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**AVALIAÇÃO DO USO DE AGENTES DESIDRATANTES E CATALISADORES METÁLICOS
IMPREGNADOS EM DIFERENTES SUPORTES NA SÍNTESE DIRETA DE
DIMETILCARBONATO**

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Pontifícia Universidade Católica do Rio Grande do Sul
 ESCOLA POLITÉCNICA
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Esta Tese de Doutorado foi julgada para obtenção do título de DOUTOR EM ENGENHARIA E TECNOLOGIA DE MATERIAIS e aprovada em sua forma final pelo Programa de Pós-Graduação em Engenharia e Tecnologia de Materiais da Pontifícia Universidade Católica do Rio Grande do Sul.

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**TESE PARA A OBTENÇÃO DO TÍTULO DE DOUTOR EM ENGENHARIA E
TECNOLOGIA DE MATERIAIS**

**Porto Alegre
Setembro, 2022**



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Tese realizada no Programa de Pós-Graduação em Engenharia e Tecnologia de Materiais (PGETEMA) da Pontifícia Universidade Católica do Rio Grande do Sul, como parte dos requisitos para a obtenção do título de Doutor em Engenharia e Tecnologia de Materiais.

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**Porto Alegre
Setembro, 2022**

*Lembre-se que as pessoas podem
tirar tudo de você, menos o seu
conhecimento.*

(Albert Einstein)

DEDICATÓRIA

Dedico este trabalho à minha mãe Leila e minha irmã Michelly, que sempre estiveram presentes mesmo estando longe. Também dedico ao meu namorado e amigo Eduardo, que presenciou todas as dificuldades e conquistas, participando delas juntamente comigo. E por fim, a todos os amigos e colegas de trabalho do laboratório, em especial Leonardo, Franciele e Sandra que me apoiaram nas ideias, agregaram com conhecimento e auxiliaram em tudo o que foi necessário.

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LISTA DE SÍMBOLOS

DMC	Dimetilcarbonato
DEC	Dietilcarbonato
CA-Fe	Ferro impregnado em carvão ativado
CA-Cu	Cobre impregnado em carvão ativado
CA-Mg	Magnésio impregnado em carvão ativado
CA-Ni	Níquel impregnado em carvão ativado
PQ	Sílica
SB	Alumina
CO	Casca de ovo
CE	Carbonato de etileno
CP	Carbonato de propileno
CB	Carbonato de butileno
CG	Carbonato de glicerol
LI	Líquidos iônicos
TGA	Análise Termogravimétrica
BET	Análise de Brunauer, Emmett e Teller de área superficial
MEV-FEG	Microscopia Eletrônica de Alta Resolução
EDS	Espectroscopia de Raios X por Energia Dispersiva
DRX	Difratometria de Raios X
FTIR-UDR	Espectroscopia no Infravermelho
MTBE	Éter metil-terc-butílico

RESUMO

FARIA, Douglas. **Avaliação do uso de agentes desidratantes e catalisadores metálicos impregnados em diferentes suportes na síntese direta de dimetilcarbonato**. Porto Alegre. 2022. Tese. Programa de Pós-Graduação em Engenharia e Tecnologia de Materiais, PONTIFÍCIA UNIVERSIDADE CATÓLICA DO RIO GRANDE DO SUL.

A transformação química do CO₂ é uma maneira interessante de reduzir a concentração desse gás na atmosfera e, como exemplo, coloca-se o uso de CO₂ para a produção de dimetilcarbonato (DMC) via síntese direta, cuja rota é uma das mais promissoras do ponto de vista ambiental. Porém, a síntese direta apresenta termodinâmica desfavorável e desativação catalítica devido à formação de água. Tal problema motivou a investigação do efeito da desidratação na síntese de DMC. Aqui, diferentes agentes desidratantes (2,2-dimetoxipropano, sulfato de sódio, óxido de magnésio e óxido de butileno) foram combinados com peneiras moleculares para remover a água e minimizar a reação reversa, além da análise do uso de catalisadores impregnados em carvão ativado, sílica, alumina e casca de ovo. Um novo reator com compartimento para acomodar peneiras moleculares na fase gasosa também foi desenvolvido. Os catalisadores foram sintetizados pelo método de impregnação e caracterizados por TGA, MEV-FEG, BET, TPD-NH₃, EDS, mapeamento, FTIR-UATR e DRX. A análise química dos produtos foi realizada por cromatografia gasosa. A otimização da quantidade de catalisador, pressão, temperatura e reciclabilidade do melhor catalisador em condições otimizadas e na presença de diferentes agentes desidratantes também foram realizadas. Para a síntese de DMC, a maior conversão de metanol foi para peneiras moleculares na fase gasosa com 2,2-dimetoxipropano na fase líquida e metóxido de potássio como catalisador (conversão = 48,6%; seletividade de 88%), ainda, a análise dos catalisadores impregnados mostrou que AC-Fe é o mais eficiente na síntese de DMC, com conversão de 23,5% e seletividade de 100% (80 ° C, 40 bar e 24h). A otimização da reação (120 °C, 40 bar e 24h) usando AC-Fe resultou no rendimento de DMC de ~ 30%. O reciclo dos sistemas catalíticos provou que a combinação de peneira molecular e AC-Fe pode manter a seletividade em 100%, diminuindo ligeiramente o rendimento.

Palavras-Chaves: DMC, CO₂, catalisadores, suportes, rendimento.

ABSTRACT

FARIA, Douglas. **Evaluation of the use of dehydrating agents and metallic catalysts impregnated in different supports in the dimethylcarbonate direct synthesis.** Porto Alegre. 2022. PhD Thesis. Graduation Program in Materials Engineering and Technology, PONTIFICAL CATHOLIC UNIVERSITY OF RIO GRANDE DO SUL.

CO₂ chemical transformation is an exciting way to reduce this gas concentration in the atmosphere. CO₂ is used to produce dimethylcarbonate (DMC) via direct synthesis, a promising route from the environmental perspective. However, direct synthesis has unfavorable thermodynamics and catalytic deactivation due to water formation. This problem motivated us to investigate the dehydration effect on the DMC direct synthesis. Here, different dehydrating agents (2,2-dimethoxypropane, sodium sulfate, magnesium oxide and butylene oxide) were combined with molecular sieves to remove water and minimize the reverse reaction, in addition to the analysis of the use of catalysts impregnated in activated carbon, silica, alumina and eggshell. A new reactor with compartment to accommodate molecular sieves in the gas phase was also developed. The catalysts were synthesized by the impregnation method and characterized by TGA, SEM-FEG, BET, TPD-NH₃, EDS, mapping, FTIR-UATR and XRD. Chemical analysis of the products was performed by gas chromatography. The optimization of the amount of catalyst, pressure, temperature and recyclability of the best catalyst under optimized conditions and in the presence of different dehydrating agents were also carried out. For the synthesis of DMC, the highest conversion of methanol was for molecular sieves in the gas phase with 2,2-dimethoxypropane in the liquid phase and potassium methoxide as catalyst (conversion = 48.6%; selectivity of 88%), still, the analysis of the impregnated catalysts showed that AC-Fe is the most efficient in the synthesis of DMC, with a conversion of 23.5% and a selectivity of 100% (80 °C, 40 bar and 24h). Reaction optimization (120 °C, 40 bar and 24h) using AC-Fe resulted in a DMC yield of ~30%. The recycling of the catalytic systems proved that the combination of molecular sieve and AC-Fe can maintain the selectivity at 100%, slightly decreasing the yield.

Keywords: DMC, CO₂, catalysts, supports yield.

1. INTRODUÇÃO

O dióxido de carbono (CO_2) é um dos gases do efeito estufa que se acumulam na atmosfera, sendo um dos principais contribuintes do aquecimento global. Para lidar com esse tipo de problema, uma possível solução é a captura, armazenamento e utilização de CO_2 . A utilização do CO_2 permite produzir diferentes compostos de alto valor agregado, como diversos carbonatos orgânicos, sendo eles, dimeticarbonato (DMC), dietilcarbonato (DEC), entre outros [1]–[13]. Dentre os diversos produtos de interesse, o DMC é um composto químico ambientalmente amigável que tem sido usado em diversas aplicações, como reagente de carbonilação e metilação ou na transesterificação de glicerol, precursor de corantes, produtos farmacêuticos, adesivos, detergentes e biolubrificantes [14], [15].

Nos últimos anos, foram realizadas inúmeras publicações referentes a produção e utilização de carbonatos orgânicos (DMC) segundo banco de dados Chemical Abstract, destacando o crescente interesse dedicado a esta área em poucos anos, como mostra a Figura 1.1 [16].

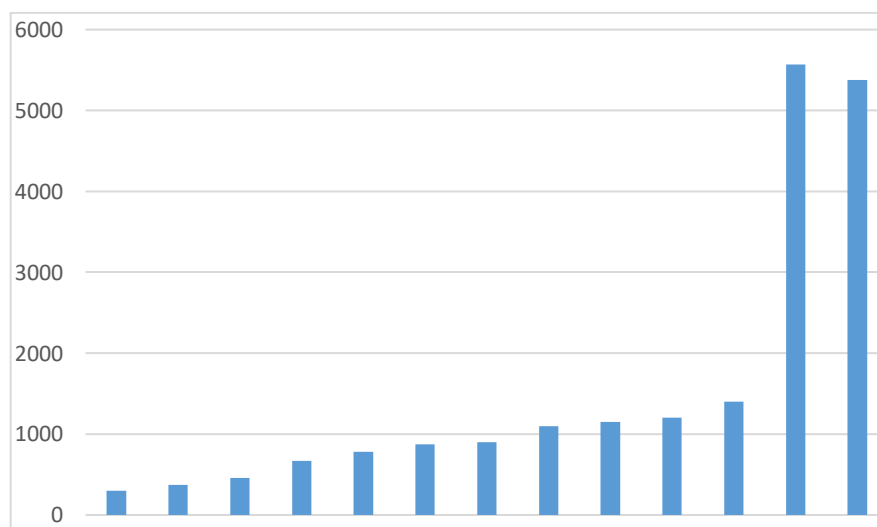


Figura 1.1. Publicações referentes à síntese de DMC de 2010-2022[17].

A busca por catalisadores e processos mais eficientes para atender aos padrões de rendimento e seletividade de DMC tem criado um forte incentivo no campo tecnológico e industrial, estimulando e impulsionando a pesquisa nessa área, principalmente a partir de 2021, onde o aumento de artigos publicados alcançou o patamar de mais de 5000 manuscritos [18].

O foco crescente na síntese direta de DMC com diferentes catalisadores, como nitratos e óxidos, ocorre porque torna a síntese cerca de 1000 vezes menos tóxica que a síntese com o catalisador comumente utilizado (fosgênio) [16]. Ainda, há uma grande aplicabilidade do DMC como reagente em sínteses orgânicas, pois possui uma boa reatividade para moléculas nucleofílicas, como fenóis e aminas primárias[19].

Outro carbonato orgânico muito importante é o DEC, além de ser proveniente do CO₂, utiliza o etanol que pode ser produzido através da biomassa, como a cana-de-açúcar, tornando sua rota de síntese mais sustentável. DEC é um carbonato orgânico linear usado como aditivo de combustíveis devido ao alto teor de oxigênio, maior do que o éter metil-terc-butilíco (MTBE), tendo aplicações na produção de policarbonatos, fármacos e fertilizantes [20].

Até o momento, muitas rotas têm sido utilizadas para síntese de DMC, como a rota do fosgênio, a rota de transesterificação, a rota da alcoólise da ureia, rota de carbonilação oxidativa do metanol e a síntese direta de DMC via metanol e dióxido de carbono [21], [22]. Dentre essas rotas, fosgenação, transesterificação e carbonilação oxidativa do metanol em fase líquida alcançaram a industrialização [23]. Para a síntese de DEC, temos a rota do fosgênio, carbonilação oxidativa do etanol, carbonilação do nitrato de etila, etanólise catalítica da ureia e a síntese direta via CO₂ e etanol [24]. Porém, para DMC e DEC, a fosgenação foi um processo descontinuado devido ao uso de um reagente tóxico, o fosgênio [25].

Como forma de amenizar o impacto ambiental, a síntese direta de DMC e DEC são os processos mais estudados para produção dos carbonatos, entretanto, a termodinâmica da reação é desfavorável [26], [27]. As restrições aos problemas termodinâmicos podem ser tratadas alterando o equilíbrio da reação com variações de temperatura, pressão, tempo e utilização de agentes desidratantes [23], [28].

Portanto, o presente estudo visa sintetizar DMC utilizando metanol, CO₂, agentes desidratantes orgânicos e/ou inorgânicos na fase líquida e gasosa, agente promotor e catalisadores, comercial (CH₃OK) e heterogêneos suportados em carvão

ativado, além de otimizar os parâmetros de temperatura, pressão e quantidade de catalisador necessários para se obter melhores resultados de rendimento e seletividade de DMC.

2. OBJETIVOS

O objetivo geral do presente trabalho é avaliar a síntese direta de dimetilcarbonato (DMC) através do uso de agentes desidratantes e diferentes catalisadores.

2.1. Objetivos Específicos

Reproduzir a síntese direta de DMC usando iodometano como promotor e CH_3OK como catalisador;

Avaliar o uso de peneiras na parte gasosa (superior) e líquida (inferior) no reator, com intuito de diminuir a quantidade de água do meio reacional na síntese direta de DMC;

Otimizar o tempo de síntese de DMC;

Analisar a combinação de agentes desidratantes orgânicos e inorgânicos (2,2-dimetoxipropano, sulfato de sódio, óxido de magnésio e óxido de butileno) em fase líquida com peneiras moleculares na fase gasosa;

Sintetizar catalisadores metálicos (nitrato de ferro, nitrato de cobre, nitrato de magnésio e nitrato de níquel) impregnados em carvão ativado, sílica, alumina e casca de ovo;

Caracterizar os catalisadores suportados em CA, PQ, SB e CO através de técnicas de TGA, IFTR, MEV-FEG, DRX e BET;

Avaliar o uso dos catalisadores suportados em CA, PQ, SB e CO na síntese direta de DMC, utilizando iodometano como promotor e peneiras moleculares na fase gasosa;

Otimizar os parâmetros de temperatura, pressão e quantidade de catalisador para produção de DMC;

Analisar o reciclo do catalisador suportado em CA com melhor desempenho na síntese de DMC.

3. REVISÃO BIBLIOGRÁFICA

3.1. Panorama da emissão de CO₂

A necessidade de reduzir as emissões de dióxido de carbono da produção energética e de outras atividades industriais tem recebido grande atenção global. O aumento dos estudos referentes ao uso de energias renováveis e nuclear, cuja aplicabilidade para produzir eletricidade e demais componentes energéticos globais conta com emissão zero de CO₂ também vem crescendo[29], [30].

As emissões globais alcançaram 33Gt em 2019, tal nível é similar ao que havia sido previsto e, tem relação com o crescimento global da economia em torno de 2,9% [29]. A relação entre a emissão de CO₂, crescimento econômico e produção de energia renovável e não-renovável na China, no período de 1980-2014 foi analisada [31]. O uso de energias não renováveis e o crescimento econômico acarretaram no aumento considerável de emissão de CO₂, por outro lado, o uso de energias renováveis aliado com o crescimento econômico proporcionou diminuição da emissão de CO₂ na atmosfera e crescimento econômico estável, logo, existe a possibilidade de conciliar economia e meio ambiente sem perdas de ambos os lados[31].

Os dados mais recentes em torno do uso de energia global mostram que há uma redução drástica da atividade econômica e da mobilidade durante o primeiro trimestre de 2020, o que alavancou a decaída da demanda global de energia em 3,8% em relação ao primeiro trimestre de 2019 [32]. Entretanto, mesmo com a segunda onda da pandemia, as reduções na demanda de energia e emissões de CO₂ são pequenas, indicando que retomarão crescimento mesmo que lentamente. As quedas impressionantes na demanda de energia resultaram numa queda nas emissões globais de CO₂, superando qualquer expectativa como mostra Figura 3.1.

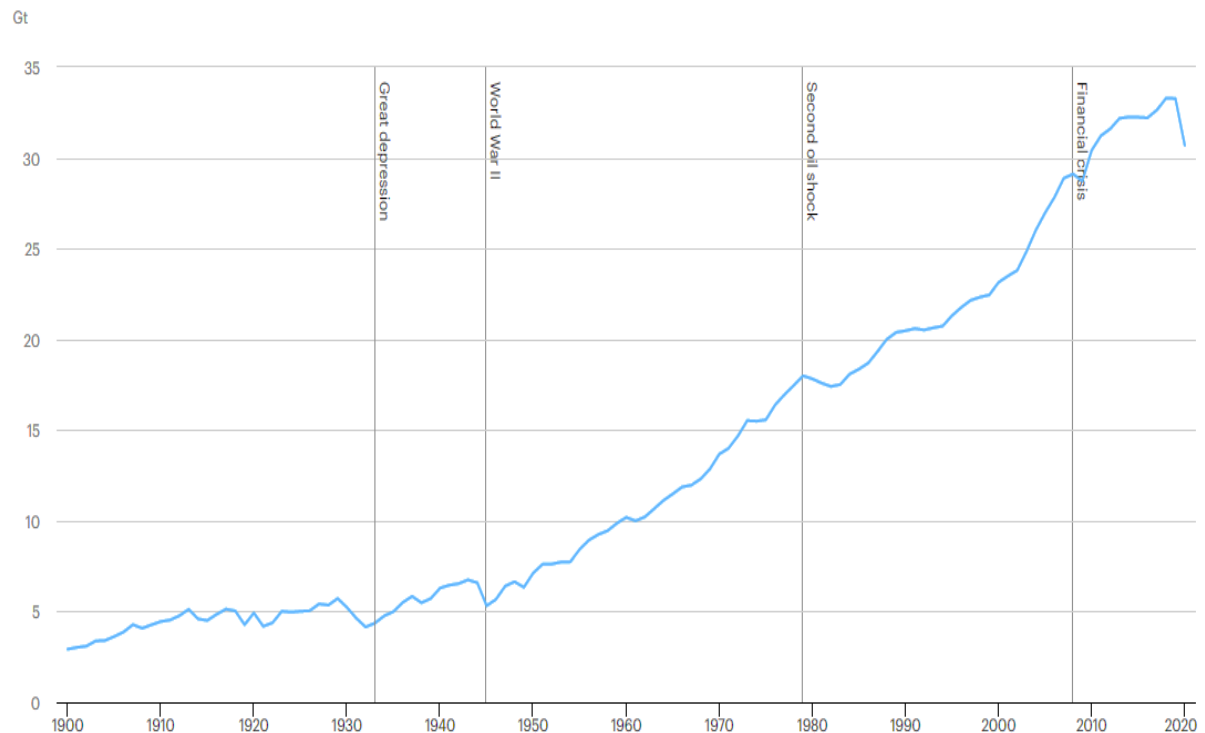


Figura 3.1. Gráfico de emissão de CO₂ de 1900-2020 [32].

A taxa de diminuição das emissões de CO₂ deverá ser quase duas vezes maior do que todas as quedas anteriores desde o final da Segunda Guerra Mundial [32]. As emissões globais de CO₂ foram 5% menores no primeiro trimestre de 2020 do que em 2019, principalmente devido a uma redução de 8% nas emissões de carvão, 4,5% de petróleo e 2,3% de gás natural [32]. A queda drástica de emissão de CO₂ ocorreu principalmente nas regiões que sofreram os primeiros e maiores impactos do COVID-19, sendo eles China, União Europeia e Estados Unidos [32].

Apesar da queda da demanda de energia e, conseqüentemente, do declínio das emissões de CO₂ devido a pandemia do COVID-19, ainda há a preocupação ambiental de redução deste gás na atmosfera, visando a utilização de CO₂ em processos industriais, como forma de sintetizar compostos de alto valor agregado [33]–[35].

3.2. Transformação química do CO₂ em compostos orgânicos

O aumento na quantidade de emissão de dióxido de carbono proveniente da queima de combustíveis fósseis é retratado como maior contribuinte para o

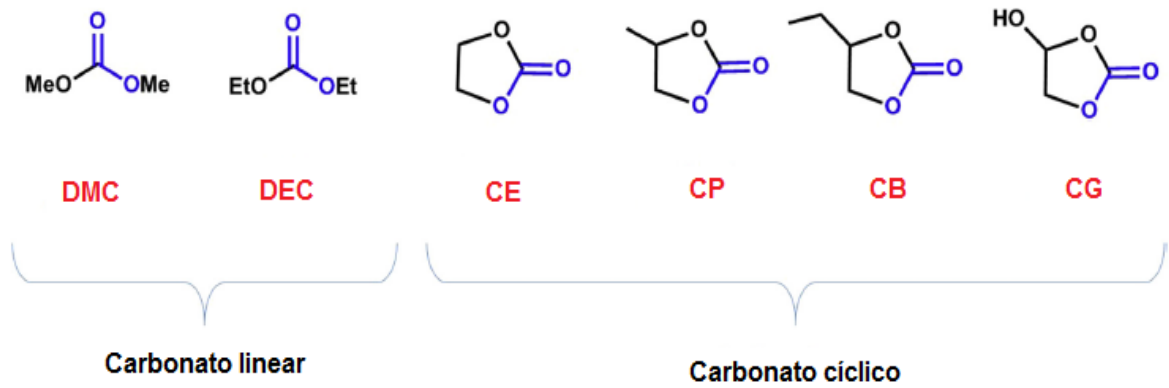


Figura 3.2. Principais carbonatos orgânicos e subdivisões em lineares e cíclicos [36].

3.3. Dimetilcarbonato (DMC)

O dimetilcarbonato (DMC) é um intermediário químico de fácil degradabilidade, alta polaridade, baixa viscosidade e toxicidade, utilizado em uma gama de aplicações [19], [23], [37]. Dentre elas, o uso na síntese de policarbonato, polímero amplamente usado nas indústrias de construção, automóveis e dispositivos médicos. O DMC também é utilizado como solvente de eletrólito para baterias de lítio, devido a sua constante dielétrica, e, usado como reagente ambientalmente amigável para metilação e carbonilação [23], [40]. Algumas das possíveis vias de reação do DMC estão listadas na Figura 3.3.

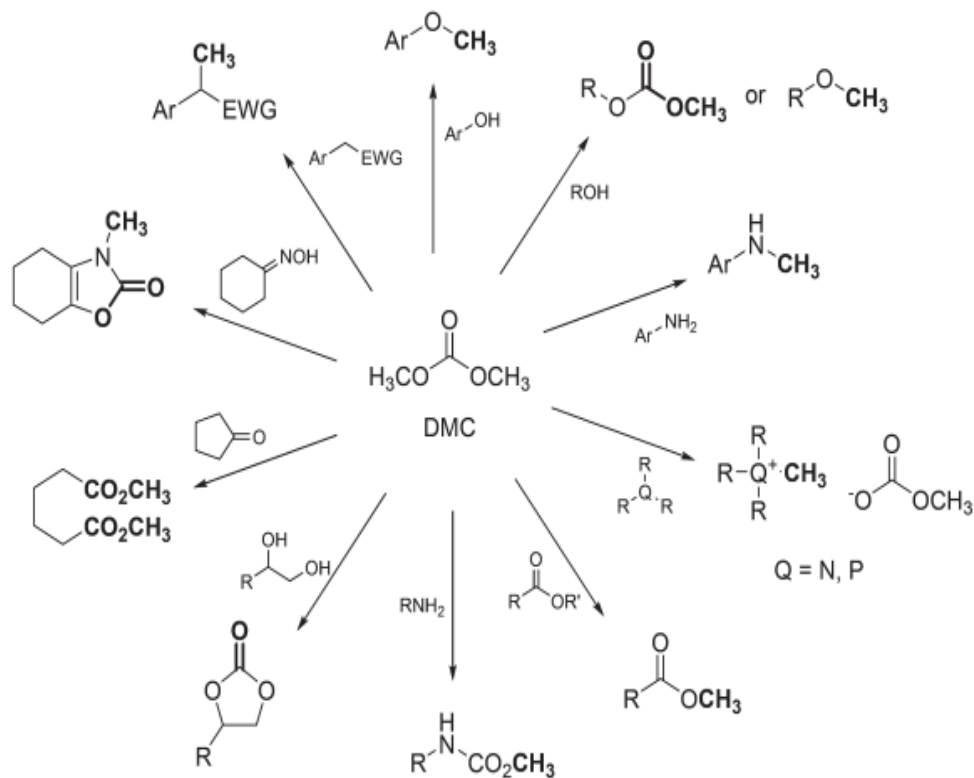


Figura 3.3. Vias típicas de reatividade de DMC [19].

Além disso, o DMC tem sido considerado um aditivo com grande potencial para o óleo combustível, devido ao alto teor de oxigênio (53%), número de octano (105), bom coeficiente de distribuição de gasolina/água, baixa toxicidade e rápida biodegradabilidade, ainda, a adição adequada de DMC ao diesel pode diminuir a emissão de partículas de fuligem dos motores e, conseqüentemente, reduzir a poluição ambiental [23], [37].

3.3.1. Principais rotas para produção de dimetilcarbonato (DMC)

Existem diversas propostas de rotas para sintetizar o DMC, tais como: rota do fosgênio, transesterificação, alcoólise da ureia, carbonilação oxidativa e a síntese direta a partir de CO₂ e metanol. Dentre essas rotas, a fosgenação, carbonilação oxidativa e transesterificação alcançaram a industrialização [23]. Entretanto, a rota do fosgênio foi descontinuada devido à alta toxicidade da matéria prima (fosgênio),

enquanto as demais continuam sendo utilizadas de forma intensiva na produção industrial em larga escala [23].

Até a década de 80, o DMC foi produzido industrialmente pela *Bayer Company* (Alemanha) e pela *Société National des Poudres et Explosifs* (França) apenas com base na fosgenação do metanol (Figura 3.4), embora as condições de processamento sejam simples, a tecnologia envolve o uso de compostos muito tóxicos que promovem severa corrosão de equipamentos devido a produção de HCl (subproduto) durante o processo [23], [37].

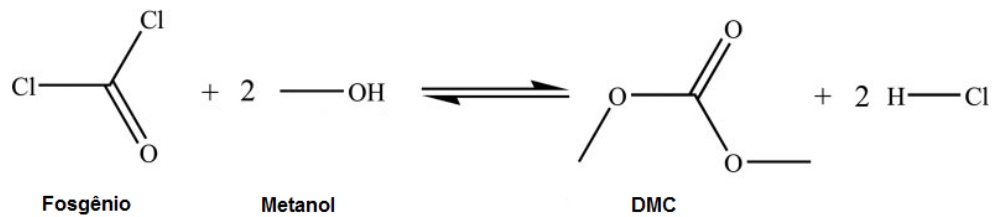


Figura 3.4. Fosgenação do metanol para síntese de DMC [37].

Em 1983, a empresa italiana *Enichem Company* desenvolveu uma rota livre de fosgênio para síntese de DMC, a chamada rota de carbonilação oxidativa do metanol em fase líquida com cloreto de cobre como catalisador (Figura 3.5).

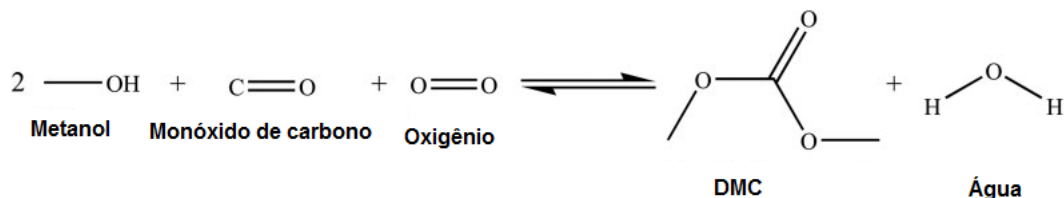


Figura 3.5. Carbonilação oxidativa do metanol [37].

Embora haja um ganho econômico no uso da rota de carbonilação oxidativa, ocorre a produção de água durante o processo, causando a diminuição da estabilidade do catalisador, e ainda, há o risco de explosão quando o conteúdo de O₂ excede 4 mol%, além disso, há a possibilidade da produção de um subproduto competitivo na reação, o CO₂, que diminuiria a eficácia do processo. Logo, apesar da industrialização da rota de carbonilação oxidativa, muitos problemas ainda devem ser abordados e otimizados [23].

Na década de 90, empresas como a Texaco (EUA), Shell (Holanda) e outras sediadas na China implementaram a rota de transesterificação em duas etapas para síntese de DMC (Figura 3.6) [23], [40]. Esta rota é amplamente estudada devido à alta produtividade e seletividade de DMC e, também, a co-geração de carbonato de glicerol, produto com alto valor comercial [23], [37]. Apesar da alta produtividade, há um alto custo no processo e considerável limitação termodinâmica devido ao favorecimento dos reagentes durante o equilíbrio reacional [23], [36], [37].

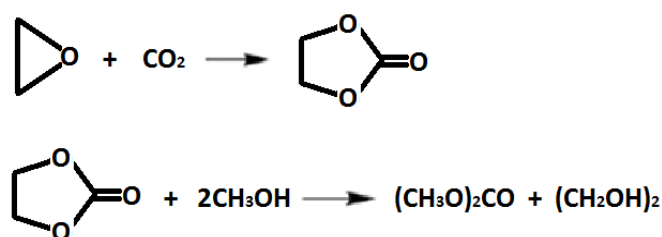


Figura 3.6. Rota de transesterificação em duas etapas [23].

O primeiro passo na rota de transesterificação é a conversão do óxido de etileno em carbonato de etileno, realizado sob condições moderadas e com rendimento e seletividade próximos a 100%, entretanto, a reação subsequente entre o carbonato de etileno e o metanol é o passo determinante da reação, pois requer condições adversas no processo como altas temperaturas e pressões [14], [39]. Com objetivo de contornar as condições que prejudicam o processo reacional, foram desenvolvido diversos catalisadores homogêneos como aminas terciárias e líquidos iônicos [23].

3.3.2. Rota alternativa para produção de DMC: síntese direta de DMC

Do ponto de vista ambiental e econômico, a síntese direta de DMC utilizando CO_2 como matéria prima é altamente atraente para indústria. A utilização de CO_2 como fonte alternativa de carbono pode fornecer produtos químicos de alto valor agregado e mitigar os danos ambientais do efeito estufa [27], [38], [41]. Entretanto, a estabilidade termodinâmica e as limitações cinéticas das moléculas de CO_2 tornam tal rota foco de pesquisas para superar os baixos rendimentos através do uso de novos catalisadores, técnicas de remoção de água *in situ* e demais alterações

processuais [23], [28], [36], [37]. A Figura 3.7 apresenta a equação química para a síntese direta de DMC usando metanol e CO₂.

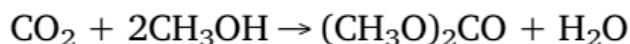


Figura 3.7. Síntese direta de DMC.

Como forma de melhorar o rendimento e seletividade de DMC, diversos catalisadores homogêneos e heterogêneos tem sido empregados para a síntese direta de DMC, como dimetóxido de dibutilestanho (IV) [37], [40], carbonato de potássio [23], [42], [43], carbonato de sódio [42], carbonato de lítio [42], óxido de cério [38], misturas de óxidos com cério [38], [41], [44]–[46], óxido de zircônia [47], [48], dióxido de estanho dopado com zinco, cobre ou potássio e suportado em alumina[49], líquidos iônicos[50]–[53],etc.

3.3.3. *Catalisadores homogêneos e heterogêneos na síntese direta de DMC*

Inúmeros catalisadores vêm sendo utilizados para síntese de DMC com objetivo de produzir um catalisador barato e que alcance rendimento e seletividade eficaz para ser utilizado na indústria. O dimetóxido de dibutilestanho (IV) (Bu₂Sn(OMe)₂) é um catalisador bem conhecido para conversão direta de CO₂ a DMC. No entanto, em presença de água este catalisador pode se degradar em Bu₂SnO + CH₃OH [37], sendo assim, a produção de subprodutos acaba encarecendo o processo e alterando o equilíbrio da reação, o que diminui o rendimento. Os autores [40] relataram que na temperatura de 423K e pressão de 20 MPa é possível obter cerca de 1% de conversão em reações catalisadas com dimetóxido de dibutilestanho (IV), porém ocorre uma diminuição significativa da atividade catalítica entre a primeira e a segunda reação devido a desativação do catalisador em presença de água.

Compostos de elementos do grupo I (Li, Na e K) foram utilizados como catalisadores básicos na síntese de DMC [23], [42]. Neste sistema catalítico, usou-se também um promotor (co-catalisador) e um agente desidratante para melhorar o rendimento da reação. O rendimento de DMC com os diferentes catalisadores de

metal alcalino foi classificado na seguinte ordem: $K > Na > Li$. Os catalisadores compostos por metal- CO_3 foram mais eficazes do que os formados por metal-OH na síntese de DMC e o melhor rendimento (~12 %) foi obtido na presença de K_2CO_3 (catalisador), CH_3I (promotor) e 2,2-dimetoxipropano (agente desidratante) [23], [42], [43].

Outro catalisador básico, o metóxido de potássio (CH_3OK) foi investigado para a síntese direta de DMC a partir de metanol e CO_2 em presença do promotor (CH_3I) [43]. Os resultados mostraram que o uso de CH_3OK em presença de CH_3I pode promover um rendimento de 16,2% e alta seletividade (100%) para formação de DMC sob condições amenas para este processo. O mecanismo de síntese proposto para a produção de DMC a partir de CO_2 usando CH_3OK e CH_3I envolve a ativação do metanol, a inserção de CO_2 e a produção de DMC. Neste processo, a basicidade do catalisador é muito importante para a ativação do metanol, ou seja, quanto mais forte a basicidade, maior será a concentração de formação de CH_3O^- . Assim, o maior rendimento com alta seletividade (100%) em condições reacionais amenas (7,3 MPa e $80^\circ C$), foi obtido com a substituição do catalisador K_2CO_3 (~12%) por CH_3OK (16,2%), atribuído a alta basicidade do CH_3OK em comparação ao K_2CO_3 [43].

A literatura aponta que as condições reacionais (tempo, pressão e concentração dos reagentes) possuem grande influência sobre o rendimento de DMC obtido [18], [19], [27], [28], [54]–[58]. A Figura 3.8 mostra o efeito da pressão de CO_2 sobre os rendimentos de DMC na presença de CH_3OK e CH_3I .

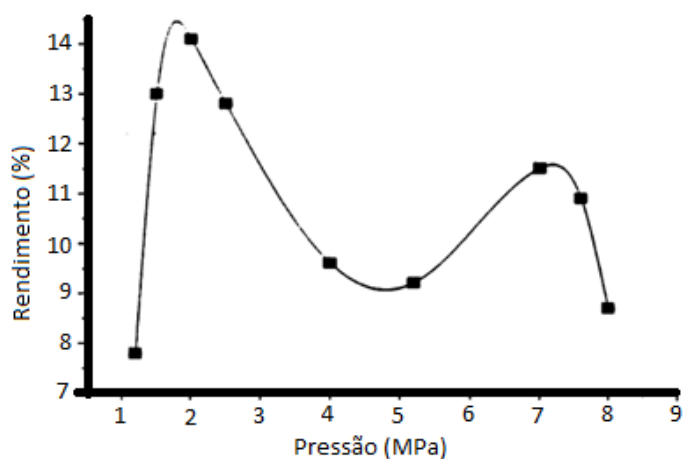


Figura 3.8. O efeito da pressão no rendimento do DMC. T: $80^\circ C$, CH_3OK / CH_3OH : 3/50 (mol), CH_3I : 0,048 mol, tempo: 6 h.[43].

Pode-se observar que o gráfico de rendimento de DMC mostra dois pontos máximos, um em 2,0 MPa e outro a 7,3 MPa. Tem sido relatado que, quando CO_2 é usado como solvente ou reagente, as taxas de reação são máximas próximo da pressão crítica (7,3 MPa), no entanto os resultados mostrados na Figura 3.8 indicam que altas pressões de CO_2 não são necessárias para a síntese de DMC, visto que o maior rendimento de DMC foi atingido entre 1,5 e 2,0 MPa [43]. A diminuição no rendimento de DMC observada na região de 2,0 a 7,3 MPa ou em pressões superiores a 7,3 MPa resultaria do efeito de diluição, porque a quantidade de fase líquida aumenta em maior proporção com aumento na pressão de 2 a 7,3 MPa e além 7,3 MPa [43].

Os resultados experimentais obtidos para a síntese de DMC [59], utilizando CO_2 e metanol na presença de iodeto de metila e K_2CO_3 , também mostraram que condições supercríticas de CO_2 são prejudiciais a formação de DMC. Quando o efeito da pressão foi investigado na faixa de 0 até 15 MPa, o maior rendimento de DMC foi alcançado na pressão de 4,5 MPa [59].

O efeito da temperatura e do tempo de reação sobre os rendimentos de DMC na presença de CH_3OK e CH_3I é apresentado nas Figuras 3.9 e 3.10. Conforme pode-se observar na Fig 3.9, o rendimento de DMC aumenta de ~6% para ~13% quando a temperatura de reação é elevada de 60°C para 80°C, exibindo em seguida, uma pequena diminuição no rendimento. Estes dados experimentais mostram que existe uma temperatura ideal, para que a formação de produto seja favorecida [43], [59]. A mudança no rendimento de DMC com o aumento de temperatura mostrado na Fig.3.9 pode estar relacionado com a ação mútua da cinética e da termodinâmica [60].

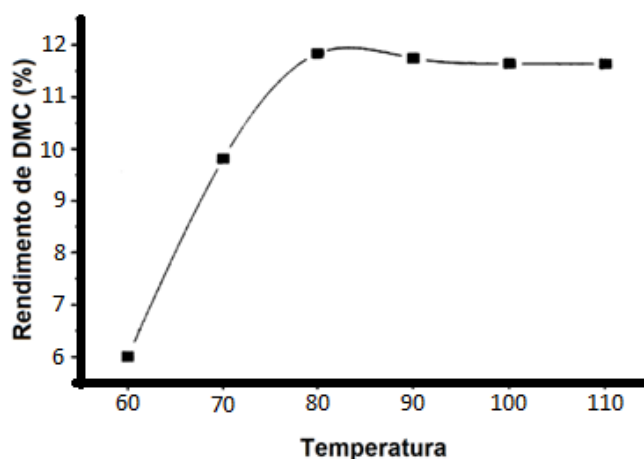


Figura 3.9. Efeito da temperatura ($^{\circ}\text{C}$) no rendimento de DMC Pressão: 2 MPa, tempo: 6 h, $\text{CH}_3\text{OK} / \text{CH}_3\text{OH}$: 3/50 (mol), CH_3I : 0,048 mol [43].

A Figura 3.10 mostra o rendimento de DMC em função do tempo de reação. O aumento no rendimento quando o tempo de reação é elevado de 1h para 6 h é evidente [43]. No entanto, comportamento diferente é observado quando o tempo aumenta de 6h para 10h [43]. Estes resultados indicam que a taxa de formação de DMC diminui após o tempo de reação de 6h, o que poderia ser atribuído ao equilíbrio de reação alcançado [43]. Por outro lado, diversos fatores influenciam no melhor rendimento, como o catalisador usado, presença de promotor, tamanho do reator e pressão, sendo assim, para o estudo citado, tempos reacionais maiores dificultam o processo, porém, outros estudos evidenciam que tempos maiores de reação podem aumentar o rendimento na síntese de DMC [28].

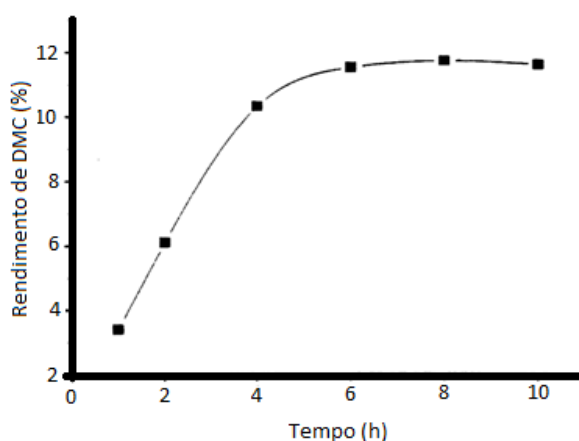


Figura 3.10. Efeito do tempo de reação no rendimento de DMC Temperatura: 80°C , Pressão 2 MPa, $\text{CH}_3\text{OK} / \text{CH}_3\text{OH}$: 3/50 (mol / mol), CH_3I : 0,048 mol[43].

Catalisadores como os óxidos metálicos constituem uma importante classe de materiais catalíticos. Óxido de cério (CeO_2), dióxido de zircônio (ZrO_2), misturas de óxidos ($\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$) têm sido utilizados como catalisadores para a síntese direta de DMC [61][48], [53], [61], [62]. Estudos que utilizaram ZrO_2 como catalisador revelaram que a taxa de formação de DMC é dependente da morfologia, da fase e estrutura cristalina, propriedades e número de sítios ácido/base presentes na estrutura do catalisador ZrO_2 [47], [49].

Resultados experimentais revelaram que tanto a acidez quanto a basicidade dos catalisadores desempenharam um papel fundamental na síntese direta de DMC a partir de metanol e dióxido de carbono [44]. De acordo com o mecanismo de formação de DMC, o metanol é ativado a espécies metila e espécies metoxi nos sítios ácidos e básicos catalisador, respectivamente. O ânion metoxi carbonato é então formado pela reação de espécies metoxi com o CO₂ adsorvido nos sítios básicos do catalisador [42], [44]. O ânion metoxi carbonato reage ainda com grupos metila nos sítios ácidos do catalisador para produzir DMC. Portanto, espera-se que os catalisadores bifuncionais ácido-base mostrem uma excelente atividade catalítica nesta reação [44].

O catalisador apropriado para a síntese de DMC a partir de CO₂ e metanol deve gerar simultaneamente grupos metoxi a partir de metanol e espécies carboxilato ou carbonato a partir de CO₂ [49]. Para satisfazer estes requisitos, pode-se utilizar óxidos metálicos de natureza básica ou anfotérica fraca na composição do catalisador juntamente com a adição de CuCl₂, ZnCl₂ ou KF que atuam na melhora da geração de compostos de carbonato na superfície do catalisador [49]. Outros catalisadores como os líquidos iônicos também estão sendo alvo de estudos na síntese de DMC [50], [51], [63]–[66]

Os LIs são uma classe de sais orgânicos, formados pela combinação de cátions orgânicos e ânions inorgânicos ou orgânicos, que possuem temperatura de fusão inferior a 100°C [64], [67]–[71]. Estes compostos exibem propriedades únicas como a capacidade de não inflamar, pressão de vapor extremamente baixa e boa estabilidade térmica [27], [63], [65], [67], [69], [71]. Além disso, são versáteis e menos prejudiciais ao meio-ambiente do que os solventes orgânicos convencionais. A grande variabilidade estrutural de cátions e ânions permite a criação de compostos com características e propriedades específicas para uma determinada aplicação [66], [68], [70], [72].

Em geral, os LIs são divididos em duas grandes categorias: Líquidos Iônicos à Temperatura Ambiente (RTILs: do inglês “Room Temperature Ionic Liquids”) considerados os LIs tradicionais ou convencionais e, os líquidos iônicos específicos (TSILs: do inglês “task-specific ionic liquids”), isto é, que apresentam grupos funcionais reativos em sua estrutura [63], [64], [66], [70].

A síntese direta de DMC usando o catalisador K_2CO_3/CH_3I em presença de LI (cloreto de 1-butil-3-metilimidazólio – Bmim Cl, tetrafluoroborato de 1-butil-3-metilimidazólio - bmim BF_4 e hexafluorofosfato de 1-butil-3-metilimidazólio - bmim PF_6) sob irradiação de micro-ondas foi descrita [50]. A presença de LI no meio reacional promoveu o aumento do rendimento de DMC, dentre os LIs utilizados, o cloreto de 1-butil-3-metilimidazólio foi o promotor mais eficaz.

Estudos de simulação computacional mostraram que o LI pode atuar como meio de reação, regulando a polaridade intermediária e o momento dipolar do estado de transição, o que potencializa a absorção seletiva de energia de micro-ondas e aumenta a solubilidade do CO_2 no sistema de reação [50]. Desse modo, a presença de LI reduz a energia de ativação da reação interfacial, aumenta o transporte de CO_2 e o número de colisões de moléculas reativas (CO_2 e CH_3OH) em torno das moléculas de K_2CO_3 , promovendo a melhora da atividade catalítica [50]. Além disso, o tamanho da cadeia do LI também interfere na ação catalítica, pois alguns resultados indicaram que o LI com menor comprimento de cadeia de carbono ligada ao cátion exibe atividade relativamente mais alta para a reação de metanol com CO_2 , uma vez que possui maior polaridade. A polaridade e o campo eletrostático dos LIs usados como catalisador e meio de reação podem estabilizar o intermediário carregado, tornando a reação mais fácil de prosseguir [23], [51]. O LI funcionalizado com hidroxila EtmimOH demonstrou mais atividade catalítica do que o EmimOH, enquanto o EtmimBr não apresentou atividade [51]. Isto sugere um efeito sinérgico entre o grupo hidroxila do álcool e o ânion básico OH^- , esta sinergia desempenha um papel muito importante na fixação e ativação de CO_2 e metanol, posteriormente convertido em DMC.

Em relação aos suportes, eles são empregados para manter os catalisadores interligados em sua matriz, dessa forma, há a possibilidade de reutilização desses catalisadores suportados, além de auxiliar na separação do meio reacional [26], [73]–[75]. Diferentes tipos de suportes são estudados e podem ser analisados de acordo com sua porosidade e quantidade de catalisador impregnado, logo, a análise de suportes como sílica, alumina e carvão ativado pode auxiliar no aumento da conversão de carbonatos e na reutilização dos catalisadores para aumentar a eficiência processual nas indústrias [75]–[77].

Portanto, o estudo de catalisadores suportados torna-se de grande valia na aplicação para síntese de carbonatos orgânicos, sendo que, a dificuldade de alcançar resultados satisfatórios é influenciada pela escolha e estudo do catalisador presente no meio reacional [78]. Apesar dos inúmeros catalisadores estudados, a presença de matrizes celulósicas e resíduos de biomassa como forma de suporte ainda é pouco analisada, já que além da dificuldade reacional ainda se tem o obstáculo de sintetizar um excelente catalisador. Entretanto, as estruturas dos suportes podem aumentar a capacidade de impregnação e ligação de metais em sua estrutura e, conseqüentemente, acarretar numa melhor ação catalítica frente a diferentes condições de temperatura, pressão e tempo reacional.

A celulose é um suporte muito estudado para inserção de metais em sua estrutura proveniente de fontes residuais de biomassa, como por exemplo a casca de ovo. A celulose é o polímero orgânico mais abundante do planeta, presente na estrutura de todas as células vegetais, sendo composta por celulose (35%), hemicelulose (25%), lignina (20%), proteína bruta (3%) e cinzas (17%). Grupos hidroxila presentes na celulose podem ser desprotonados prontamente, criando um grupo O^- extremamente reativo que pode ser modificado através da ligação de metais. Sendo assim, o uso de um resíduo com possibilidade de modificação em sua estrutura para aplicação na sorção e transformação de CO_2 torna a casca de ovo extremamente utilizável para a síntese de DMC e DEC, logo, concede um valor econômico e ambiental para a casca do ovo [79].

Ovos de galinha são amplamente utilizados como um alimento de baixo custo e alta qualidade nutricional. Na Europa, mais de 100 bilhões de ovos são consumidos ou incorporados como ingrediente em muitos produtos alimentícios [80]. No Brasil, de acordo com o IBGE, a produção de ovos de galinha em 2021 foi de 3,976 bilhões de dúzias. Dados divulgados pela Associação Brasileira de Proteína Animal (ABPA) dão conta de que nos primeiros dois meses do corrente ano de 2022, foram contabilizadas 4,411 mil toneladas de ovos exportados para países como Emirados Árabes Unidos, Omã e Japão, o que representa um volume 38,9% maior em relação ao mesmo período de 2021[81].

O resíduo proveniente da casca do ovo é uma matéria-prima natural, abundante, não tóxica e apresenta elevado potencial econômico. Este material é

composto, em sua maior parte, por CaCO_3 na forma de calcita (94% p/p), além de traços de fosfato de cálcio (1% p/p), carbonato de magnésio (1% p/p) e matéria orgânica (cerca de 4% p/p) [82]. Assim, resíduos de casca de ovo têm sido aplicados como catalisadores e suportes para impregnação de metais em diferentes processos, como tratamento de água, suporte de catalisadores e adsorventes.

Portanto, diferentes catalisadores podem ser utilizados e analisados quanto a síntese de DMC. E, cada catalisador pode influenciar de modo diferente os parâmetros reacionais e, conseqüentemente, a formação de DMC. Por outro lado, como temos a formação de água durante o processo, também torna-se necessário contornar esse problema e, por isso, alguns agentes desidratantes vem sendo testados, como DMP, óxido de butileno, entre outros [28].

3.3.4. Agentes desidratantes na síntese de DMC

O maior desafio referente a síntese direta de DMC são as limitações termodinâmicas da reação, que nos mostra um desfavorável equilíbrio para os produtos [28]. Com intuito de aumentar o rendimento de DMC, agentes desidratantes são inseridos no meio reacional de modo a diminuir a concentração de água nos produtos e, assim, tornar o equilíbrio da reação favorável para a síntese de DMC.

Diversos agentes desidratantes como as nitrilas e acetal/cetals vem sendo usados na síntese de DMC [48], [61], [64], [83]–[85]. A cianopiridina é um agente desidratante que gera bons resultados na síntese de DMC usando CeO_2 como catalisador, entretanto, a hidrólise da cianopiridina produz diversos subprodutos (amidas, carbamatos, etc.), causando uma diminuição da seletividade do processo e, conseqüentemente, do rendimento [48].

A influência de diferentes agentes secantes como peneiras moleculares 4A, 2,2 dimetoxipropano (DMP), acetonitrila, óxido de cicloexeno e óxido de estireno também foram avaliadas [86]. As melhores condições de reação (ou seja, 1g de catalisador, temperatura de 140°C e 7,5 MPa de pressão) foram usadas para esses experimentos[86]. Dentre os agentes desidratantes utilizados, o DMP mostrou ser o melhor, produzindo 23,57 mmol de DMC, enquanto a peneira molecular 4A produziu 18,61 mmol de DMC. Curiosamente, os epóxidos tais como óxido de ciclohexeno e óxido de estireno produziram quantidade altas de DMC, 22,32 e 22,68 mmol,

indicando que o agente desidratante desempenha um importante papel na síntese direta de DMC a partir de CO₂ e metanol, aumentando o rendimento do produto de interesse.

O uso de peneiras moleculares para captura de água na fase gasosa e, também, o uso de DMP (dimetoxipropano) combinado com peneiras a fim de melhorar a conversão e seletividade de DMC foi avaliado [28]. O DMP é um agente desidratante que reage com a água gerando como subproduto a cetona (Figura 3.11), sendo assim, a seletividade tende a ser alterada[28].



Figura 3.11. Reação de DMP na presença de água [28].

Logo, nota-se a importância da utilização de agentes desidratantes no meio reacional, devido a grande eficácia no deslocamento do equilíbrio da reação para síntese de produto (DMC), melhorando o rendimento do processo.

3.3.5. Avaliação econômica da produção e venda de DMC

O uso de dióxido de carbono como matéria-prima representa um desafio comercial, que é desenvolver produtos alternativos a custos mais baixos e com menores impactos de fabricação. Muitos produtos podem ser desenvolvidos através do CO₂ usando reações de carboxilação ou hidrogenação[87]. Na captura de carbono e utilização, uma determinada tecnologia de utilização de dióxido de carbono mostra aspectos específicos para emissão potencial de redução, restrições termodinâmicas intrínsecas e nível de maturidade comercial[87]. Cada produto traz algumas vantagens e penalizações, por isso é importante definir alguns critérios para avaliar e escolher os produtos mais atraentes.

O rápido crescimento da indústria de eletrônicos tem resultado numa alta demanda de baterias para smartphones e outros eletrônicos portáteis. O DMC é um componente essencial para produção das baterias o que acarreta na sua crescente produção no mercado. Algumas das companhias chaves no mercado global de

síntese de DMC são: Merck KgaA, Henan GP Chemicals Co.Ltd., WEGO Chemical Group, Hefei THJ Chemical Industry Co. Ltd., Akzo Nobel, UBE Industries, ThermoFisher Scientific, Alfa Aesar, Aceto Corporation, Connect Chemicals e Silver Fern Chemicals[88].

As indústrias de grande produção são localizadas na Ásia, onde a demanda por DMC é maior, porém, a demanda está se expandindo com a criação de veículos híbridos e elétricos por empresas como a Tesla. Além disso, o mercado de combustíveis da Europa está seguindo os passos de empresas norte americanas com pesquisas relacionadas ao uso de DMC como promissor aditivo de combustíveis[87], [88].

Prevê-se que o mercado de DMC cresça de US\$ 847 milhões em 2021 para US\$ 1.148 milhões em 2026, com um CAGR de 6,3% de 2021 a 2026[89]. Espera-se que a crescente demanda por policarbonatos e baterias de íon-lítio impulse o DMC no mercado global. Shandong Shida Shenghua Chemical Group Co., Ltd. (China) é o terceiro maior produtor operando no mercado de DMC[88], [89]. Atualmente, a empresa possui 13 conjuntos de equipamentos de produção que podem produzir mais de 20 tipos de produtos. Alguns dos principais produtos oferecidos pela empresa são carbonato de dimetila, carbonato de propileno, carbonato de etileno, carbonato de etilmetila, hexafluorofosfato de lítio e aditivos especiais para eletrólitos e éter metil terc-butilico. A empresa é um fornecedor de matéria-prima solvente de alta qualidade para muitos fabricantes de eletrólitos de baterias de íon-lítio[89], [90]. Ela afirma produzir cerca de 100.000 toneladas de carbonato de dimetila anualmente, que é vendido para a Europa, Américas, Japão, Coreia e Sudeste Asiático[90].

Pacheco, Bresciani e Alves (2021)[91] conduziu um estudo com pesquisa sistemática da literatura para apontar critérios relevantes como ferramentas de análise de decisão multicritério, dados termodinâmicos, tamanho e crescimento, preço do produto e taxa de utilização de dióxido de carbono. Os resultados da avaliação demonstram que a síntese de dimetilcarbonato é um dos produtos com maior viabilidade econômica e de crescimento industrial.

Kuennen et al. (2016)[92], analisaram a síntese direta de DMC utilizando membranas e avaliaram a sua eficácia em relação a parte econômica e, conseqüentemente, energética. O design do trabalho no uso de reatores com contínua retirada de água do processo, com intuito de manter o equilíbrio reacional e aumentar o rendimento catalítico. As simulações realizadas em Aspen Plus mostraram que o uso de excesso de metanol acarreta na diminuição da conversão e em uma concentração de DMC menor do que 1,5mol%. Além disso, devido à baixa seletividade, a purificação dos produtos presentes no reator demandava alta energia (13,61kWh/kg DMC) e alto custo, o que não tornaria o processo viável. Assim, concluíram que o estudo em torno do uso das membranas e remoção de água durante o processo pode ocasionar o aumento da seletividade e, conseqüentemente, diminuir os custos calculados, uma vez que não seria necessária outra etapa de purificação de DMC.

Yu, Chen e Chien (2018)[93] usaram ferramenta de simulação para avaliar a conversão de CO₂ a DMC. Em relação a avaliação econômica, duas conclusões foram retiradas do trabalho. Uma delas é que o desempenho econômico é muito influenciado pela flutuação dos preços. Já a outra, envolve a aplicação dos reatores e custos envolvidos na obtenção dos mesmos, podendo proporcionar uma melhora significativa no desempenho econômico geral. Uma forma de melhora do desempenho econômico é o estudo de diferentes catalisadores e agentes desidratantes que ultrapassem o obstáculo termodinâmico da reação, favorecendo a síntese de DMC e diminuindo etapas de purificação que encarecem sua produção.

3.4. Dietilcarbonato (DEC)

O dietilcarbonato, da família do dialquilcarbonato, é um dos mais importantes produtos químicos verdes dos ésteres de carbonato, também chamado de carbonato de etila [94]. É um líquido incolor e transparente em condições normais e, possui perfil toxicológico brando[13]. Algumas propriedades do DEC estão resumidas na Tabela 3.1.

Tabela 3.1 Propriedades físicas do dietilcarbonato[95].

Ponto de fusão	-43 °C
Ponto de ebulição	126–128 °C
Densidade	0.975 g/cm ³
Ponto de fulgor	25 °C
Solubilidade em água	Insolúvel
Toxicologia	Levemente tóxico

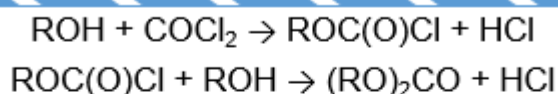
Além disso, quando comparado ao DMC, o DEC apresenta menor volatilidade e maior coeficiente de distribuição gasolina/água, tornando-o um excelente aditivo de combustível [96]. O DEC pode ser usado em lubrificantes, na indústria de cosméticos, em produtos farmacêuticos e como eletrólito em baterias de íon de lítio [97], [98]. Ainda, pode ser usado como aditivo em óleo diesel, devido ao alto teor de oxigênio (~40%) [99]. O carbonato de etila ainda pode ser usado como agente de carbonilação e etilação devido a presença de grupos CH₃CH₂O e -CO- [100].

3.4.1. Principais rotas para produção de dietilcarbonato (DEC)

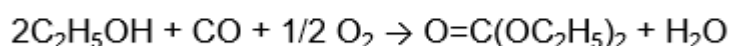
O uso de fosgênio (COCl₂) e etanol é o método mais antigo de produção de DEC, sendo relatado seu uso em 1941 [16]. Porém, atualmente, o processo de fosgenação está sendo abandonado devido ao uso de gases corrosivos de cloro e excesso de piridina, gerando grandes quantidades de sais residuais de NaCl [101].

Levando em consideração os princípios da química verde, que usa produtos mais seguros à saúde e ao meio ambiente, rotas livres de fosgênio para síntese de DEC foram apresentadas e tomaram a atenção da comunidade científica. Entre as mais destacadas temos as apresentadas na Figura 3.12.

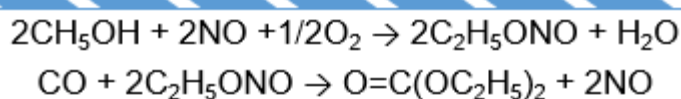
Fosgenação do etanol



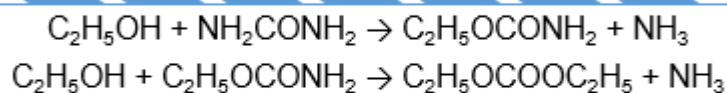
Carbonilação oxidativa do etanol



Carbonilação de nitrato de etila



Etanólise catalítica da ureia



Síntese direta de CO₂ e etanol

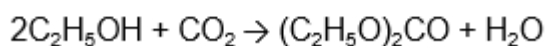


Figura 3.12. Rotas de síntese de DEC. Adaptado de [95].

A carbonilação oxidativa do etanol é um método viável e promissor para síntese de DEC, devido à alta seletividade do produto [102]. A reação pode ocorrer nas fases líquida e gasosa, porém possui dificuldades, como por exemplo, a difícil separação dos produtos e catalisadores na fase líquida, assim como a corrosão dos equipamentos em ambas as fases [103].

As reações oxidativas usando nitratos de alquila como agente oxidante foram desenvolvidas em 1980 pela *Ube Industries Ltd*, no Japão [104]. Os substratos, como CO e/ou compostos insaturados e/ou carbonilados são oxidados pelo nitrato de alquila, usando catalisador de paládio e na ausência de oxigênio [105].

Dentre as sínteses citadas, o uso da ureia tem sido um processo industrial tradicional para a utilização de dióxido de carbono. Ureia é barato, amplamente disponível e, portanto, foi pensado como uma rota potencial para a síntese de

compostos orgânicos, como os carbonatos. Existem várias vantagens nesse processo, como baixo custo de matérias-primas, nenhuma formação azeotrópica entre álcool e água, bem como fácil separação e purificação do produto. Entretanto, ainda é necessário avaliar o uso de catalisadores que apresentem melhor atividade e, além disso, os parâmetros cinéticos e termodinâmicos precisam ser analisados e otimizados para tornar a rota comercializável [24].

Já a síntese direta de DEC vem sendo estudada como a mais promissora, devido ao uso direto de CO₂ e etanol, sem formação de compostos intermediários durante o processo, porém, assim como no uso da ureia, a reação não ocorre de forma espontânea [24].

3.4.2. Rota alternativa para produção de DEC: síntese direta de DEC

A síntese direta de DEC vem ganhando enorme interesse devido a sua importância comercial e ambiental [106]. Além disso, o etanol utilizado na reação é altamente abundante, não tóxico, mas, em comparação ao metanol, é menos ácido e, portanto, menos reativo[24].

Além de ser sustentável, devido ao uso de CO₂, reduzindo sua emissão, também utiliza o etanol, proveniente de fonte renovável, por processo fermentativo nas biorrefinarias [107]. A reação de síntese direta de DEC, assim como na síntese de DMC, forma água como produto e desloca o equilíbrio da reação para os reagentes, diminuindo os rendimentos de DEC. Devido a esses problemas, o uso de sistemas catalíticos diferenciados e otimização dos parâmetros de síntese vem sendo estudados [108], [109].

A síntese direta de DEC utilizando o catalisador bimetálico Cu-Ni ocorre segundo a Figura 3.13. Primeiramente, o catalisador (M) origina C₂H₅O⁻ proveniente do etanol, depois o CO₂ é ativado e forma espécies CO₂-M. Os grupos C₂H₅O⁻-M e CO₂-M interagem transformando-se no complexo M-O(C₂H₅)-C(O)-M e, por fim, outra molécula de etanol ativada reage com o complexo formado e produz DEC e sítios M são regenerados [110].

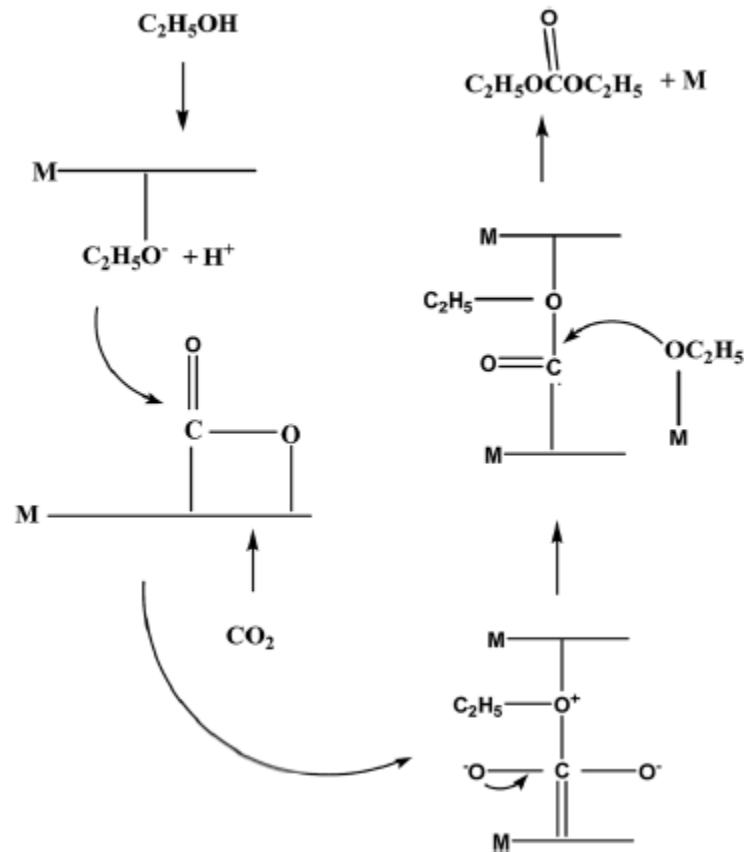


Figura 3.13. Reação direta de etanol, CO_2 e catalisador para formação de DEC[111].

3.4.3. Catalisadores homogêneos e heterogêneos na síntese direta de DEC

Catalisadores para a síntese direta de DEC vem sendo estudado nos últimos anos, sejam eles heterogêneos ou homogêneos [13], [24], [103], [109], [112], [113]. Catalisadores Cu-Ni suportados em carvão ativado mostraram-se mais ativos para a síntese de DEC do que os catalisadores monometálicos. Em condições experimentais da reação (90 °C e 13 bar) os maiores rendimentos obtidos foram com razão molar Cu-Ni de 3:1 e 2:1 [111].

O uso de CeO_2 sintetizado pelo método de precipitação foi usado para avaliar os parâmetros na síntese de catalisadores e tempos reacionais, chegando a conclusão de que quando sintetizado em pH 11, apresenta melhores resultados de produção de DEC [114].

Na Tabela 3.2 são mostrados diferentes catalisadores e seus respectivos rendimentos na síntese de DEC.

Tabela 3.2. Rendimento de diferentes catalisadores na síntese de DEC [115].

Catalisador	Rendimento de DEC (mmol)
ZrO₂	0,150
La₂O₃	0,003
Nu₂O₃	0,004
K₂O/ZrO₂	0,005
H₃O₄₀PW₁₂.xH₂O	0,007
H₃O₄₀PMO₁₂.xH₂O	0,008
H₃O₄₀PW₁₂/ZrO₂	0,063

3.4.4. Agentes desidratantes na síntese de DEC

A água é um dos produtos de muitas reações que utilizam catalisadores e sua presença pode inibir a reação catalítica devido a limitação do equilíbrio termodinâmico [116]. Nas reações reversíveis de conversão de CO₂, nas quais há produção de água, a conversão acaba sendo limitada devido a desativação dos catalisadores [117]. Segundo o princípio de Le Chatelier, a remoção da água *in situ* no reator pode ser um meio eficaz de deslocar o equilíbrio da reação para a formação de produtos, permitindo o aumento da conversão de CO₂ e produção de DEC [118].

O uso de peneiras moleculares é um excelente exemplo de agente desidratante, uma vez que seu uso acarreta numa melhora de até 2,5 vezes no rendimento de DEC juntamente com zircônia como catalisador. O tamanho do poro da peneira molecular e as propriedades ácido-básicas do catalisador foram os principais fatores responsáveis pelo sucesso da catálise [119].

O conhecimento das condições reacionais de interesse é essencial para seleção de um adsorvente como agente desidratante do processo. A temperatura de reação é um dos principais parâmetros de impedimento do uso de agentes

desidratantes, uma vez que necessita de altas temperaturas (~250 °C). Portanto, o adsorvente deve ter boa ação em temperaturas elevadas e excelente seletividade, além da estabilidade estrutural durante a síntese [120].

O óxido de butileno foi usado como agente desidratante na síntese direta de DEC, assim como em DMC, e mostrou resultados satisfatórios, uma vez que, com uso de CeO₂ como catalisador o rendimento de DEC aumentou 9 vezes em comparação à reação sem a presença de agente desidratante [121]. Acetronila e aminas também foram usadas como agentes desidratantes, entretanto, produtos complexos foram formados durante a síntese diminuindo drasticamente a seletividade de DEC dificultando a purificação do produto [85], [122].

Diversas rotas de síntese de DMC e DEC podem ser realizadas, assim como alterações e otimizações processuais com intuito de aumentar o rendimento e a seletividade do produto. Dentre as possíveis mudanças reacionais, temos a aplicação de agentes desidratantes e, também, a utilização de catalisadores heterogêneos, os quais agem diferentemente na síntese dos carbonatos. Apresentada a necessidade e relevância do tema abordado, as metodologias e resultados conseguintes focam na melhora das condições reacionais para aumento de rendimento e seletividade da síntese de DMC.

4. MATERIAIS E MÉTODOS – RESULTADOS E DISCUSSÕES

4.1. ARTIGO 1

Inicialmente serão reportados os resultados já publicados no artigo intitulado “*Dehydrating agent effect on the synthesis of dimethyl carbonate (DMC) directly from methanol and carbon dioxide*” (coloca o DOI aqui) publicado no periódico científico “*RSC Advances*”, que integra o trabalho de doutorado.

O artigo descreve a síntese direta de DMC utilizando CH_3OK como catalisador e CH_3I como promotor. Além disso, avalia o uso de um compartimento no reator para acomodar peneiras moleculares, com intuito de retirar a água da parte gasosa do meio reacional. Sendo assim, o trabalho avaliou o uso de peneiras na parte gasosa e na parte líquida visando a síntese direta de DMC, e, analisou a combinação de peneiras na parte gasosa com demais agentes desidratantes na parte líquida (2,2-dimetoxipropano, sulfato de sódio, óxido de magnésio e óxido de butileno). Como resultado, o uso de peneiras na fase gasosa combinadas com DMP na fase líquida gerou uma conversão de metanol de 48,6% e seletividade de 88%, em condições de 80 °C de temperatura, 40 bar de pressão e tempo de 24 horas.

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Dehydrating agent effect on the synthesis of dimethyl carbonate (DMC) directly from methanol and carbon dioxide

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CO₂ emissions and global warming have increased with the growth of the world economy and industrialization. Direct synthesis of dimethyl carbonate (DMC) from CO₂ and methanol (CH₃OH) has been considered a promising route from a green chemistry point of view due to global warming mitigation by CO₂ emission reduction. However, DMC yield, when obtained by direct synthesis, is limited due to unfavorable thermodynamics and catalyst deactivation by water formation in the reaction process. This problem motivated us to investigate the effect of dehydration on DMC production by direct synthesis. Herein, different dehydrating agents (2,2-dimethoxypropane, sodium sulfate, magnesium oxide and butylene oxide) were combined with molecular sieves to remove the water and minimize the reverse reaction. A new reactor presenting a compartment to accommodate molecular sieves in the gas phase was developed as well. The chemical/product analysis was carried out by gas chromatography and the results were used to calculate methanol conversion and DMC selectivity. The highest methanol conversion value was found for the combination of molecular sieves in the gas phase with 2,2-dimethoxypropane in the reaction liquid phase (methanol conversion = 48.6% and 88% selectivity). The results showed that dehydration systems may promote increased yield in direct DMC synthesis under mild conditions. The dehydration systems tested in this work exhibited excellent conversion and yield as compared to other reported studies.

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1. Introduction

The growth of the world economy allied to human and industrial activities is the main origin of the increase in CO₂ emission in the atmosphere.¹ CO₂ emission reached 24 Gt in 1995, growing about 1% a year from 1990 to 1999 and arriving at 35 Gt in 2015. The CO₂ level is expected to reach 40 Gt in 2020, growing 2.0% by year over the decade.² This scenario corroborates the need for exploring new ways of using CO₂ as a raw material in innovative industrial processes obtaining high added value products and reducing the environmental impact.³ Direct synthesis reactions from CO₂ and alcohol producing organic carbonates, such as dimethylcarbonate (DMC) are being investigated.⁴ Alkyl carbonate production allows the use of excess CO₂ generating low toxicity, biodegradable and non-corrosive products.⁵

DMC is an important carbonate being used in several niches, such as intermediate in polycarbonate production for building utilization, medical devices, automobiles and electrolytic solvent in lithium batteries due to the high dielectric constant. Yet, due to the high oxygen composition (53%) and octane number (105) dimethyl carbonate has been described as an excellent diesel additive reducing the emission of soot particles and, consequently, the environmental impact.⁶ Methyl *tert*-butyl ether (MTBE) is used as additive in fuels, however, several countries are banning its use due to the generated environmental impacts. Therefore, DMC comes as a substitute, since, in the concentration of 40% (v/v) in relation to the MTBE concentration achieves the same effectiveness as MTBE reducing waste generation by 50%.^{7–10}

Industrial production of DMC is environmentally friendly, however the Gibbs energy for DMC production by direct reaction is greater than zero. Reaction equilibrium constant around 10⁻⁵ indicates that the formation reaction does not occur spontaneously. DMC synthesis has traditionally occurred through three routes. In the first, DMC is synthesized from phosgene and methanol (phosgene method) having a high environmental impact.¹¹ The second route uses methanol, oxygen and carbon monoxide (oxidative carbonylation)

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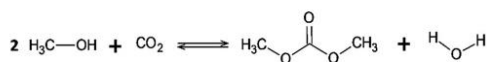


Fig. 1 DMC direct synthesis.

presenting an inherent health and safety risk by using CO as reagent in addition to the high process and feedstock cost.^{12–14} The third route uses dimethyl sulfate and sodium carbonate (transesterification method), products from the oil refinery, presenting the highest total cost per DMC produced.^{13,15} In addition to the traditional methods, DMC can be obtained by direct synthesis using carbon dioxide and methanol. This route provides the lowest total cost per DMC produced and safer chemicals besides a favorable carbon balance. The main drawback of DMC direct synthesis is the low yield and selectivity.^{13,14} Therefore, to improve yield and selectivity in DMC direct synthesis modelled reactors, changes in pressure and temperature and the use of techniques for directing the equilibrium constant for product formation must be evaluated.¹⁶ In addition, DMC direct synthesis from methanol and CO₂ produces water as a by-product (see Fig. 1), decreasing yield by directing the reaction balance towards reagents.^{17,18}

This scenario evidences the need of assessing efficient dehydrating agents for the removal of water produced during reaction, consequently improving DMC yield. Several dehydrating agents have been investigated for DMC synthesis.^{11,12} Among investigated dehydrating agents molecular sieves can be highlighted due to their large surface area, thermal stability and excellent adsorption.¹³ Organic and inorganic dehydrating agents, such as 2,2-dimethoxypropane (DMP) and magnesium oxide, are also described as efficient water withdrawn agents during DMC synthesis increasing product yield.^{14,15}

The main goal of this work is to evaluate a new dehydration system for direct DMC synthesis using CH₃I as promoter, CH₃OK as catalyst. In this new designed system, molecular sieves were tested in the reaction liquid phase and in the gas phase. Yet, a combination of organic and inorganic dehydrating agents (2,2-dimethoxypropane, sodium sulfate, magnesium oxide and butylene oxide) in liquid phase and molecular sieve in the gas phase were tested as well.

2. Methodology

2.1 Materials

Methanol (>99.9% – EMSURE®), potassium methoxide (>95% – ALDRICH), iodomethane (>99.5% – ALDRICH), diethyl ether (>99.9% – EMSURE®), magnesium oxide (98% – ALDRICH), 2,2-dimethoxypropane – DMP (98% – ALDRICH), sodium sulfate (>98% – ALDRICH), dimethylcarbonate – DMC (>99.5% – ALDRICH), pearl-shaped molecular sieves (3A – ALDRICH), butylene oxide (99% – ALDRICH) and CO₂ (99.8% – White Martins).

2.2 DMC synthesis

Two 120 ml reactors (made of titanium alloy) with constant magnetic stirring were used to perform the experiments (see

Fig. 2). Temperature was controlled by means of a thermocouple connected to a temperature controller and kept constant using a resistive thermal band in both reactors. A reactor was equipped with a compartment metallic support in the gas phase filled with molecular sieves (see Fig. 2A). For a typical reaction 213 mmol of methanol, 10 mmol of CH₃OK, 20 mmol of CH₃I, the desired dehydrating agent and 40 bar of CO₂ were used. Reactions were carried out using different dehydrating agents (molecular sieve, 2,2-dimethoxypropane, sodium sulfate, magnesium oxide and butylene oxide) added direct to the liquid phase or by combining a molecular sieve placed in the gas phase with dehydrating agent added in the liquid phase. The reactor was pressurized with CO₂ at 40 bar and heated at 80 °C. Reaction time ranged from 6 h to 30 h. At the end of the reaction, the reactor was cooled to room temperature and slowly depressurized. The new reactor designed in this work (Fig. 2) contains an apparatus in the upper part to supporting the molecular sieves (A) capturing water in the gaseous phase. As a way of comparison of the results for the DMC synthesis using the new reactor and the already described process the sieves were also tested in the liquid part (B). Yet, the use of molecular sieves in the gaseous phase combined with different dehydrating agents in the liquid phase in the DMC obtainment reaction by direct synthesis will also be tested using the system described in Fig. 2A.

In order to compare the results a reaction without dehydrating agent was also performed. All tests were performed in triplicate. The products of catalytic tests were analyzed by gas chromatography (GC) in order to determine yield, conversion and selectivity. Gas Chromatograph Shimadzu GC-2014 equipped with SH-Rtx-5 column using a heating ramp of 31 °C for 0.5 minutes, 10 °C min⁻¹ to 50 °C for 1 minute, 20 °C min⁻¹ to 100 °C for 2 minutes and 50 °C min⁻¹ to 220 °C for 2 minutes. Samples were diluted with a concentration of 4% (v/v) in ethyl

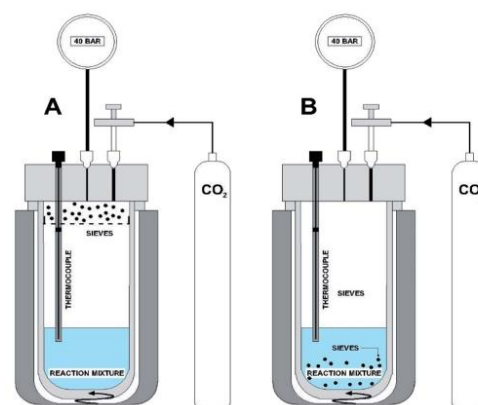


Fig. 2 Scheme of experimental apparatus: (A) reactor 1 equipped with a compartment to accommodate molecular sieves in the gas phase; (B) reactor 2 used to add molecular sieve and/or dehydrating agent in the liquid phase.



ether and the peak area of DMC (2.4–2.7 minutes) was used to define the concentration through the calibration curve of pure DMC following procedures described by Valente, Riedo and Augusto (2003).²³ Conversion and selectivity were performed as described by Chen *et al.* (2012).²⁰

Methanol conversion was calculated using eqn (1).

$$\text{Methanol conversion (\%)} = \frac{(\text{Methanol reacted})}{(\text{Methanol total})} \times 100 \quad (1)$$

where methanol reacted (mol) = 2 × DMC produced (mol).

DMC selectivity was obtained by eqn (2).

$$\text{DMC selectivity (\%)} = \frac{(\text{DMC})}{(\text{DMC} + (\text{by-products}))} \times 100 \quad (2)$$

DMC yield was determined using eqn (3).

$$\text{DMC yield (\%)} = \frac{(\text{Methanol conversion (\%)} \times (\text{DMC selectivity (\%))})}{100} \quad (3)$$

In addition, water content was determined (in triplicate) using the Karl Fischer test by digital automatic titration equipment with the Karl Fischer solution.

2.3 Statistical analysis

Minitab 18 Statistical Software-ANOVA was used to perform statistical analysis in order to assess the standard deviation of tests performed in triplicate and analyze the Tukey test with 95% reliability, where equal letters show statistical equality between the samples averages.

3. Results and discussion

3.1 Direct synthesis of DMC using molecular sieve (3A) and combination of dehydrating agents

Thermodynamic limitations and/or catalyst deactivation due to water formation during DMC direct synthesis makes this

reaction unfavorable resulting in low DMC yield.^{5,24,25} Aiming to evaluate the effect of dehydrating agents (chemical or physical) on the yield of DMC obtained by direct synthesis reaction CH₃OK was used as catalyst and CH₃I as promoter. Table 1 presents methanol conversion, DMC selectivity and DMC yield values, reaction parameters and Tukey test results used to evaluate statistical equality between samples (see letters a to g in conversion column, Table 1).

One of the acceptable mechanisms for DMC direct synthesis from CO₂ and methanol (CH₃OH) using CH₃OK as catalyst and iodomethane CH₃I (Table 1, entry 1) is shown in Fig. 3. CH₃I can act as reaction promoter or as a reagent.²⁶ In this mechanism the hydrogen of the methanol hydroxyl is abstracted by the catalyst producing a methoxy anion, which reacts with CH₃I or CO₂, forming dimethyl ether or methyl carbonate anion which successively reacts with CH₃I to form DMC. The iodine anion formed during the reaction steps reacts with the proton recycling the catalyst. Produced HI reacts with methanol recovering the CH₃I.²⁶

Results obtained in this work suggest that CH₃I may be acting as a promoter as no selectivity reduction was observed by gas chromatography when only CH₃I and CH₃OK were used (Table 1, entry 1).

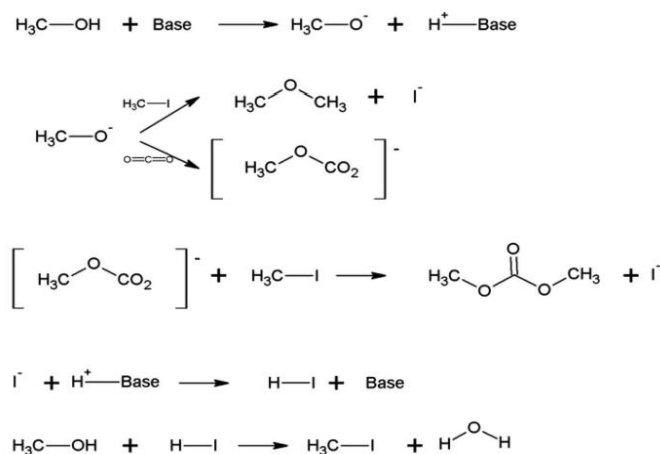
The catalytic system employed by Cai *et al.* 2005 (ref. 27) using CH₃OK (catalyst) and CH₃I (promoter) in the direct synthesis of DMC from CO₂ was selected to evaluate the efficiency of dehydrating agents. In this work, catalyst content and reactor size were different from that used by Cai *et al.* (2005).²⁷ The reaction described in literature obtained a yield of ~9.7% with 100% of selectivity using reaction conditions of 80 °C, 40 bar and 6 h of reaction time. Different catalyst content and promoter combined with the use of a smaller reactor may explain the lower yield (see entry 1, Table 1) when using the same catalyst system reported by Cai *et al.* (2005).²⁷ The use of different amounts (1.0–3.0 g) of molecular sieves in the liquid phase demonstrated to be effective when compared to the reaction carried out without the presence of dehydrating agent

Table 1 Methanol conversion, DMC selectivity, DMC yield and parameters for reactions using sieves in the liquid and gaseous part with standard deviation values^a

Entry	Sieve		Dehydrating agent	Time (h)	Temperature (°C)	Pressure (bar)	DMC selectivity (%) [*]	Methanol conversion (%) ^{**}	DMC yield (%) ^{***}	Water (%)
	Phase	(g)								
1	—	0	—	24	80	40	100	7.0 ± 1.6 ^{f,g}	7.0 ± 1.6	7.1 ± 0.1
2	Liquid	1	Sieve	24	80	40	100	13.6 ± 1.9 ^d	13.6 ± 1.9	3.7 ± 0.1
3	Liquid	2	Sieve	24	80	40	100	17.2 ± 1.1 ^{c,e}	17.2 ± 1.1	1.6 ± 0.1
4	Liquid	3	Sieve	24	80	40	100	9.3 ± 0.7 ^f	9.3 ± 0.7	1.5 ± 0.3
5	Gas	1	Sieve	24	80	40	100	7.0 ± 0.7 ^g	7.0 ± 0.7	3.3 ± 0.2
6	Gas	2	Sieve	24	80	40	100	30.5 ± 2.3 ^a	30.5 ± 2.3	0.5 ± 0.1
7	Gas	3	Sieve	24	80	40	100	8.7 ± 0.5 ^f	8.7 ± 0.5	4.5 ± 0.1
8	Gas	2	Sieve	6	80	40	100	9.7 ± 1.2 ^f	9.7 ± 1.2	2.5 ± 0.1
9	Gas	2	Sieve	12	80	40	100	14.3 ± 0.7 ^d	14.3 ± 0.7	2.6 ± 0.2
10	Gas	2	Sieve	18	80	40	100	16.1 ± 0.4 ^e	16.1 ± 0.4	3.9 ± 0.8
11	Gas	2	Sieve	30	80	40	100	26.2 ± 0.8 ^b	26.2 ± 0.8	6.1 ± 1.2

^a Fixed parameters → methanol: 213 mmol; catalyst (CH₃OK): 10 mmol; promoter (CH₃I): 20 mmol. *: eqn (1); **: eqn (2); ***: eqn (3) described in Methodology section.



Fig. 3 Proposed mechanism for CH_3I reaction in DMC synthesis.

(entry 1, Table 1: yield = 7.0%), as statistically proved by the Tukey test represented in Table 1 by unequal letters. The highest DMC yield was obtained using 2.0 g of molecular sieves (entry 3, Table 1: yield = 17.2%) followed by reaction yields obtained with 1.0 g (entry 2, Table 1: yield = 13.6%) and 3.0 g (entry 4, Table 1: yield = 9.3%) of molecular sieve respectively. The use of molecular sieve reduced the water content from 7.1% to 3.7% (entry 2, Table 1: 1.0 g of molecular sieve), 1.6% (entry 3, Table 1: 2.0 g of molecular sieve) and 1.5% (entry 4, Table 1: 3.0 g of molecular sieve). These results indicate that increasing the amount of molecular sieve in the liquid phase from 2.0 to 3.0 g can hinder the interaction of reagents with the catalytic active sites reducing catalytic activity. The use of 1.0 g of molecular sieve may not be sufficient to remove the formed water and achieve optimal yield values.

Surprisingly tests performed with molecular sieve in the gas phase showed an increase of more than 300% when using 2.0 g of molecular sieve (entry 6, Table 1: yield = 30.5%), 22%, 3.0 g (entry 7, Table 1: yield = 8.7%) and 0%, 1.0 g (entry 5, Table 1: yield = 7.0%) when compared to the reaction without molecular sieve addition (entry 1, Table 1, yield = 7.0%). Increasing molecular sieve content from 1.0 g (entry 5, Table 1: water = 3.3%) to 2.0 g (entry 6, Table 1: water = 0.5%) significantly reduced the water content present in the reaction medium. However, increasing molecular sieve content from 2.0 g (entry 6, Table 1: water = 0.5%) to 3.0 g (entry 6, Table 1: water = 4.5%) increased the water content present in the reaction medium. This result indicates that the increase in molecular sieve content is probably reducing the contact surface of molecular sieves with water vapor due to the sieves agglomeration in the reactor metallic support. These results are corroborated by the

Table 2 Methanol conversion, DMC selectivity, DMC yield, water content and reactions parameters using molecular sieves in the gas phase and dehydrating agents in the liquid phase, with standard deviation values^a

Entry	Sieve Phase	Sieve (g)	Dehydrating agent	Temperature (°C)	Pressure (bar)	DMC selectivity (%) [*]	Methanol conversion (%) ^{**}	DMC yield (%) ^{***}	Water (%)
1	—	—	DMP	80	40	55	6.4 ± 0.9 ^c	3.5 ± 0.9	0.6 ± 0.1
2	—	—	Na ₂ SO ₄	80	40	100	5.0 ± 1.4 ^{c,d}	5.0 ± 1.4	1.1 ± 0.3
3	—	—	Butylene oxide	80	40	ND	ND ^b	ND	Traces
4	—	—	MgO	80	40	ND	ND ^b	ND	Traces
5	Combined-gas	2	Sieve/DMP	80	40	88	48.6 ± 1.9 ^a	42.8 ± 1.9	0.6 ± 0.1
6	Combined-gas	2	Sieve/Na ₂ SO ₄	80	40	100	14.8 ± 2.0 ^e	14.8 ± 2.0	2.3 ± 0.2
7	Combined-gas	2	Sieve/butylene oxide	80	40	15	2.5 ± 1.4 ^{c,d}	0.3 ± 1.4	2.3 ± 0.8
8	Combined-gas	2	Sieve/MgO	80	40	100	4.5 ± 0.9 ^c	4.5 ± 0.9	0.7 ± 0.1

^a Fixed parameters → methanol: 213 mmol; catalyst (CH₃OK): 10 mmol; promoter (CH₃I): 20 mmol; dehydrating agent: 10 mmol; time: 24 hours. ND = not detected. *: eqn (1); **: eqn (2); ***: eqn (3) described in Methodology section.





Fig. 4 Gradual dehydration reaction between DMP and water during DMC synthesis.

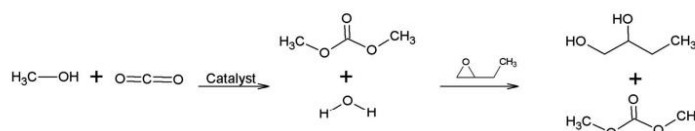


Fig. 5 Direct synthesis of DMC in the presence of butylene oxide as a dehydrating agent.

Tukey test. It should also be emphasized that the use of molecular sieves in the gas phase facilitates the dehydrating agent separating process from the reaction mixture reducing cost and steps in DMC production process.

Effect of reaction time on DMC yield when molecular sieves are used in the gaseous phase was also evaluated. In 6 hours of reaction time a yield of around 9.7% (entry 8, Table 1) was achieved. This result is similar to Cai *et al.* (2005)²⁷ founds using the same reaction conditions. However, after 6 hours an increase in DMC production was observed. Yield of 14.3% (entry 9, Table 1) was achieved in 12 h, 16.1% (entry 10, Table 1) 18 hours and the highest yield value of 30.5% (entry 6, Table 1) in 24 hours. After the 24 hour period, a small decrease in the amount of DMC yield was observed reaching 26.2% (entry 11, Table 1). According to literature,²⁸ water withdrawal from the reaction medium has great interference in the DMC synthesis optimization time since smaller amount of water allows greater catalytic activity and catalyst durability. From these results one can infer that the molecular sieve porosity improved catalytic activity and increased DMC production by withdrawing the water produced during the reaction. Therefore, probably after 24 hours of reaction time the molecular sieve become less effective decreasing reaction yield. The use of 2.0 g of molecular sieve in the gas phase for 24 hours was the best result for the experimental conditions tested. Therefore, it was used in combination with other dehydrating agents in the liquid phase (DMP, Na₂SO₄, MgO and butylene oxide) aiming further yield improvement as shown in Table 2.

DMP was evaluated as dehydrating agent (Table 2, entry 1) due to its quick action by chemical hydrolysis making it easy to use in dehydration processes. In addition DMP is stable during storage.²⁹ As seen in Fig. 4 acetone is produced as by-product decreasing reaction selectivity.^{21,22}

Butylene oxide is an effective dehydrating agent promoting an increase in product conversion due to the excellent dehydration capacity into the reaction medium.³⁰ When reacting with water, produces ethylene glycol decreasing DMC selectivity due to by-product formation,³¹ as show in Fig. 5.

When combining molecular sieve with dehydrating agents different yield values were obtained (DMP 42.8% (entry 5, Table 2), Na₂SO₄ 14.8% (entry 2, Table 2), MgO, 4.5% (entry 4, Table 2)

and 0.3% butylene oxide (entry 3, Table 2)). Although the addition of solid dehydrating agent (Na₂SO₄ or MgO) in the liquid phase promotes the reduction of the amount of water formed in the reaction medium the presence of these compounds may be reducing the interaction between the reactants and the catalyst active sites. Yet, the use of DMP decreases selectivity due to the ketone production in the reaction medium, consequently decreasing yield. However, even with this setback the yield is superior when using this system. Ketone removal step, by distillation, can be added to the process in order to improve selectivity increasing it to 100%.^{19,32}

Butylene oxide decreased DMC selectivity by 15%, reaching a methanol conversion of 2.5% being inefficient. So, it is clear from results that the best performance was obtained by combining the molecular sieve and DMP resulting in a yield increase of almost 50% when compared to the reaction performed using only molecular sieve in the gaseous phase (entry 6, Table 1). The dehydrating agents DMP (entry 1, Table 2), Na₂SO₄ (entry 2, Table 2), butylene oxide (entry 3, Table 2) and MgO (entry 4, Table 2) were also evaluated. Obtained yield values were lower/similar when compared to the reaction carried without dehydrating agent (entry 1, Table 1: yield = 7.0%).

DMP (entry 1, Table 2) showed a methanol conversion value statistically equal when compared to the reaction carried without dehydrating agent (entry 1, Table 1). However, a reduction in selectivity of 55% was observed and attributed to acetone formation as a by-product. When using sodium sulfate a lower yield was achieved when comparing with the reaction without dehydrating agent addition. Sodium sulfate is an effective dehydrating agent for use at room temperature and is considered a slow-acting dehydrating agent. These features can influence the process of water removing from the reaction medium.^{33,34}

When using butylene oxide (entry 3, Table 2) and MgO (entry 4, Table 2) as dehydrating agent no methanol conversion was detected under the tested reaction conditions. When using butylene oxide as dehydrating agent and more drastic reaction conditions (150 °C and pressure of 90 bar) a methanol conversion of 11.7% was reached as described elsewhere.³¹ Magnesium oxide suffers a large dilation when retaining water. This



Table 3 Catalyst, promoter/dehydrating agent, temperature, pressure and DMC yield of different works

Entry	Catalyst	Promoter/dehydrating agent	Temperature (°C)	Pressure (bar)	DMC yield (%)	Literature
1	CH ₃ OK	CH ₃ I/sieves (gas phase)	80	40	30.5	This work
2	CH ₃ OK	CH ₃ I/sieves (gas phase) + DMP (liquid phase)	80	40	42.8	This work
3	Cu/Ce	—	140	50	1.6	Marciniak <i>et al.</i> (2019) ³⁸
4	Chitosan/IL	—	100	75	16.7	Tamboli <i>et al.</i> (2016) ³⁹
5	Cu-Ni/graphene	—	110	30	13.0	Deeratraku <i>et al.</i> (2020) ⁴⁰
6	K ₂ CO ₃ + EmimBr	CH ₃ I	80	73	5.7	Kabra <i>et al.</i> (2016) ⁴¹
7	CH ₃ OK	CH ₃ I	80	73	16.2	Fang and Fujimoto (1996) ³⁷
8	K ₂ CO ₃	CH ₃ I, DMP	140	200	12.0	O'Neil, Clayton and Mayeda (1969) ⁴²
9	CeO ₂	Molecular sieves (4A)	120	6	3.2	Zhang <i>et al.</i> (2015) ¹³
10	Dibutyltin dimethoxide	Molecular sieves (3A)	180	300	31	Choi <i>et al.</i> (2002) ²⁵
11	Dibutyltin dimethoxide	—	180	300	3	Choi <i>et al.</i> (2002) ²⁵
12	Cu/Ce	2-Cyanopyridine	140	50	5.0	Marciniak <i>et al.</i> (2019) ³⁸
13	Cu/Ce	Methyl trichloroacetate	140	50	12	Marciniak <i>et al.</i> (2019) ³⁸

feature can reduce the contact of reagents and catalyst favoring DMC synthesis.^{35,36}

Temperature and pressure range used for DMC synthesis described in literature (see Table 3) were varied from 80 °C to 140 °C and 6 bar up to 200 bar respectively. Our results, using mild conditions (80 °C, 40 bar) and molecular sieves placed in the gas phase or the combination of molecular sieve placed in the gas phase/DMP placed in the liquid phase were superior to results described in literature (see Table 3, entries 1 and 2). Molecular sieves effect on DMC yield obtained by direct synthesis was described elsewhere obtaining a yield up to 31% using dibutyltin dimethoxide (catalyst), high pressure (300 bar) and 180 °C of temperature (see Table 3, entry 10) using a facility that allow to place the dehydrating agent at room temperature and circulate the reaction mixture through the dehydration tube by a high-pressure circulation pump.²⁵ DMC synthesis using CH₃OK and CH₃I, without the presence of dehydrating agents, at a pressure of 73 bar and 80 °C of temperature was described achieving a conversion of 16.2% (ref. 37) (see Table 3, entry 7). Our results evidenced that the use of molecular sieves in the gas phase allied to DMP in the liquid phase increases DMC yield up to 42.8%. This yield value is superior when compared to current literature as seen in Table 3. Yet, a DMC yield of 30.5% was obtained when placing molecular sieves in the gas phase using mild temperature and pressure conditions (80 °C and 40 bar) as seen in Table 3, entry 1. The placement of the molecular sieves in the gas phase is somehow facilitating the water withdrawing besides being very important in terms of easiness of molecular sieve separation.

4. Conclusions

Different dehydrating agents (molecular sieve, 2,2-dimethoxypropane, sodium sulfate, magnesium oxide and butylene oxide) were evaluated in the DMC direct synthesis. Yet, a new

system for dehydration under mild conditions was proposed. The best results were obtained when 2.0 g of molecular sieve was placed in the gas phase (yield = 30.5%) or when 2.0 g of molecular sieve was combined in the gas phase with 10 mmol DMP in the liquid phase (yield = 42.8%). In the dehydrating system proposed in this work the sieves can be easily separated, since they are deposited in the gas phase and the acetone formed from the DMP can be easily separated from the reaction medium using the distillation technique. This catalytic system also achieved higher yield values when compared to other systems reported in literature for direct synthesis of DMC. Thus, the proposed dehydration system in this work may be an effective way to promote increase in DMC direct synthesis yield whereas can be used with different catalysts.

Conflicts of interest

There are no conflicts of interest to declare.

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4.2. ARTIGO 2

O artigo 2 foi publicado pela revista “*Journal of CO₂ Utilization*” intitulado “*Performance of supported metal catalysts in the dimethyl carbonate (DMC) production by direct synthesis using CO₂ and methanol*” (coloca o DOI aqui) , e suas metodologias e resultados são parte da tese de doutorado.

O artigo visa a síntese direta de DMC com uso de metais suportados em carvão ativado como catalisadores, sendo eles: AC-Fe, AC-Cu, AC-Mg e AC-Ni. Houve uma análise estrutural dos catalisadores suportados e, também do suporte puro, com intuito de explorar as alterações causadas pela impregnação dos metais na matriz do carvão. Visto que ocorreu a impregnação, foram realizados testes que mostraram a capacidade de síntese de DMC, com maior eficácia para o catalisador AC-Fe com rendimento de 23,5% e seletividade de 100% (80 °C, 40 bar e 24h). A fase experimental de otimização mostrou que 120 °C, 40 bar e 24h são as definições de variáveis que melhoram o desempenho catalítico, alcançando um rendimento de DMC de ~ 30% com uso de AC-Fe. Por fim, o reciclo dos sistemas catalíticos provou que a combinação de peneira molecular (fase gasosa) e AC-Fe (catalisador) manteve a seletividade em 100% e o rendimento diminuiu ligeiramente.



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Performance of supported metal catalysts in the dimethyl carbonate production by direct synthesis using CO₂ and methanol

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ABSTRACT

CO₂ chemical transformation is an exciting way to reduce CO₂ concentration in the atmosphere. The use of CO₂ to produce dimethyl carbonate (DMC), a linear, biodegradable, low toxicity carbonate via direct synthesis, is one of the most promising routes from the environmental point of view. However, DMC direct synthesis presents obstacles such as unfavorable thermodynamics and catalytic deactivation due to the water produced as a by-product. Therefore, the development and optimization of a catalytic system that can overcome these obstacles are crucial. This study investigated the catalytic activity of iron nitrate (AC-Fe), copper nitrate (AC-Cu), magnesium nitrate (AC-Mg), and nickel nitrate (AC-Ni) impregnated in activated carbon for DMC direct synthesis. Catalysts were synthesized by the impregnation method and characterized by several techniques. Simulation results evidenced the major reaction steps and simplified models of a complex involving metallic catalysts and reactants. The optimization of the catalyst amount, pressure, temperature, and recyclability of the best catalyst under optimized conditions and in the presence of different dehydrating agents was also performed. Results showed that the AC-Fe catalyst is the most efficient in the DMC direct synthesis, with a yield of 23.5 % and a selectivity of 100 % (80 °C, 40 bar, and 24 h). Reaction optimization (120 °C, 40 bar, and 24 h) using (AC-Fe) as catalyst resulted in a DMC yield of approximately 30 %. The catalytic systems recycling proved that using the dehydrating agent right combination (molecular sieve) and catalyst (AC-Fe) can maintain selectivity at 100 %, slightly decreasing yield.

1. Introduction

The application of carbon dioxide as a raw material in the chemical industries is vital from an environmental perspective. However, industrial processes using CO₂ as a starting material are few, mainly due to the large amount of energy required for its transformation [1]. Thus, some of the methodologies for transposing the CO₂ transformation into useful chemical products consist of using high-energy starting materials, such as hydrogen, unsaturated compounds, low-carbon, and organometallic rings. Also, choosing low-energy oxidized synthetic targets, such as organic carbonates, represents a crucial strategy [2,3]. Besides, in reactions to synthesize DMC, it is necessary to use a catalyst, which can be homogeneous, heterogeneous, or enzymatic. Promoting agents, such as iodomethane, can also be used [4,5].

Carbonates produced from CO₂ chemical transformation must be mentioned because they can selectively and efficiently replace hazardous reagents in organic processes [6,7]. Organic carbonates can be divided into two groups: linear carbonates (DMC and diethyl carbonate (DEC)); and cyclic carbonates: ethylene carbonate (CE), propylene carbonate (CP), butylene carbonate (CB), and glycerol carbonate (CG) [6–10]. Fig. 1 shows the structures of the main carbonates.

DMC is an essential chemical intermediate of easy degradability, high polarity, low viscosity, and toxicity used in various applications. For example, DMC is a raw material in polycarbonate synthesis, a widely used polymer in construction, automobiles, medical devices, and electrolyte solvent for lithium batteries due to its high dielectric constant and an environmentally friendly reagent for methylation and carbonylation [4,10–13].

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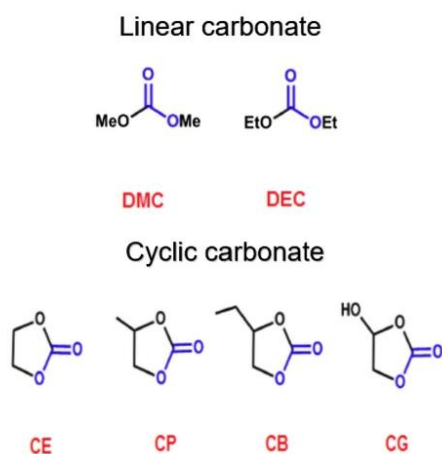


Fig. 1. Main linear and cyclic organic carbonates [9].

DMC can be synthesized by several routes, such as phosgene, transesterification, urea alcoholization, oxidative methanol carbonylation, and direct synthesis from methanol and CO₂ [11]. Phosgenation, oxidative carbonylation of methanol (oxycarbonylation) in a liquid phase, and transesterification processes reached industrialization. However, due to the high toxicity of the raw material (phosgene), the phosgenation route was discontinued. In contrast, DMC industrial production by oxycarbonylation and transesterification routes is a mature technology. The use of these routes in DMC production has some drawbacks, including the high toxicity of reagents and equipment corrosion [11,12,14].

To overcome these disadvantages, the direct synthesis of DMC is extensively studied to promote an increase in DMC yield and, at the same time, use non-toxic reagents that do not enable corrosion of tanks and other equipment [6,7,12,15–25]. Fig. 2 shows the scheme of the direct synthesis of DMC.

Homogeneous catalysts can produce DMC through direct synthesis. Among them are thallium (I) hydroxide, tin (IV) tetralkoxides, dialkyltin dialkoxides, bases, C/N-chelated organotin (IV) trifluoromethane sulfonates [4,12,26–34]. However, the use of homogeneous catalysts presents, as the central challenge, catalyst separation from the reaction medium. Therefore, heterogeneous catalysts, such as CeO₂ and ZrO₂ [7, 15], Ce_{0.5}Zr_{0.5}O₂ [31], Ce_{0.4}Zr_{0.6}O₂ [20], and Cu-CeO₂ can overcome this drawback [35].

In addition to using several kinds of catalysts, one can use catalytic supports, such as silica, activated carbon, alumina, among others [36]. The use of supports should be explored to increase DMC production yield due to the structural, chemical, and thermal properties that help catalytic activity [37]. One of the most studied supports is activated carbon. Oxygen-containing sites in the carbon's structure facilitate the adsorption of metal ions (catalysts). Besides, hydroxyls kept on inorganic supports tend to destabilize more easily impregnated catalysts, whose disruption does not occur with the use of activated carbon [36, 38]. Several studies have analyzed the use of activated carbon to support impregnation of the metal ions and concluded that the catalytic activity is increased by support porosity, allowing the reuse of supported

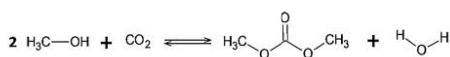


Fig. 2. Direct synthesis of DMC [4].

catalysts [39–41]. Thus, the support efficiency can be rated as follows: activated carbon > alumina > zeolite > silica [37].

Herein, we report the impregnation of different metals in activated carbon. The obtained samples were characterized and evaluated as catalysts in the DMC direct synthesis. The results from the simulation evidenced the main reaction steps providing simplified models for the metals-reactants complexes. The use of molecular sieves as dehydrating agents and iodomethane (CH₃I) as a promoter was also tested. The recycling of the best-supported catalyst was evaluated in the DMP synthesis using different dehydrating agents and sieves.

2. Methodology

2.1. Materials

Methanol (> 99.9 % - EMSURE®), iodomethane (> 99.5 % - ALDRICH), diethyl ether (> 99.9 % - ALDRICH), dimethyl carbonate - DMC (> 99.5 % - ALDRICH), activated carbon (CarboActiv G Plus Brascarbo- 325mesh), iron (III) nitrate nonahydrate (> 98.5 % - ALDRICH), copper (II) nitrate trihydrate (> 99.0 % - ALDRICH), nickel (II) nitrate hexahydrate (> 99.5 % - ALDRICH), magnesium nitrate hexahydrate (> 99.9 % - ALDRICH), pearl-shaped molecular sieves (3A - ALDRICH), 2,2-dimethoxypropane (98 % - ALDRICH) and CO₂ (99.8 % - White Martins).

2.2. Synthesis of metallic catalysts by the impregnation method in substrates

The catalysts were synthesized using the evaporation impregnation method [42]. This method consists of preparing a solution containing 10 g of the support material (activated carbon) and 1.7 g of different metal nitrates (iron, copper, magnesium, and nickel) in 250 ml of distilled water. Afterward, the solution is kept under constant agitation and at a temperature of 60 °C for 24 h; it is placed in an oven at 100 °C overnight and, finally, calcined at 600 °C for 3 h.

2.3. Characterization of supported metal ions

2.3.1. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed using a TA Instruments model Q600 equipment, ranging from room temperature to 1000 °C, with a heating rate of 20 °C/min under a synthetic air atmosphere. The calculation to determine the actual impregnation (%) of the metals in the activated carbon sample was carried out according to Eq. 1, where the difference among the metal impregnated carbon (ACX) sample weight and the weight of the pure carbon (AC) sample in the temperature range of 25–800 °C gives the percentage of impregnation [43].

$$\% = (\text{wt}\% \text{ACX } 25 - 800^\circ\text{C}) - (\text{wt}\% \text{AC } 25 - 800^\circ\text{C}) \quad (1)$$

2.3.2. Scanning electron microscopy with field emission (SEM-FEG)

Analysis of Scanning Electron Microscopy with Field Emission (SEM-FEG) was performed using FEI Inspect F50 equipment in the mode of secondary electrons (SE). The films were placed in a stub and covered with a gold foil.

2.3.3. BET

The specific surface area was calculated based on the Brunauer-Emmet-Teller (BET) method. The pore size and the pore volume were determined by the Barret-Joyner-Halenda method. Before all analysis, samples were degassed at 150 °C for at least 3 h.

2.3.4. FTIR-UATR

The chemical structures of supported catalysts and activated carbon were assessed by infrared spectroscopy technique using a Perkin - Elmer

100 Spectrum at wavenumber range 4000–650 cm⁻¹ with accessory UATR (universal attenuated total reflectance). All samples were analyzed in the form of powder.

2.3.5. XRD

The samples were placed in the sample holder of the Shimadzu model XRD 7000 (X-Ray Powder Diffraction) equipment and analyzed between 2 and 70 degrees (the region where the most intense peaks can appear). Copper k alpha radiation was used for analysis, and parallel geometry support was used for the surface analysis.

2.4. DMC synthesis

A 120 mL reactor (made of a titanium alloy) with constant magnetic stirring was used to perform the experiments. The temperature was controlled using a thermocouple connected to a temperature controller and kept steady using a resistive thermal band in both reactors. The reactor was equipped with metallic compartment support in the gas phase filled with molecular sieves [4]. For a typical reaction, 213 mmol of methanol, 0.7 g metal impregnated activated carbon, 20 mmol of CH₃I, 2.0 g of molecular sieves, and 40 bar of CO₂ were used. The reactor was pressurized with CO₂ at 40 bar and heated at 80 °C. At the end of the reaction, the reactor was cooled to room temperature and slowly depressurized.

The best-performance catalyst was used to optimize the temperature (80, 105, and 130 °C) and pressure (40, 45, and 50 bar) parameters in direct DMC synthesis. Finally, an analysis of 4 recycles was performed using the best catalyst supported on the activated carbon. After each reaction, the catalyst was washed several times in methanol and dried in an oven overnight. Catalyst reuse evaluation was performed using three different systems, namely A: 3A molecular sieve (dehydrating agent); B: DMP (dehydrating agent); C: molecular sieve (gas phase) combined with DMP (liquid phase), as described in previous work [4]. The reaction conditions were as follows: pressure: 40 bar; temperature: 120 °C; time: 24 h; 0.7 g of AC-Fe; 2.0 g molecular sieve; 10 mmol of DMP; 213 mmol of methanol; 20 mmol of CH₃I.

All reaction tests were performed in triplicate and analyzed by gas chromatography (GC) to determine yield, conversion, and selectivity [4]. The equipment used was the Gas Chromatograph Shimadzu GC-2014 with SH-Rx-5 column and the programming of 31 °C for 0.5 min, rate of 10 °C / min to 50 °C for 1 min, rate of 20 °C / min to 100 °C for 2 min and rate of 50 °C / min to 220 °C for 2 min. The samples were diluted with a concentration of 4 % (v/v) in ethyl ether and injected into the GC to determine the DMC peak area (2.4–2.7 minutes). The calculations performed to determine conversion, selectivity, and yield were achieved according to Faria et al. [4].

Methanol conversion was calculated using Eq. 2.

$$\text{Methanol conversion (\%)} = \left(\frac{\text{Methanol reacted}}{\text{Methanol total}} \right) * 100 \quad (2)$$

DMC selectivity was obtained by Eq. 3.

$$\text{DMC selectivity (\%)} = \left(\frac{\text{DMC}}{\text{DMC} + (\text{by-products})} \right) * 100 \quad (3)$$

DMC yield was determined using Eq. 4.

$$\text{DMC yield (\%)} = \left(\frac{\text{Methanol conversion (\%)} * \text{DMC selectivity (\%)}}{100} \right) \quad (4)$$

2.5. Statistical analysis

Minitab 18 Statistical Software-ANOVA was used to do statistical analysis to assess the standard deviation of tests performed in triplicate and analyze the Tukey test with 95 % reliability. Equal letters show statistical equivalence of the sample averages. Also, temperature and pressure parameters were optimized by analyzing the surface and contour graph.

2.6. Simulation methodology

Electronic-structure calculations and potential energy minimum search for multiple molecular structures were conducted using the GAMESS-US (2014) package of programs [44], Atomic Simulation Environment Toolkit (ASE) [45], Gabedit 2.8 [46], Visual Molecular Dynamics (VMD 1.9.1) [47], Avogadro [48], and in-home programs [49–51]. Molecular geometries corresponding to local-minimum structures (only positive vibrational frequencies) were subject to the calculation of thermochemical properties at different conditions.

The electronic structure of the simulated species was optimized by the hybrid density functional theory (M11 functional) [52] that includes dispersion interactions [53] and provides a generally decent quality of results in the case of organic moieties. The MIDI split-valence basis set [54] was used to construct molecular wave functions for every reactant and product. The electronic wave function convergence criterion was set to 1×10^{-3} kJ mol⁻¹. The steepest descent geometry optimization criterion was set to 0.5 kJ mol⁻¹ for potential energy surface investigation and to 0.05 kJ mol⁻¹ to derive thermochemical parameters. Frequency analysis was performed for optimized molecular structures, and the absence of negative frequencies in the profile was assured.

The Gibbs free energy of the reaction was calculated as a difference of the total Gibbs free energy of the products and the total Gibbs free energy of the reactants.

3. Results

3.1. Metal impregnated support characterization

3.1.1. TGA

Fig. 3 presents TGA analysis. All samples showed two stages of mass loss. In the first stage, moisture evaporation occurs (temperatures below 150 °C) [55–57], and AC presented the most significant loss of mass (18 %), followed by AC-Fe (14 %), AC-Ni (12 %) and, AC-Cu and AC-Mg (10 %). In the second degradation stage, the sample AC started the degradation at T = 420 °C, but the other impregnated metal-containing samples began the second degradation stage near T = 400 °C, which may be related to the loss of components from the lignin present in the coal [58]. The bare activated carbon (AC) sample showed a total mass loss of approximately 35.51 % due to structural decomposition. Samples mass loss were as follows: AC-Fe 17.13 %, AC-Cu (22.10 %), AC-Mg (27.34 %), and AC-Ni (29.48 %). Therefore, metals impregnation in the activated carbon is following the order: AC-Fe (18.38 ± 1.2 %) > AC-Cu (13.41 ± 0.7 %) > AC-Mg (8.17 ± 1.1 %) > AC-Ni (6.03 ± 0.9 %) in close agreement with ICP-OS analysis (see Table S1).

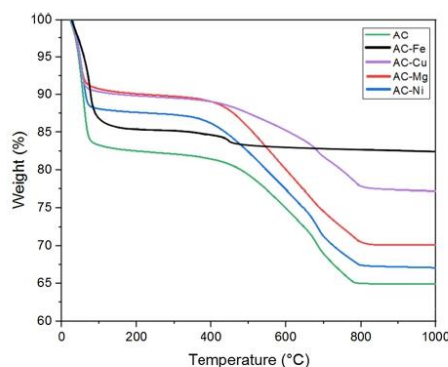


Fig. 3. TGA analysis of samples containing pure support and metals impregnated with activated carbon.

3.1.2. SEM-FEG

Different metal nitrates were impregnated in the activated carbon sample to evaluate their anchoring capacity with the support surface. Fig. 4 shows the SEM-FEG images of activated carbon (AC) and AC impregnated with different metals.

The micrographs of pure AC showed a surface with pores (mesopores/macropores/micropores). Such regions are essential because they serve to anchor metals on the support surface [59]. Activated carbon can be considered a very efficient support due to porous channels in its structure, facilitating metal impregnation [60]. Yet, dispersed and agglomerated particles in the activated carbon structure were observed in all samples. However, the anchoring of metals tends to occur more efficiently in the pores of the support structure, avoiding the anchored metal being leached as the catalyst is reused. EDS analysis for all samples is presented in Fig. S1 [61,62].

Metal insertion in the activated carbon porous cavities could cause changes in its structure [63]. One noticed particle agglomerates from the added metals in the impregnated activated carbon samples, indicating that the impregnation occurred satisfactorily [64–67]. The literature describes AC as a support with a relatively high surface area. Pore presence in AC is responsible for this morphological and structural characteristic facilitating CO₂ diffusion through the structure, benefiting its use when applied in catalysis [64,67,68].

3.1.3. BET

The specific surface area, pore-volume, and pore radius analysis are essential to determine the ability of the materials to impregnate the metal ions used as catalysts in the DMC direct synthesis [69,86]. Table 1 shows the specific surface area, pore-volume, and pore radius of synthesized samples analyzed by BET (Brunauer, Emmett, and Teller).

Activated carbon (AC) has a specific surface area value of 985 m²/g, a pore volume of 0.58 cm³/g, and an average pore radius of 1.5 nm. Yet, the N₂ adsorption-desorption isotherm (Fig. S2) is a type IV isotherm and type H4 hysteresis following Teng et al. [70]. The narrow hysteresis curve corresponds to the moderate presence of micropores in the material structure and a more important number of mesopores [71]. For all samples, metal impregnation promoted the increasing or maintenance of the pore radius, except for the case of copper impregnation, where we noticed an increase in the pore radius caused by the support structure disruption during impregnation [73,74]. A decrease in the AC-specific surface area and pore volume is expected due to metals impregnation in the micropores and deposition in the mesopores, causing channel

Table 1

Specific surface area, volume, and radius of pores of AC and impregnated iron nitrate (AC-Fe), copper nitrate (AC-Cu), magnesium nitrate (AC-Mg), and nickel nitrate (AC-Ni) samples.

Sample	BET (m ² /g)	Pore volume (cm ³ /g)	Average pore radius (nm)
AC	985	0.58	1.5
AC-Fe(NO ₃) ₃	620	0.48	1.6
AC-Cu(NO ₃) ₂	177	0.22	2.5
AC-Mg(NO ₃) ₂	797	0.57	1.5
AC-Ni(NO ₃) ₂	569	0.42	1.5

blockage that decreases the pore volume. This behavior agrees with SEM-FEG results, indicating metal impregnation in porous channels and deposition on the support surface [39,60,72].

3.1.4. FTIR

Fig. 5 presents FTIR spectra for the pure AC and AC-impregnated metal samples.

All samples showed bands around 3500 cm⁻¹ attributed to OH (hydroxyl) groups. The AC sample showed a band at 900–1200 cm⁻¹, attributed to silicon present in the activated carbon structure (Fig. S1) related to two types of bonds (Si–OH and C–O). The band at approximately 3333 cm⁻¹ for activated carbon indicates –OH bonds, and small bands at 1582 cm⁻¹ and 1192 cm⁻¹ C=C and C–O bonds, respectively [63,75–77].

For AC support impregnated with iron nitrate, bands close to 1550 cm⁻¹ and 1400 cm⁻¹ can indicate the presence of iron hydroxide particles, FeO(OH). Bands in the range of 701–709 cm⁻¹ indicate hematite (Fe₂O₃) formation due to the support structure-metal interaction. Bands at 1000–1200 cm⁻¹ show CO-type bonds present in the activated carbon support [78,79]. For AC-Cu, bands between 2100–2200 cm⁻¹ can indicate C–H, and small bands close to 3000 cm⁻¹ refer to the Cu–N bond [80]. A band around 1400 cm⁻¹ is attributed to the metal (copper) attached to the hydroxyl group [81,87].

In the case of magnesium nitrate, the metal is in its oxidized form. A small absorption band around 1635 cm⁻¹ refers to the Mg–NO₂ bond, vibrations of the carbonate groups on the surface were identified at 1384 cm⁻¹, and bands referring to MgO at 825 cm⁻¹ [82,83]. For the composite AC-Mg, the –OH and –CH bonds are seen at 3427 cm⁻¹ and 2921 cm⁻¹, respectively [84]. Vibration bands from carbonate groups of MgCO₃ appear at 1466, 1384, and 1124 cm⁻¹ [84,85]. The band of metal in the oxidized form appears in the range of 900–400 cm⁻¹ [85,

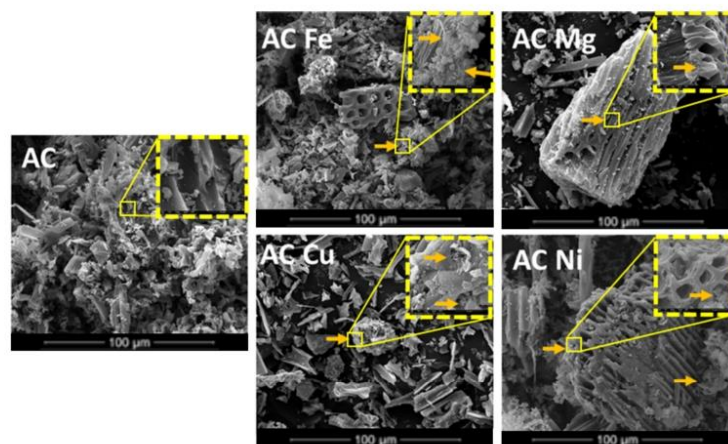


Fig. 4. MEV-FEG image of samples AC and AC-Fe, AC-Cu, AC-Mg, AC-Ni (augmentation 1000x and insert 10000x).

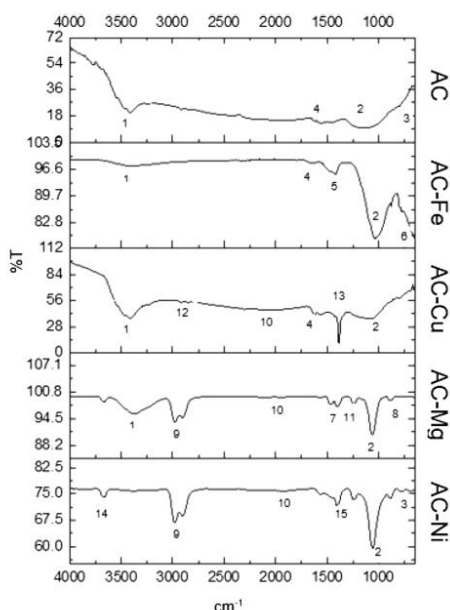


Fig. 5. FTIR spectra for pure and impregnated support with metals. ** caption □ 1: OH; 2: SiOH or C-O; 3: Si-O-Si; 4: C=C; 5: FeOOH; 6: Fe₂O₃; 7: Mg-NO₂; 8: MgO; 9: -CH; 10: C=O/NH⁺; 11: MgCO₃; 12: Cu-N; 13: copper attached to the hydroxyl group; 14: oxidation state (+2) of impregnated Ni; 15: region of the conjugation of the di-aryl group.

99].

For AC samples impregnated with nickel nitrate, a band at 3459 cm⁻¹ can evidence the oxidation state (+2) of the impregnated nickel. Methylene (-CH₂) and the methyl (-CH₃) groups stretching bands appear at 2848–3032 cm⁻¹. Around 1450–1650 cm⁻¹, one can see the band referring to C=C, and at 670–900 cm⁻¹, the -CH bond. Carbonyl and carboxyl group bands appear between 1860–1650 cm⁻¹ [67,101].

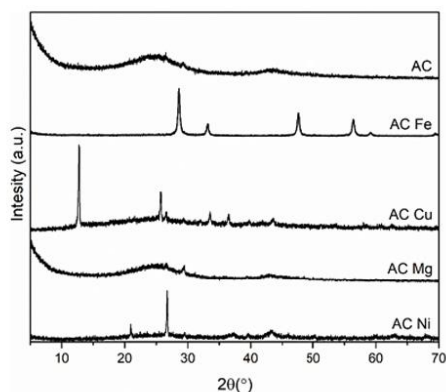


Fig. 6. XRD of activated carbon (AC) and AC impregnated with metals.

3.1.5. DRX

The XRD analysis samples of pure AC and AC impregnated with iron nitrate, copper nitrate, magnesium nitrate, and nickel nitrate is shown in Fig. 6.

The AC sample showed carbon and graphite carbon planes at an angle of 2θ close to 25° and 43°. Diffraction peaks below 25° and close to 44° are probably related to the carbonic graphite hexagonal structure. The absence of diffraction peaks below 25° is most likely due to a disturbance of the graphitic carbon structure due to the iron interaction with carbon atoms [88].

For AC-Fe samples, the graphite structure formed by the catalytic action of iron particles (ion Fe³⁺) impregnated in carbon appears at 26.2° [89]. Diffraction peaks around 59° and 62.5° correspond to (511) and (440) planes of Fe₃O₄ [88,90–93]. Besides, a peak near 25° corresponds to goethite (120) (JCPDS Card n°. 29-0713), at 35° and 45° to hematite (104) (JCPDS Card n°. 33-0664) or goethite (021), at 45° and 55° to hematite (024) and (116) [94]. According to Ramirez et al. [95], peaks at 26° and 43° are associated with AC typical turbostratic structure and, close to 35°, FeO (111) (JCPDS Card n°. 74-1886) phases may be present.

Copper impregnation caused interference in the structural plane due to copper in the form of copper oxide at 35.4° and 38.6°, which correspond to CuO (JCPDS Card n°. 48-1548) [96]. The small peak around 44.2° corresponds to the metallic copper plane (111) (JCPDS Card n°. 4-836). Besides, the peak around 25.0° is attributed to the plane (002) of amorphous carbon [97].

The X-ray diffractogram of AC-Mg showed no significant difference to the pure support, presenting a broad peak between 20° and 30° attributed to activated carbon. The absence of peaks in the AC-Mg sample is attributed to the amorphous MgO structures formed in the activated carbon [98].

For the AC-Ni sample, peaks around 22° and 27° were attributed to carbon structures of activated carbon. The peak at 45° corresponds to the crystalline plane (200) of NiO (JCPDS Card n°. 04-0835) [100].

3.2. DMC synthesis reactions

3.2.1. DMC synthesis reactions using activated carbon impregnated with metals as catalysts

Table 2 presents methanol conversions, DMC yield, and selectivity values for reactions using the supported catalysts.

Surprisingly, bare AC is active in the DMC synthesis resulting in a yield of 5.5 % (Entry 1, Table 2). The catalytic activity occurred most likely due to metals present in the pure coal structure, mainly iron, according to the ICP-OS analysis performed on the samples (Table S1). The AC-Fe sample obtained the highest yield, reaching 23.5 % with 100 % selectivity (Entry 2, Table 2). The AC-Cu also showed an acceptable

Table 2

Conversions, yields, and selectivity of reactions using catalysts supported on activated carbon. Reactions were performed using 213 mmol of methanol, 20 mmol of CH₃I, 2.0 g of molecular sieves, 40 bar pressure, the temperature of 80 °C and the time of 24 h. The letters refer to the Tukey Test, where the same letters mean the statistical equality between the samples.

ENTRY	CATALYST	DMC SELECTIVITY (%)	METHANOL CONVERSION (%)	DMC YIELD (%)
1	AC	100	5.5 ± 0.6 ^c	5.5 ± 0.6 ^c
2	AC-Fe (NO ₃) ₃	100	23.5 ± 0.8 ^a	23.5 ± 0.8 ^a
3	AC-Cu (NO ₃) ₂	100	18.4 ± 0.9 ^b	18.4 ± 0.9 ^b
4	AC-Mg (NO ₃) ₂	100	4.0 ± 0.2 ^c	4.0 ± 0.2 ^c
5	AC-Ni (NO ₃) ₂	100	4.8 ± 0.6 ^c	4.8 ± 0.6 ^c
6	Fe(NO ₃) ₃	100	2.8 ± 0.6 ^d	2.8 ± 0.6 ^d
7	Ni(NO ₃) ₂	-	Traces	Traces

catalytic activity resulting in a DMC yield of 18.4 % and selectivity of 100 % (Entry 3, Table 2). AC-Mg (Entry 4, Table 2) and AC-Ni (Entry 5, Table 2) showed low catalytic activity resulting in 4.0 % and 4.8 % of DMC yields with 100 % selectivity. We also tested pure iron nitrate as a catalyst (see Entry 6, Table 2), resulting in low DMC yield (2.8 %) and 100 % of selectivity and Ni(NO₃)₂ (see Entry 7, Table 2), producing only DMC traces. As seen in Table 2, the selectivity was 100 % for all catalytic systems. Fig. S3 shows a typical chromatographic analysis for Ac-X samples exemplified when using Ac-Fe as catalyst (Table 2, entry 2), evidencing only the peaks belonging to methanol in 1.7 min, the solvent in 2.0, and DMC close to 2.6 min. These results corroborate that metal impregnation in AC improves the catalytic activity in DMC direct synthesis. Simulation results confirmed the need for the catalyst to foster the reaction (see Table 4), decreasing the reaction barrier due to the electrostatic interaction of the oxygen atom and the metal ion.

The letters above the results represent the Tukey Test to demonstrate statistical equality among the supported catalyst performance. As seen, AC, AC-Mg, and AC-Ni are statistically equal and, AC-Fe and AC-Cu are statistically different from the others. Therefore, among the evaluated, supported catalysts, AC-Fe proved to be the best. Thus, the catalytic performance follows the order: AC-Fe > AC-Cu > AC = AC-Mg = AC-Ni > Fe(NO₃)₃ > Ni(NO₃)₂.

TGA findings showed that the iron nitrate impregnation on activated carbon was more satisfactory than Cu, Mg, and Ni (Fe = 18.38 %; Cu = 13.41 %; Mg = 8.17 %; Ni = 6.03 %). The higher catalytic performance is most likely related to the higher metal-impregnated content in the support, corroborated by simulation findings (see section 3.2.3). Yet, metal acidity is a determining factor for catalytic activity. Fe³⁺ presents a hard acid character reacting efficiently with a hard base (methanol) [102–104]. On the other hand, Cu²⁺, Mg²⁺, and Ni²⁺ have an intermediate acid character, making them less susceptible to react with a hard base (methanol) [102–104].

Table 1 shows no concrete relation between the specific surface area and the supported catalyst activity. Therefore, the impregnated support structure analysis may indicate that metals are present on the support surface and pores. However, it does not show direct influence on the catalytic action [38,39,63,67,75,105].

Li et al. [106] evaluated the combination of iron and zirconia, in different proportions, as a catalyst in the DMC direct synthesis (110 °C, 5 bar, and 4 h of reaction). They evidenced that the increase in the number of iron particles increases DMC yield. Therefore, the use of Fe_{0.7}Zr_{0.3}O₇ presented a DMC yield of 4 % and 100 % selectivity, concluding that the combination of zirconia with iron was fundamental to increase yield and selectivity. Chen et al. [38] evaluated the use of copper chloride impregnated in activated carbon in the DMC direct synthesis (25 °C and 140 bar), reaching around 5.0 % of methanol conversion and up to 90 % selectivity. Therefore, the combination of copper with the activated carbon structure influenced the increase in conversion and the product selectivity, obtaining a DMC yield of 4.5 %. Table 3 presents some literature related to DMC synthesis and different catalysts used to increase DMC yield.

We noticed that several studies refer to catalysts and dehydrating

Table 4

Gibbs free energies computed from electronic wave functions and vibrational frequencies for different reaction pathways at different conditions corresponding to the experimental setups in this research work. DMC and HI are produced out of CH₃OH, CH₃I, and CO₂. Thermochemistry for DMC and H₂O produced out of two methanol molecules and one carbon dioxide molecule (alternative transformation) was computed to show that this reaction is less energetically favorable at all physically sound conditions, as compared to the reaction involving the methyl iodide promoter: CH₃OH + CH₃I + CO₂ = DMC + HI. The precise procedure of thermochemistry calculation is described elsewhere [120].

Conditions		Gibbs free energy for different products, kJ mol ⁻¹	
T, °C	P, bar	CH ₃ OH + CH ₃ I + CO ₂ = DMC + HI	2CH ₃ OH + CO ₂ = DMC + H ₂ O
25	1	46	69
25	50	36	60
80	50	43	67
130	50	49	74
80	1	54	79
80	40	44	68
80	100	41	65
80	200	39	63

agents in the DMC direct synthesis (Table 3). The present work (Entry 1 and 2, Table 3) presents good DMC yield values compared to the literature. Each catalyst interacts differently in the reaction, so pressure and temperature parameters influence DMC yield and selectivity, as demonstrated by simulation results (see Section 3.2.3). Entry 1 and Entry 2 showed that a combination of the temperature of 80 °C and a pressure of 40 bar was efficient to promote an effective yield, however, we expect that changing these two parameters can lead to a considerable improvement in DMC yield.

Stoian et al. [110] used Mg-Al hydrotalcite on silica Lyogel at 130 °C and 10 bar, reaching a yield of approximately 16 %. On the other hand, Wang et al. [112] and Chen et al. [112] chose to insert dehydrating agents (DMP and molecular sieves), achieving low DMC yields (3.2 % and 5.0 %).

Thus, parameters such as pressure, temperature, time, catalyst amount, and the presence of dehydrating agents and promoters influence the catalytic activity of catalysts in the direct DMC synthesis.

3.2.2. Parameter optimization for direct DMC synthesis

As seen, AC-Fe is the most effective catalyst; however, factors such as catalyst amount, temperature, and pressure parameters can improve the reaction yield [6,8,10,12,42,85,113]. Fig. 7 shows the conversion and selectivity when using the AC-Fe catalyst in different quantities.

We noticed that the use of 0.4 g of AC-Fe showed a low methanol conversion (~4.0 %), whereas the increase of catalyst content to 0.55 g increased the conversion to ~16.0 %. When expanding to 0.7 g, a significant methanol conversion increase was observed, reaching 23.5 %. Also, a decrease in conversion was observed when increasing the AC-Fe catalyst content to 1.0 g and 1.3 g. The addition of a more significant amount of AC-Fe does not increase the methanol conversion. The selectivity was 100 % in both reactions. Al-Darwish et al. [114] observed the same behavior for cobalt oxide, showing that concentrations in the

Table 3
Available literature data in the area of DMC synthesis.

Entry	Catalyst	Promoter/ dehydrating agent	Temperature (°C)	Pressure (bar)	Yield (%)	Literature
1	AC-Fe	CH ₃ I/molecular sieves	80	40	23.5	This work
2	AC-Cu	CH ₃ I/molecular sieves	80	40	18.4	This work
3	Cu-Ni/graphene	–	110	30	13	Deeratraku et al. [107]
4	K ₂ CO ₃	–	120	50	~3	Liu et al. [91]
5	Fe _{0.7} Zr _{0.3} O ₇	–	110	50	~4.0	Li et al. [106]
6	Ti _{0.44} Ce _{0.56} O ₂	–	120	80	~4.0	Fu et al. [108]
7	Cu-Ni/Zeolitic Imidazolate	–	110	20	~7.0	Poungsombate et al. [109]
8	Mg-Al Hydrotalcite/Silica Lyogel	–	130	10	~16.0	Stoian et al. [110]
9	CeO ₂	DMP	140	50	3.2	Wang et al. [111]
8	Cu-Ni/molecular sieves	Molecular sieves 4A	120	110	5.0	Chen et al. [112]

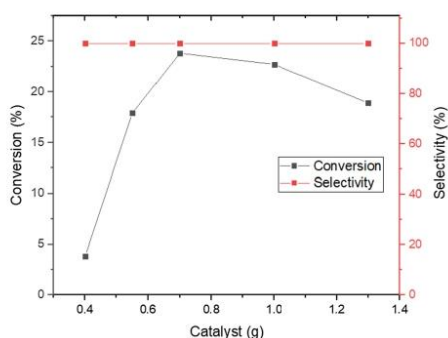


Fig. 7. Methanol conversion and selectivity using different amounts of the supported catalyst (AC-Fe). Reactions were performed using 213 mmol of methanol, 20 mmol of CH₃I, 40 bar pressure, the temperature of 80 °C and the time of 24 h.

range of 2.5 %–10.0 % were efficient in the DMC synthesis; however, higher values decrease the DMC yield. Thus, with the use of 0.7 g of AC-Fe, the study of temperature and pressure parameters optimization was carried out. Fig. 8 presents the contour chart for DMC direct synthesis at different pressures and temperatures.

To achieve the highest DMC yield (above 25 %), a higher temperature (120 °C) and pressure around 40 bar will be needed, as seen in Fig. 8. The response surface graph (Fig. S4) proves that higher temperatures and medium pressures favor DMC yield when using AC-Fe as a catalyst (0.7 g) and 24 h of reaction time.

Xuan et al. [115] evaluated the use of MOF-808-X as a catalyst in DMC direct synthesis, concluding that increasing temperature up to 140 °C results in a DMC yield improvement. Also, they noticed that pressure and catalyst amount improved process efficiency to the point of stabilization. The yield curve of the synthesis remains constant. Chen et al. [116] analyzed the use of Ti_xCe_{1-x}O₂, concluding that at higher temperatures (120–140 °C) and mild pressures (12–24 bar), methanol conversion becomes more efficient, enabling to reach up to 24.3 % conversion, 70.5 % of selectivity, approximately 17 % of DMC yield (140 °C and 24 bar) and, 10.1 % conversion and 88 % selectivity, with about 8.8 % yield (100 °C and 12 bar). They also evidenced that oxygen species from adsorbed CO₂ can fill the catalyst surface vacancies playing a crucial role in promoting methanol and carbon dioxide catalytic conversion into DMC. Functional theory suggests that the cleavage of O=C=O bonds is energetically less endothermic when an oxygen atom

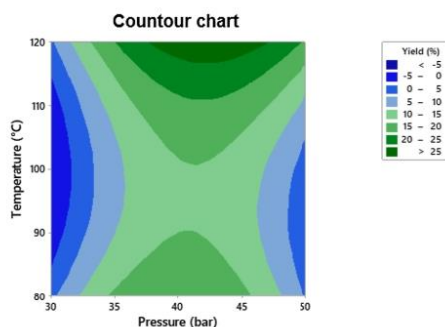


Fig. 8. Contour chart for DMC yield at different temperatures and pressures. Reactions were performed using 213 mmol of methanol, 20 mmol of CH₃I, 0.7 g of catalyst (AC-Fe), and 24 h time.

of CO₂ fills an empty oxygen site [116].

According to the DMC direct synthesis thermodynamics, the excessive temperature increase is unfavorable for the energetic process efficiency [117]. Studies indicate that the increase in yield for carbonate production occurs at a specific temperature. Pressure intervals need to be optimized and other reaction parameters such as catalyst, dehydrating agents, among others [118,119]. Therefore, for the use of AC-Fe as a catalyst in DMC direct synthesis, higher temperatures, and mild pressures are necessary to achieve higher conversion, selectivity, and, consequently, yield. In the tested system, the temperature of 120 °C using AC-Fe as a catalyst combined with the other reaction conditions (pressure = 40 bar, time = 24 h, catalyst = 0.7 g) is efficient for DMC direct synthesis. Stepwise simulations of the DMC formation reaction and the energy barrier detected (see Fig. 9 and Table 4) corroborated the need for elevated temperatures to produce DMC as a primary reaction product.

3.2.3. Simulation results

The major reaction steps are depicted in Fig. 9. We also exemplify simplified models of complexes involving metallic catalysts and reactants (carbon dioxide and methanol). The reaction starts with CO₂ attachment to CH₃OH (Fig. 9a) that is fostered by the catalyst. Transfer of the hydrogen atom becomes possible. Next, DMC and hydrogen iodide are formed (Fig. 9b). Thanks to possessing non-zero electric moments (dipole one in case of CH₃OH and quadruple one in case of CO₂), both reactants strongly interact with the catalyst particle, see Fig. 9c,d, that is adsorbed on AC.

The synthesis of DMC, despite a positive role of the metal ions, is energetically tough (Table 4). We provide thermochemistry calculations for DMC formation out of CH₃OH, CO₂, and CH₃I along with a simplified pathway that involves 2 methanol molecules and CO₂. Comparison of mechanisms involving CH₃OH + CH₃I + CO₂ = DMC + HI and 2CH₃OH + CO₂ = DMC + H₂O clearly reveals that the former one is more thermodynamically favorable at all considered experimental conditions. Thus, the presence of CH₃I as a promoter in this work makes practical sense.

Analysis of the Gibbs free energies at different confirms the principal impossibility to achieve high yields of DMC using the proposed reaction schemes become the reaction Gibbs free energy is directly proportional to the reaction equilibrium constant. Pressure increase shifts equilibrium towards the products for both reactions, but the effect of a significant pressure increase is rather modest (Table 4). Elevated temperatures used in our experimental setups are unfavorable for the reaction Gibbs free energies and hence shifts equilibrium towards reactants. However, they were absolutely necessary to get an essential fraction of DMC as a major reaction product in the experimental studies. This observation allows us to hypothesize that the DMC formation reaction is associated with rather high energy barriers that are only partially decreased by the metallic catalysts adsorbed on AC.

3.2.4. Evaluation of the reuse of the AC-Fe catalyst

As discussed earlier, the AC-Fe catalyst at 120 °C of temperature and mild pressures (40 bar) were the reaction conditions optimized for DMC direct synthesis. AC-Fe catalyst recycling (4 cycles), using different dehydrating agent systems (sieve and DMF) separately and combined, and the optimized reaction conditions can be seen in Fig. 10.

We noticed that system A (molecular sieve in the gaseous phase) presented the highest methanol conversion since the initial recycling (recycle 0) reached approximately 30 % methanol conversion and 100 % selectivity. A methanol conversion decrease was observed in the first recycle (recycle 1 = approximately 22 %). However, a slight decrease was observed in the other cycles (recycle 2 = approximately 20 %; recycle 3 = approximately 19 % and recycle 4 = approximately 18 %). Selectivity in all recycles for system A remained 100 %; there was no by-products formation during the process in all recycles.

For the B system (DMP in the liquid phase), the initial methanol

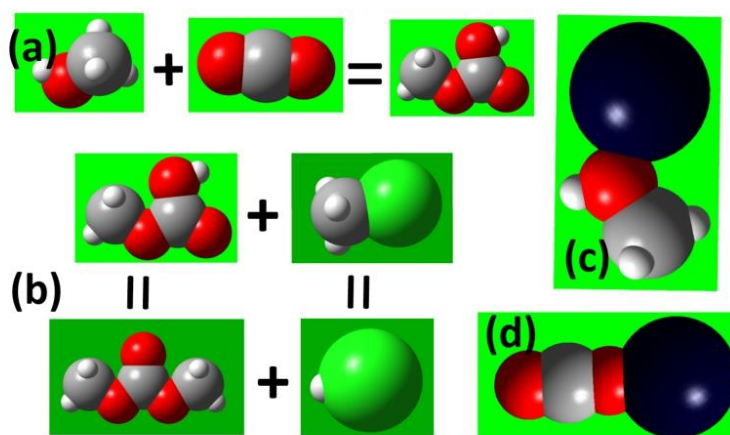


Fig. 9. Major intermediates detected during the formation of DMC out of methanol, carbon dioxide, and methyl iodide: (a) $\text{CH}_3\text{OH} + \text{CO}_2 = \text{CH}_3\text{O-COO-H}$; (b) $\text{CH}_3\text{O-COO-H} + \text{CH}_3\text{I} = \text{CH}_3\text{-O-C(O)-O-CH}_3 + \text{HI}$; (c) electrostatically bound complex of Fe^{3+} and CH_3OH ; (d) electrostatically bound complex of Fe^{3+} and CO_2 . The geometries of the depicted molecules and molecular complexes were optimized quantum chemically to minimize the potential energy of the system in each case. The resulting Z-matrices were subsequently used to calculate Gibbs free energies for the proposed reaction stages.

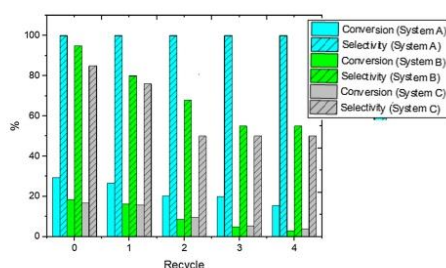


Fig. 10. The conversion and the selectivity of DMC synthesis using the AC-Fe catalyst. A: molecular sieve 4A (dehydrating agent); B: DMP (dehydrating agent); C: molecular sieve (gas phase) combined with DMP (liquid phase). * Pressure: 40 bar; Temperature: 120 °C; Time: 24 h; 0.7 g of AC-Fe; 2.0 g of molecular sieve; 10 mmol of DMP; 213 mmol methanol; 20 mmol of CH₃I.

conversion (recycle 0) of approximately 18 % remained constant in the first recycle (recycle 1). However, we noticed a drastic methanol conversion decrease, down to 3 %, in the recycle 4. Also, DMP in the liquid phase produces a by-product (ketone), decreasing DMC yield and selectivity during the reuse needing a DMP purification step [4]. Therefore, the DMP in the liquid phase does not improve methanol conversion and selectivity when used for catalyst recycling. On the other hand, system C (sieve combined with DMP) showed similar methanol conversion and selectivity to system B throughout the recycles. Thus, the DMP present in the liquid phase may be preventing the action of molecular sieves in the gas phase and impairing the system's dehydration.

Several studies on catalyst recycling are described in the literature, aiming to reduce DMC production costs [114,117,121,122]. Al-Daewish et al. [114], analyzed CeO₂ as a catalyst in different forms for DMC synthesis, namely: CeO₂, CoO/CeO₂, NiO/CeO₂, CaO/CeO₂ and CuO/CeO₂. Reuse was evaluated under reaction conditions of 140 °C, 30 bar, 3 h, and 0.5 g catalyst. The maximum yield for CeO₂ was found to be at 1.6 mmol of DMC. Through the four recycles, the catalyst activity decreased each cycle. CaO/CeO₂ only feature activity for two cycles. CuO/CeO₂ was effective only in the first one showing that each catalyst interacts differently in the reaction medium, possibly reused or not in the DMC synthesis [114].

4. Conclusions

The characterization analysis of the catalysts (AC-Fe, AC-Cu, AC-Mg, and AC-Ni) showed that the activated carbon metal impregnation was successful, most likely due to numerous pores in its structure, and the best impregnation occurred for AC-Fe. The catalytic reactions stressed that the use of AC-Fe catalyst has proved to be the most efficient in the DMC direct synthesis than other metals, with a yield of 23.5 % and selectivity of 100 %. Simulation results evidenced the need for the metal catalyst to foster the reaction.

The process optimization indicated that in the amount of 0.7 g of the catalyst (AC-Fe), 40 bar of pressure, and 120 °C of temperature, the best conversion, selectivity, and, consequently, DMC yield (approximately 30 %) occurs. Stepwise simulations of the DMC formation reaction and the energy barrier explained the need for elevated temperatures in experimental setups to get an essential fraction of DMC as a primary reaction product.

The evaluation of catalytic systems A, B, and C proved that system A is the most suitable for catalyst reuse since it does not alter the product selectivity and does not abruptly decrease reaction yield.

CRedit authorship contribution statement

Douglas José Faria worked on conceptualization, investigation, Methodology, and writing. Leonardo Moreira dos Santos worked on conceptualization, investigation, Project administration, and writing. Franciele L. Bernard worked on conceptualization, investigation, Project administration. Ingrid Selbach Pinto worked on investigation and validation. Ivan Pacheco Romero worked on resources and supervision. Vitaly V Chaban worked on Methodology, formal analysis, Investigation, validation and writing. Sandra Einloft worked on conceptualization, Methodology, Project administration, funding acquisition, and writing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jcou.2021.101721>.

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4.3. ARTIGO 3

O artigo 3 é intitulado “*Dimethyl carbonate direct synthesis using CO₂, methanol and metals supported in different matrices as catalyst*”.

Coloca o resumo do trabalho aqui e no e-mail que vais enviar com a tese explica que estamos aguardando a parte de simulação e também as contribuições da banca para depois submeter pois para a **Defesa de doutorado em formato de artigo de acordo com o regulamento do PGETEMA - PUCRS:**

Requisitos: publicação de artigos em revistas indexadas como A, sendo primeiro autor no mínimo em 1 dos artigos, ou publicação de 2 artigos em revista indexada como B no Engenharia II da CAPES.

5. COMPARAÇÃO ENTRE CATALISADORES AVALIADOS

A partir dos 3 artigos produzidos por este trabalho, podemos comparar os diversos catalisadores aplicados na síntese direta de DMC. De início, verificamos que o uso da peneira molecular na fase gasosa permitiu um grande aumento do rendimento na síntese direta de DMC e, por isso, todas as reações subsequentes foram realizadas com esse agente desidratante. Além disso, concluímos que o uso do iodometano como agente promotor também foi parte fundamental para o avanço nos resultados de rendimento.

O uso de carvão ativado, sílica, alumina e resíduo da casca de ovo foram os suportes escolhidos para serem avaliados, uma vez que são apontados na literatura como excelente matrizes para impregnação de metais. A tabela 5.1 aponta os melhores resultados alcançados por cada suporte impregnado com metal.

Tabela 5.1 Melhores resultados de rendimento para cada tipo de catalisador.

CATALISADOR	RENDIMENTO (%)
CA-Fe	23,5
CO-Fe	12,7
PQ-Fe	7,2
SB-Cu	8,9

Dentre todos os catalisadores avaliados, o uso de carvão ativado impregnado com ferro demonstrou ser o mais eficaz, com rendimento de 23,5% e seletividade de 100%. Além disso, o estudo da sua reutilização mostrou que a ação catalítica permanece constante durante 5 reações seguidas. Portanto, para uma produção industrial de DMC, o mais adequado seria utilizar o sistema com CA-Fe como catalisador, pois proporcionaria um rendimento eficiente, diminuição de custo relacionados ao catalisador e exclusão de gastos com equipamentos de separação

na etapa final do processo. Além disso, o uso de catalisadores heterogêneos demonstraram maior eficiência, uma vez que podem ser reutilizados sem causar danos à ação catalítica no que se refere ao rendimento e seletividade do DMC.

Ferreira (2014)[123] realizou uma análise econômica, como modelo ASPEN HYSYS da síntese de DMC comparando resultados da literatura. O autor se baseou em uma planta com capacidade produção de 50 kton/ano de DMC e seguiu as seguintes premissas: 1) 8000 horas de operação da planta por ano; 2) Recuperação de apenas 90% do DMC produzido, lembrando que a estequiometria da reação exige consumo de 2 mols de MeOH para produção de 1 mol de DMC; 3) Conversão de 11,7% de MeOH em DMC, que é o valor experimental para condições reacionais de 80°C e 20bar; 4) Alimentação de mistura equimolar de CO₂ e MeOH no reator.

Com todas as premissas respeitadas, a vazão total de alimentação do reator foi fixada em 2640 kmol/h e CSTR foi considerado o reator mais adequado para a síntese.

Dessa forma, o autor alcançou um dimensionamento de custos para a temperatura de 120 °C e 120 bar com alcance de rendimento de 29,6%, gerando uma receita de, aproximadamente \$1.574.243.313 por ano.

O processo de análise econômica para a síntese de DMC é muito complexo, uma vez que leva em consideração todos os equipamentos, quantidades de reagentes, tipos de reatores, separadores, entre outros. Assim, não só o rendimento, mas a seletividade do processo se torna necessário, já que o aumento da seletividade diminui custos de equipamentos e processos de separação do produto (DMC).

O catalisador utilizado como base de estudo para Ferreira (2014)[123] foi o CH₃OK e, neste trabalho utilizamos catalisadores heterogêneos, o que possibilita seu reuso, como demonstrado pelo CA-Fe e, conseqüentemente, diminuição dos custos processuais.

A síntese direta de DMC, apesar de extremamente difícil, devido a barreira termodinâmica da reação, é um processo com alto valor agregado e com capacidade de inúmeros estudos envolvendo a otimização de variáveis como temperatura, pressão, tempo, tipos de catalisadores. Dessa forma, a análise aprofundada e eficiente dos fatores já citados tende a promover uma alta eficiência industrial, ambiental e econômica.

6. CONCLUSÕES

Os melhores resultados para síntese de DMC foram para 2,0g de peneiras moleculares na parte gasosa do reator (rendimento=30,5%) ou quando 2,0g de peneira na fase gasosa foi combinada com 10mmol de DMP na fase líquida (rendimento=42,8%). O sistema proposto de peneiras no reator pode ser facilmente separado, desde que esteja na fase gasosa. A acetona formada com uso de DMP pode ser separada usando a técnica de destilação, sendo assim, não prejudicaria a diminuição da seletividade quando há DMP no meio reacional.

A análise de caracterização dos catalisadores (AC-Fe, AC-Cu, AC-Mg, AC-Ni) mostrou que a impregnação dos metais no carvão ativado foi bem-sucedida, provavelmente devido à presença de numerosos poros em sua estrutura, e a melhor impregnação ocorreu para AC-Fe. As reações catalíticas ressaltaram que o uso do catalisador AC-Fe tem se mostrado o mais eficiente na síntese direta de DMC do que outros metais, com rendimento de 23,5% e seletividade de 100%.

A otimização do processo indicou que na quantidade de 0,7g de catalisador (AC-Fe), 40 bar de pressão e 120 ° C de temperatura, ocorre a melhor conversão, seletividade e, conseqüentemente, rendimento de DMC (~ 30%). Simulações das reações de formação de DMC e barreiras energéticas explicam a necessidade de elevadas temperaturas experimentais para sintetizar DMC como produto primário.

A avaliação dos sistemas catalíticos A (agente desidratante: peneira molecular), B (agente desidratante: DMP) e C (agente desidratante: peneira molecular combinada com DMP) comprovou que o sistema A é o mais adequado para o reaproveitamento do catalisador no processo, visto que não altera a seletividade do produto e não diminui abruptamente o rendimento da reação.

Para a análise de TGA dos suportes de casca de ovo, sílica e alumina, o suporte com melhor impregnação foi a casca de ovo, tanto para o cobre como para o ferro (13% e 7%). MEV-FEG, FTIR, EDS e mapeamento confirmaram a impregnação

dos metais na superfície porosa dos suportes. BET apontou a alta área superficial dos suportes devido a grande presença de poros, sendo maior a quantidade de mesoporos na casca de ovo do que nos demais suportes. Em relação a presença de sítios ácidos nas amostras de CO-Fe e CO-Cu, TPD-NH₃ mostrou um maior número de sítios ácidos para a amostra de CO-Fe, sendo que CO-Cu apresentou sítios ácidos mais fracos.

Para as reações, o uso de CO-Fe como catalisador na síntese direta de DMC apresentou rendimento de 12.7% seguido de CO-Cu com 11.3%, ambos com seletividades >99%.

Portanto, levando em consideração todos os suportes e metais avaliados no presente trabalho, o uso de carvão ativado com ferro impregnado em sua estrutura mostrou uma melhor performance como catalisador na síntese direta de DMC e, também, uma reutilização eficaz para o processo, como 5 reusos mantendo a ação catalítica nos resultados de rendimento e seletividade.

Propostas futuras incluem o uso de biomassa vegetal rica em celulose para agirem como matrizes catalíticas que contenham metais impregnados para aumento do rendimento de DMC. Dentre essas biomassas, temos a casca de arroz, bagaço de cana, casca de batata, entre outros.

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