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Catalytic Methylation of Aromatic Hydrocarbons using CO_2/H_2 over Re/TiO₂ and H-MOR catalysts

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Abstract: A combined catalyst comprising TiO₂-supported Re (Re(1)/TiO₂; Re = 1 wt%) and H-MOR (SiO₂/Al₂O₃ = 90) was found to promote the methylation of benzene using CO₂ and H₂. This catalytic system exhibited high performance with regard to the synthesis of methylated benzenes and gave high yields of total methylated products (up to 52% benzene-based yield and 42% CO₂-based yield) under the reaction conditions employed in this study (p_{CO2} = 1 MPa; p_{H2} = 5 MPa; T = 250 °C; t = 20 h) in a batch reactor. Catalyst screening demonstrated that a combination of Re(1)/TiO₂ and H-MOR (SiO₂/Al₂O₃ = 90) exhibited superior performance compared to other combinations of supported metal catalysts and zeolites in terms of both yield and selectivity for methylated benzenes.

The utilization of carbon dioxide (CO₂), an important greenhouse gas, as a C₁ source has been the subject of intensive research over the past several decades. The use of CO₂ as a chemical feedstock could be a means of reducing atmospheric CO₂ concentrations, and CO₂ is also abundant, nontoxic and readily available.^[1–5] There is thus significant interest in the catalytic transformation of CO₂ via hydrogenation to produce chemicals, especially methanol (MeOH), because this is an important commodity chemical that serves as a versatile C₁ building block in chemical synthesis.^[6] Although the direct production of MeOH from the hydrogenation of CO₂ has recently been achieved industrially using Cu-based catalysts under relatively harsh conditions (*T* > 200 °C; *p* = 5-10 MPa),^[7] this process suffers from a low equilibrium conversion of CO₂ due to thermodynamic limitation.^[8,9]

One possible approach to achieve high CO_2 conversion is use of a lower reaction temperature to produce MeOH.^[10–12] However, the development of a catalyst for low temperature MeOH synthesis is a formidable task. Another popular strategy to address this issue associated with the thermodynamic limitation is to employ a CO_2/H_2 mixture as the methylation reagent instead of MeOH for the one-pot synthesis of value-added chemicals (see **Figure S1** for representative equilibrium calculations).^[13] In particular, *N*-methylation through the formation of C–N bonds for the synthesis of various methylamines has been widely explored.^[14–17] Moreover, in 2014, Beller and coworkers reported

Supporting information for this article is given via a link at the end of the document.

C-methylation to form aromatic C-H bonds using CO₂/H₂ to replace MeOH as the CH₃ source.^[18] Their work involved the use of Ru-based homogeneous catalytic systems to promote the Cmethylation of electron-rich arenes. However, although this prior work was highly seminal and impactful, the reported substrate scope was limited solely to electron-rich arenes with high reactivities. It would be highly desirable to also perform the Cmethylation of unactivated aromatic hydrocarbons such as benzene to generate new aromatic compounds. Currently, Cmethylation in the petroleum industry is performed using MeOH together with disproportionation/transmethylation over zeolite catalysts to produce methylated aromatic hydrocarbons such as p-xylene, which is widely used as a precursor for plastics.^[19] It is therefore anticipated that a combination of MeOH-producing catalysts and methylation catalysts such as zeolites could afford the one-pot synthesis of methylated benzenes from benzene, CO₂ and H₂.

In the present study, a combined system consisting of a TiO_2 -supported Re catalyst (Re(1)/TiO_2; Re loading = 1 wt%) that exhibits high catalytic performance for low temperature MeOH synthesis^[12] and the zeolite H-MOR (SiO₂/Al₂O₃ = 90) was employed for the direct methylation of benzene using CO_2 and H_2 (p_{CO2} = 1 MPa; p_{H2} = 5 MPa; T = 250 °C). Catalyst screening using various combinations of supported metal catalysts and zeolites having a wide range of SiO₂/Al₂O₃ ratios showed that this combination provided the best performance for the methylation reaction. Although the methylation of arenes, including benzene, using syngas (that is, CO/H₂) has been reported,^[20-23] the direct use of CO₂ would be beneficial. In addition, while the direct synthesis of aromatic hydrocarbons, including methylated benzenes, from CO₂/H₂ mixtures that do not already contain benzene has been realized, these processes typically require harsh conditions.^[24-30] In contrast, our process provides an effective means of upgrading crude oils and should also contribute to decreasing the total CO2 emissions produced during petroleum refining processes.

Re(1)/TiO₂ was synthesized using a simple wet impregnation method, employing NH₄ReO₄ and TiO₂ (Refer to the Supporting Information for a more detailed procedure). Scanning transmission electron microscopy (STEM) images of the Re(1)/TiO₂ (**Figure S2**) confirmed that the Re was loaded on the TiO₂ support in the form of highly dispersed sub-nanometer clusters.^[31] Commercially-available zeolite catalysts were used as received. For each catalytic reaction, the active catalyst was prepared by physically mixing both materials with subsequent reduction in a quartz tube (T = 500 °C; t = 0.5 h) under a flow of H₂ (20 mL min⁻¹).

In the initial phase of this study, the methylation of benzene using CO_2/H_2 was carried out to assess the properties of various MeOH synthesis catalysts, and the results are summarized in **Figure 1** (Full data for the catalyst screening are provided in

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Figure 1. Screening of (A) hydrogenation catalysts (M/TiO₂ and Re/Support), and (B) zeolite catalysts for the methylation of benzene using CO₂ and H₂. Pre-treatment: 500 °C, 0.5 h under a H₂ flow (20 mL min⁻¹); reaction conditions: 1 wt% of supported metal catalyst (mass adjusted to contain 0.0081 mmol of loaded metal per experiment) with 0.10 g of zeolite catalyst, 1.0 mmol of benzene, CO₂ (1 MPa), H₂ (5 MPa), 250 °C, 20 h. Benzene-based yield is shown in right axis. *Includes C₉ to C₁₂ methylated benzenes.

 Table S1). First, the catalytic performances of various supported metal catalysts were compared and evaluated.

A combination of Re(1)/TiO₂ and H-MOR(90) afforded the highest yield of methylated products (52% benzene-based yield). It should be noted here that undesired dearomatized products were not observed for this catalytic system. In contrast, not only did other TiO₂-supported metal catalysts (**Figure 1A**) afforded relatively low total product yields, dearomatized products such as cyclohexane and methylcyclohexane were also detected in those calculated based on the number of protonic sites (**Figure 2**). This could be attributed to the fact that increasing SiO₂/Al₂O₃ ratio enhances the hydrophobic reaction between the zeolite pores and the substrate, which in this case, benzene, thus leading to a higher product formation rate when adjusted to the number of protonic sites.^[32]

systems. Subsequently, the performances of various supported Re catalysts were also evaluated (Figure 1A), and the product yields were found to be significantly lower than that obtained with Re(1)/TiO2. The industrial MeOH synthesis catalyst Cu/ZnO/Al₂O₃ (MDC-7; 34 wt% Cu) was also examined and found to be ineffective under the reaction conditions employed in this study. These results suggested that Re(1)/TiO₂ would be the best MeOH synthesis component for this methylation process.

After establishing TiO₂-supported Re catalyst as the MeOH synthesis catalyst, we proceeded the to zeolite screening of catalysts having various framework distinctive types with a wide

range of SiO₂/Al₂O₃ ratios for the methylation of benzene using CO₂/H₂ (Figure 1B). H-MOR was found to be more favorable for the formation of toluene and p-xylene when compared to other zeolite catalysts tested in this study. Comparisons of various H-MOR $(SiO_2/AI_2O_3 = 20,$ 90 and 220) showed that H-MOR(90) (Bracketed the number denotes SiO₂/Al₂O₃ for ratio zeolites) gave the highest yield. However, H-MOR(220) gave a higher product formation rate

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Figure 2. Effect of the SiO₂/Al₂O₃ ratio on the methylation of benzene using CO₂ and H₂ catalyzed by Re(1)/TiO₂ and H-MOR. Pretreatment: 500 °C, 0.5 h under a H₂ flow (20 mL min⁻¹); reaction conditions: 0.0081 mmol of loaded metal with 0.10 g of the zeolite, 1.0 mmol of benzene, CO₂ (1 MPa), H₂ (5 MPa), 250 °C, 1 h. *Includes C₉ to C₁₂ methylated benzenes.

H-ZSM-5, which is widely used for the alkylation of benzene due to its high activity and selectivity,^[33,34] was found to be less effective for the formation of toluene and xylenes as compared to H-MOR in this study. Although yields of methylated products are low, it is worth mentioning that a relatively large amount of light alkanes (C₂-C₄), which are considered as valuable products^[35,36] were detected when H-CHA zeolite was used. Based on these results, H-MOR(90) was identified to be the most suitable methylation catalyst for the present combined catalyst system. A series of control experiments were also performed without CO₂, H₂ or benzene, and no major products were detected following these reactions (**Table S1**). In place of a mixture of Re(1)/TiO₂ and H-MOR(90), the catalytic methylation of benzene was also attempted using either Re(1)/TiO₂ or H-MOR(90) individually. In both cases, the reaction barely proceeded with little to no methylated products detected. The reaction was also carried out using Re(1)/H-MOR(90), but the performance was far inferior to that obtained from the combination of Re(1)/TiO₂ and H-MOR(90). These results suggest that the presence of both Re(1)/TiO₂ and H-MOR(90) is crucial to obtaining a high degree of catalytic performance from this methylation process. The effect of reaction temperature on the methylation of benzene was also investigated (**Figure S4**). 250 °C was chosen as the optimal temperature for our system considering the higher relative yield of main products when compared to the yield of unwanted by-products.

Next, we proceeded to carry out the methylation of benzene employing $Re(x)/TiO_2$ (x = 0.2, 0.5, 1, 5, 10 or 20 wt%) to determine the optimal Re loading (Figure 3A) for the reaction (Refer to Figure S3 for the STEM images of Re(x)/TiO₂). The highest yields of toluene and p-xylene were obtained using Re(1)/TiO₂. This outcome can be attributed to the fact that this material gave the highest MeOH formation rate, as reported in our previous work.[31] The product selectivity appeared to shift gradually towards CH4 with increasing Re loading. This was not unexpected, since larger clusters of Re species are known to enhance the formation of CH₄.^[31] The total product yield was also found to decrease gradually as the Re loading was increased. Re/TiO₂ with a lower Re loading (< 1 wt%) may have a higher fraction of isolated atomic Re species, which has been shown to favor the formation of CO. The dearomatization of benzene was observed when using Re(x)/TiO2 with higher Re loadings (> 1 wt%). These results indicate that dearomatization was caused by aggregated Re species that appear predominantly at loadings above 1 wt%. Based on these data, Re(1)/TiO₂ was found to be the most suitable catalyst for this reaction.

The effect of the pre-treatment temperature on the methylation of benzene using CO₂ and H₂ was also investigated, employing the optimized reaction conditions (**Figure 3B**). H₂ reduction at 500 °C gave the best performance in terms of both total methylation yield and product selectivity, while higher yields of CO were observed at lower temperatures (no reduction and *T* = 200 or 300 °C). This result is partly ascribed to the higher



Figure 3. Effects of (A) Re loading and (B) reduction pre-treatment temperature on the product distribution for the methylation of benzene using CO₂ and H₂. Pre-treatment: 500 °C, 0.5 h under a H₂ flow (20 mL min⁻¹); reaction conditions: 0.0081 mmol of loaded Re with 0.10 g of H-MOR(90), 1.0 mmol of benzene, CO₂ (1 MPa), H₂ (5 MPa), 250 °C, 20 h. Benzene-based yield is shown in left axis whereas CO₂-based yield is shown in right axis. *Includes C₉ to C₁₂ methylated benzenes. The same legend is used as in Figure 1.

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proportion of isolated Re atoms on the less reduced specimens, which tend to promote the formation of CO.

A plot showing the time course of benzene methylation is presented in **Figure 4**. The product concentrations are seen to increase gradually as the reaction proceeds. The decrease in the rate of increase of the toluene yield approaching t = 20 h is possibly due to further methylation of toluene to form multimethylated benzenes, as shown by the data at a reaction time of 30 h.



Figure 4. Time course plot for the methylation of benzene using CO₂ and H₂ catalyzed by Re(1)/TiO₂ and H-MOR(90). Pre-treatment: 500 °C, 0.5 h under a H₂ flow (20 mL min⁻¹); reaction conditions: 0.15 g of Re(1)/TiO₂ and 0.10 g of H-MOR (SiO₂/Al₂O₃ = 90), 1.0 mmol of benzene, CO₂ (1 MPa), H₂ (5 MPa), 250 °C.

To gain more insights into the specifics of the reaction, methylation reactions employing various methylating agents, including MeOH, HCOOH and CO, were carried out under the comparable reaction conditions (**Scheme 1**). Note that each reaction was performed for just 1 h so as to observe the initial reaction rates. Both CO/H₂ and HCOOH (**Scheme 1**, **c & d**) were found to be ineffective when applied to this reaction and led to lower formation rates of overall methylated products compared to the reaction with CO₂/H₂ (**Scheme 1**, **a**). On the other hand, the reaction proceeded efficiently when MeOH was used even in the absence of CO₂ and H₂, suggesting that MeOH is a possible intermediate in this reaction system (**Scheme 1**, **b**). It is likely that MeOH is first produced from CO₂/H₂ over the Re(1)/TiO₂ and that subsequent methylation reactions take place between this MeOH and benzene over the H-MOR(90).

Lastly, the methylation reaction was performed by using higher amount of benzene than in the standard reaction condition. The CO₂-based yield for methylated products was 9% under standard reaction condition (1 mmol of benzene). The yields increased significantly to 32% and 42% when 10 mmol and 20 mmol of benzene was used, respectively (**Figure 5**), even surpassing the theoretical one-pass yield for CO₂-to-methanol reaction at 250 °C (theoretical methanol yield = 30%; see **Figure S1** for the equilibrium calculation). The results clearly proved that

one-pot methylation reaction using CO_2/H_2 can achieve higher CO_2 conversion in one pass compared to direct CO_2 -to-methanol reaction. Recycling tests for our catalyst system were also attempted, and the results are shown in the supporting information (**Figure S5**).



Unit = × 10⁻² mmol·h⁻¹

Scheme 1. Methylation of benzene catalyzed by Re(1)/TiO₂ and H-MOR (SiO₂/Al₂O₃ = 90) using a) CO₂, b) MeOH, c) CO and d) HCOOH as methylating agents. *Includes C₉ to C₁₂ methylated benzenes.

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Figure 5. Methylation of benzene using CO₂ and H₂ catalyzed by Re(1)/TiO₂ and H-MOR(90) with different initial amount of benzene as reactant. Pre-treatment: 500 °C, 0.5 h under a H₂ flow (20 mL min⁻¹); reaction conditions: 0.15 g of Re(1)/TiO₂ and 0.10 g of H-MOR (SiO₂/Al₂O₃ = 90), CO₂ (1 MPa), H₂ (5 MPa), 250 °C, 20 h. Benzenebased yield is shown in left axis whereas CO₂-based yield is shown in right axis. *Includes C₉ to C₁₂ methylated benzenes. The same legend is used as in Figure 1.

The catalytic methylation of naphthalene using CO₂ and H₂ was also carried out to explore the applicability of our catalyst system. Instead of Re(1)/TiO₂ and H-MOR(90), which were identified to be the best catalysts for the methylation of benzene, the combination of Re(1)/TiO₂ and H-BEA(40) was found to be the most effective in the case of naphthalene, giving the highest yield of total methylated products (up to 26% naphthalene-based yield). More detailed results can be found in Supporting Information (**Table S2**). The catalytic methylation of naphthalene using CO₂ and H₂ was performed at 230 °C rather than 250 °C as the higher temperature promoted the formation of unwanted by-products such as tetralin. The time course plot for the methylation of naphthalene is shown in **Figure 6**.





Figure 6. Time course plot for the methylation of naphthalene using CO_2 and H_2 catalyzed by $Re(1)/TiO_2$ and H-BEA(40). Pre-treatment: 500 °C, 0.5 h under a H_2 flow (20 mL min⁻¹); reaction conditions: 0.15 g of $Re(1)/TiO_2$ and 0.10 g of H-BEA(40), CO_2 (1 MPa), H_2 (5 MPa), 230 °C. *MN = Methylnaphthalene, DMN = Dimethylnaphthalene.

In conclusion, one-pot synthesis of value-added products using a mixture of CO_2/H_2 was demonstrated by employing a combination of CO_2 hydrogenation catalyst and zeolite catalyst. We developed a heterogeneous catalytic system for the methylation of benzene using CO_2 and H_2 . After a thorough catalyst screening process, the combination of Re(1)/TiO₂ and H-MOR(90) was found to promote the reaction to give a high yield of methylated products at a reaction temperature of 250 °C. The catalytic methylation of naphthalene using CO_2 and H_2 was also carried out successfully using a similar catalyst system comprising Re(1)/TiO₂ and H-BEA(40), with a reaction temperature of 230 °C. A series of control experiments showed that the reaction proceeds via a MeOH pathway, with CO_2 as the source of the methyl group.

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Keywords: CO_2 hydrogenation • C-methylation • Aromatics • Onepot synthesis

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The catalytic methylation of benzene using CO₂ and H₂ was performed in conjunction with a catalyst system TiO₂-supported comprising Re (Re(1)/TiO₂) and H-MOR (SiO₂/Al₂O₃ = 90). This catalyst combination gave high yields and selectivity for methylated benzene compounds. The catalytic methylation of naphthalene was also successfully carried out using a similar catalytic system consisting of Re(1)/TiO2 and H-BEA (SiO₂/Al₂O₃ = 40).



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