



Title	Catalytic Methylation of Aromatic Hydrocarbons using CO <sub>2</sub> /H <sub>2</sub> over Re/TiO <sub>2</sub> and H-MOR Catalysts
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# Catalytic Methylation of Aromatic Hydrocarbons using CO<sub>2</sub>/H<sub>2</sub> over Re/TiO<sub>2</sub> and H-MOR catalysts

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**Abstract:** A combined catalyst comprising TiO<sub>2</sub>-supported Re (Re(1)/TiO<sub>2</sub>; Re = 1 wt%) and H-MOR (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 90) was found to promote the methylation of benzene using CO<sub>2</sub> and H<sub>2</sub>. 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% CO<sub>2</sub>-based yield) under the reaction conditions employed in this study ( $p_{\text{CO}_2}$  = 1 MPa;  $p_{\text{H}_2}$  = 5 MPa;  $T$  = 250 °C;  $t$  = 20 h) in a batch reactor. Catalyst screening demonstrated that a combination of Re(1)/TiO<sub>2</sub> and H-MOR (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 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 (CO<sub>2</sub>), an important greenhouse gas, as a C<sub>1</sub> source has been the subject of intensive research over the past several decades. The use of CO<sub>2</sub> as a chemical feedstock could be a means of reducing atmospheric CO<sub>2</sub> concentrations, and CO<sub>2</sub> is also abundant, nontoxic and readily available.<sup>[1–5]</sup> There is thus significant interest in the catalytic transformation of CO<sub>2</sub> via hydrogenation to produce chemicals, especially methanol (MeOH), because this is an important commodity chemical that serves as a versatile C<sub>1</sub> building block in chemical synthesis.<sup>[6]</sup> Although the direct production of MeOH from the hydrogenation of CO<sub>2</sub> has recently been achieved industrially using Cu-based catalysts under relatively harsh conditions ( $T > 200$  °C;  $p$  = 5–10 MPa),<sup>[7]</sup> this process suffers from a low equilibrium conversion of CO<sub>2</sub> due to thermodynamic limitation.<sup>[8,9]</sup>

One possible approach to achieve high CO<sub>2</sub> conversion is use of a lower reaction temperature to produce MeOH.<sup>[10–12]</sup> 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<sub>2</sub>/H<sub>2</sub> mixture as the methylation reagent instead of MeOH for the one-pot synthesis of value-added chemicals (see **Figure S1** for representative equilibrium calculations).<sup>[13]</sup> In particular, *N*-methylation through the formation of C–N bonds for the synthesis of various methylamines has been widely explored.<sup>[14–17]</sup> Moreover, in 2014, Beller and coworkers reported

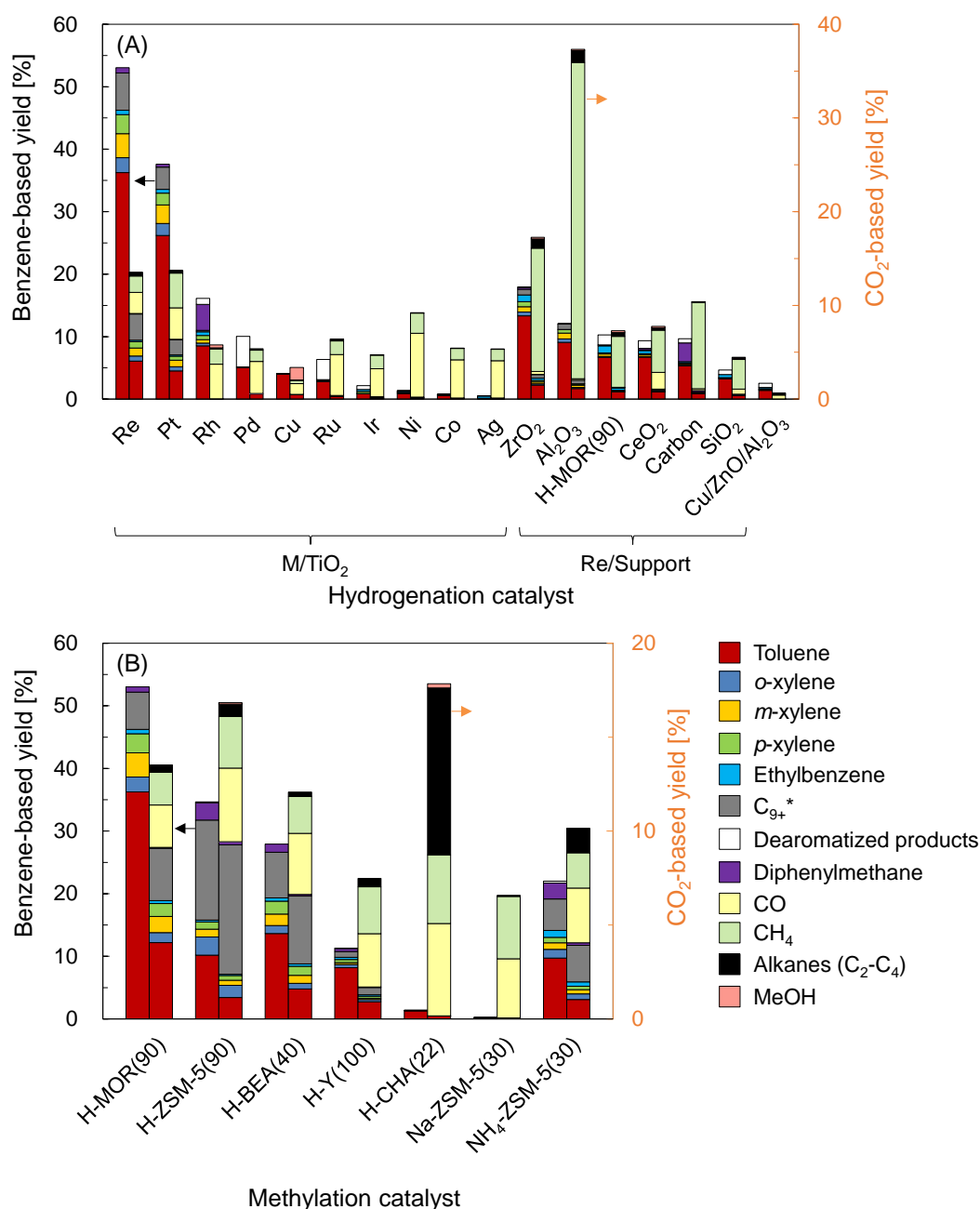
C-methylation to form aromatic C–H bonds using CO<sub>2</sub>/H<sub>2</sub> to replace MeOH as the CH<sub>3</sub> source.<sup>[18]</sup> Their work involved the use of Ru-based homogeneous catalytic systems to promote the C-methylation of electron-rich arenes. However, although this prior work was highly 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 C-methylation of unactivated aromatic hydrocarbons such as benzene to generate new aromatic compounds. Currently, C-methylation 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.<sup>[19]</sup> 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, CO<sub>2</sub> and H<sub>2</sub>.

In the present study, a combined system consisting of a TiO<sub>2</sub>-supported Re catalyst (Re(1)/TiO<sub>2</sub>; Re loading = 1 wt%) that exhibits high catalytic performance for low temperature MeOH synthesis<sup>[12]</sup> and the zeolite H-MOR (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 90) was employed for the direct methylation of benzene using CO<sub>2</sub> and H<sub>2</sub> ( $p_{\text{CO}_2}$  = 1 MPa;  $p_{\text{H}_2}$  = 5 MPa;  $T$  = 250 °C). Catalyst screening using various combinations of supported metal catalysts and zeolites having a wide range of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> 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/H<sub>2</sub>) has been reported,<sup>[20–23]</sup> the direct use of CO<sub>2</sub> would be beneficial. In addition, while the direct synthesis of aromatic hydrocarbons, including methylated benzenes, from CO<sub>2</sub>/H<sub>2</sub> mixtures that do not already contain benzene has been realized, these processes typically require harsh conditions.<sup>[24–30]</sup> In contrast, our process provides an effective means of upgrading crude oils and should also contribute to decreasing the total CO<sub>2</sub> emissions produced during petroleum refining processes.

Re(1)/TiO<sub>2</sub> was synthesized using a simple wet impregnation method, employing NH<sub>4</sub>ReO<sub>4</sub> and TiO<sub>2</sub> (Refer to the Supporting Information for a more detailed procedure). Scanning transmission electron microscopy (STEM) images of the Re(1)/TiO<sub>2</sub> (**Figure S2**) confirmed that the Re was loaded on the TiO<sub>2</sub> support in the form of highly dispersed sub-nanometer clusters.<sup>[31]</sup> 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 H<sub>2</sub> (20 mL min<sup>−1</sup>).

In the initial phase of this study, the methylation of benzene using CO<sub>2</sub>/H<sub>2</sub> 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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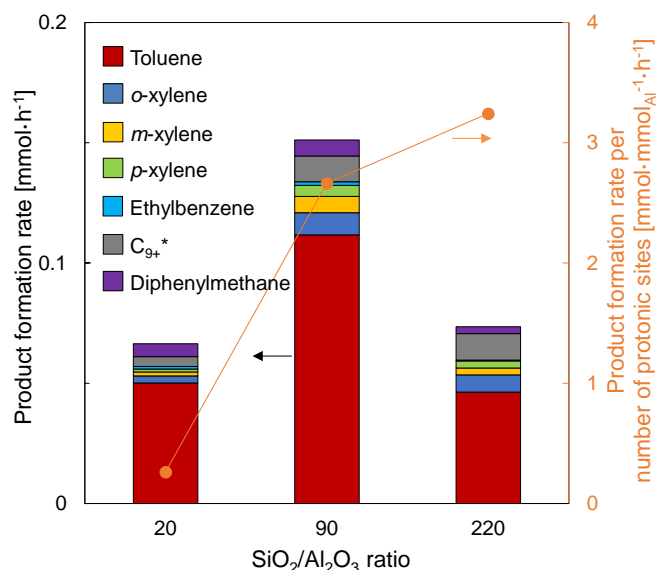
**Figure 1.** Screening of (A) hydrogenation catalysts (M/TiO<sub>2</sub> and Re/Support), and (B) zeolite catalysts for the methylation of benzene using CO<sub>2</sub> and H<sub>2</sub>. Pre-treatment: 500 °C, 0.5 h under a H<sub>2</sub> flow (20 mL min<sup>-1</sup>); reaction conditions: 1 wt% of supported 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, CO<sub>2</sub> (1 MPa), H<sub>2</sub> (5 MPa), 250 °C, 20 h. Benzene-based yield is shown in left axis whereas CO<sub>2</sub>-based yield is shown in right axis. \*Includes C<sub>9</sub> to C<sub>12</sub> methylated benzenes.

**Table S1).** First, the catalytic performances of various supported metal catalysts were compared and evaluated. A combination of Re(1)/TiO<sub>2</sub> 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 TiO<sub>2</sub>-supported metal catalysts (Figure 1A) afforded relatively low total product yields, dearomatized products such as cyclohexane and methylcyclohexane were also detected in those

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)/TiO<sub>2</sub>. The industrial MeOH synthesis catalyst Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> (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)/TiO<sub>2</sub> would be the best MeOH synthesis component for this methylation process.

After establishing TiO<sub>2</sub>-supported Re catalyst as the MeOH synthesis catalyst, we proceeded to the screening of zeolite catalysts having various distinctive framework types with a wide range of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios for the methylation of benzene using CO<sub>2</sub>/H<sub>2</sub> (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<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 20, 90 and 220) showed that H-MOR(90) (Bracketed number denotes the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio for zeolites) gave the highest yield. However, H-MOR(220) gave a higher product formation rate

calculated based on the number of protonic sites (Figure 2). This could be attributed to the fact that increasing SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> 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.<sup>[32]</sup>



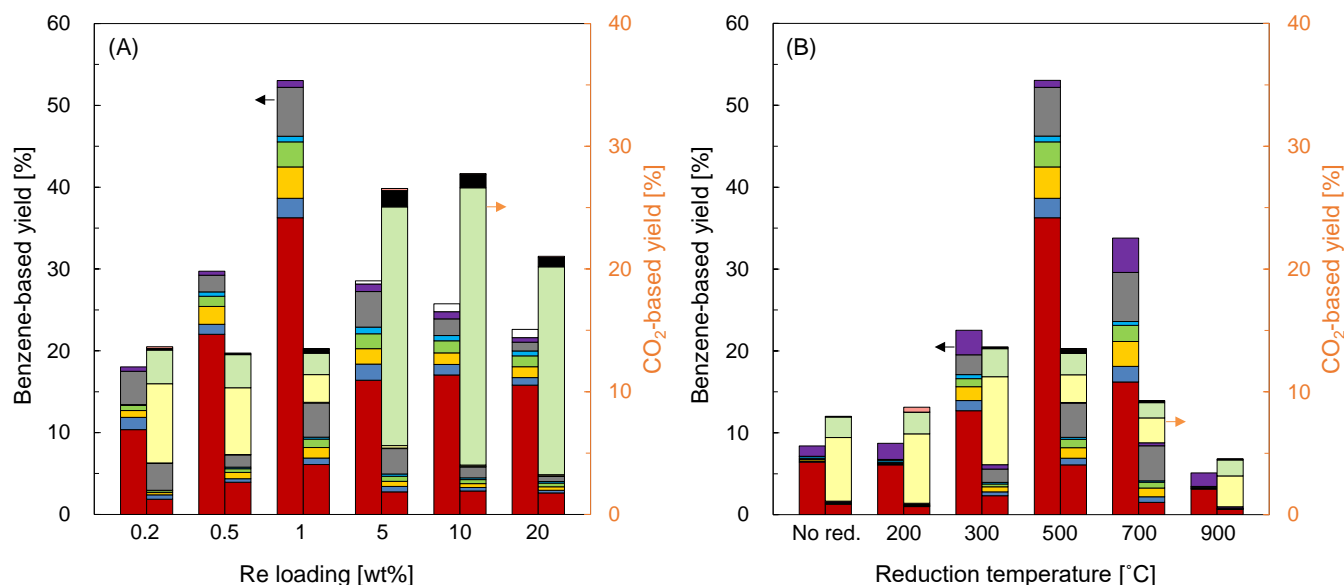
**Figure 2.** Effect of the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio on the methylation of benzene using  $\text{CO}_2$  and  $\text{H}_2$  catalyzed by  $\text{Re}(1)/\text{TiO}_2$  and H-MOR. Pre-treatment: 500 °C, 0.5 h under a  $\text{H}_2$  flow ( $20 \text{ mL min}^{-1}$ ); reaction conditions: 0.0081 mmol of loaded metal with 0.10 g of the zeolite, 1.0 mmol of benzene,  $\text{CO}_2$  (1 MPa),  $\text{H}_2$  (5 MPa), 250 °C, 1 h. \*Includes  $\text{C}_9$  to  $\text{C}_{12}$  methylated benzenes.

H-ZSM-5, which is widely used for the alkylation of benzene due to its high activity and selectivity,<sup>[33,34]</sup> 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 ( $\text{C}_2\text{--C}_4$ ), which are considered as valuable products<sup>[35,36]</sup> 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  $\text{CO}_2$ ,  $\text{H}_2$  or benzene, and no major products were detected following these reactions (Table S1). In place of a mixture of  $\text{Re}(1)/\text{TiO}_2$  and H-MOR(90), the catalytic methylation of benzene was also

attempted using either  $\text{Re}(1)/\text{TiO}_2$  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  $\text{Re}(1)/\text{H-MOR}(90)$ , but the performance was far inferior to that obtained from the combination of  $\text{Re}(1)/\text{TiO}_2$  and H-MOR(90). These results suggest that the presence of both  $\text{Re}(1)/\text{TiO}_2$  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  $\text{Re}(x)/\text{TiO}_2$  ( $x = 0.2, 0.5, 1, 5, 10$  or  $20 \text{ wt\%}$ ) to determine the optimal Re loading (Figure 3A) for the reaction (Refer to Figure S3 for the STEM images of  $\text{Re}(x)/\text{TiO}_2$ ). The highest yields of toluene and *p*-xylene were obtained using  $\text{Re}(1)/\text{TiO}_2$ . This outcome can be attributed to the fact that this material gave the highest MeOH formation rate, as reported in our previous work.<sup>[31]</sup> The product selectivity appeared to shift gradually towards  $\text{CH}_4$  with increasing Re loading. This was not unexpected, since larger clusters of Re species are known to enhance the formation of  $\text{CH}_4$ .<sup>[31]</sup> The total product yield was also found to decrease gradually as the Re loading was increased.  $\text{Re}/\text{TiO}_2$  with a lower Re loading ( $< 1 \text{ wt\%}$ ) 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  $\text{Re}(x)/\text{TiO}_2$  with higher Re loadings ( $> 1 \text{ wt\%}$ ). These results indicate that dearomatization was caused by aggregated Re species that appear predominantly at loadings above 1 wt%. Based on these data,  $\text{Re}(1)/\text{TiO}_2$  was found to be the most suitable catalyst for this reaction.

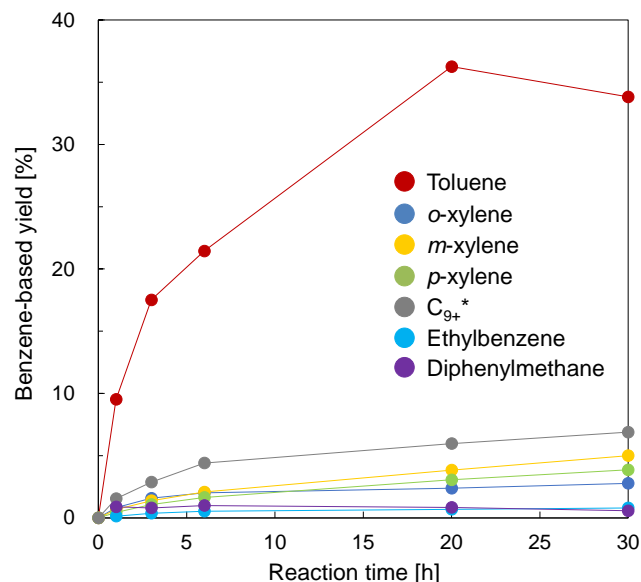
The effect of the pre-treatment temperature on the methylation of benzene using  $\text{CO}_2$  and  $\text{H}_2$  was also investigated, employing the optimized reaction conditions (Figure 3B).  $\text{H}_2$  reduction at 500 °C gave the best performance in terms of both total methylation yield and product selectivity, while higher yields of CO were observed at lower temperatures (no reduction and  $T = 200$  or  $300 \text{ °C}$ ). 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  $\text{CO}_2$  and  $\text{H}_2$ . Pre-treatment: 500 °C, 0.5 h under a  $\text{H}_2$  flow ( $20 \text{ mL min}^{-1}$ ); reaction conditions: 0.0081 mmol of loaded Re with 0.10 g of H-MOR(90), 1.0 mmol of benzene,  $\text{CO}_2$  (1 MPa),  $\text{H}_2$  (5 MPa), 250 °C, 20 h. Benzene-based yield is shown in left axis whereas  $\text{CO}_2$ -based yield is shown in right axis. \*Includes  $\text{C}_9$  to  $\text{C}_{12}$  methylated benzenes. The same legend is used as in Figure 1.

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 multi-methylated benzenes, as shown by the data at a reaction time of 30 h.

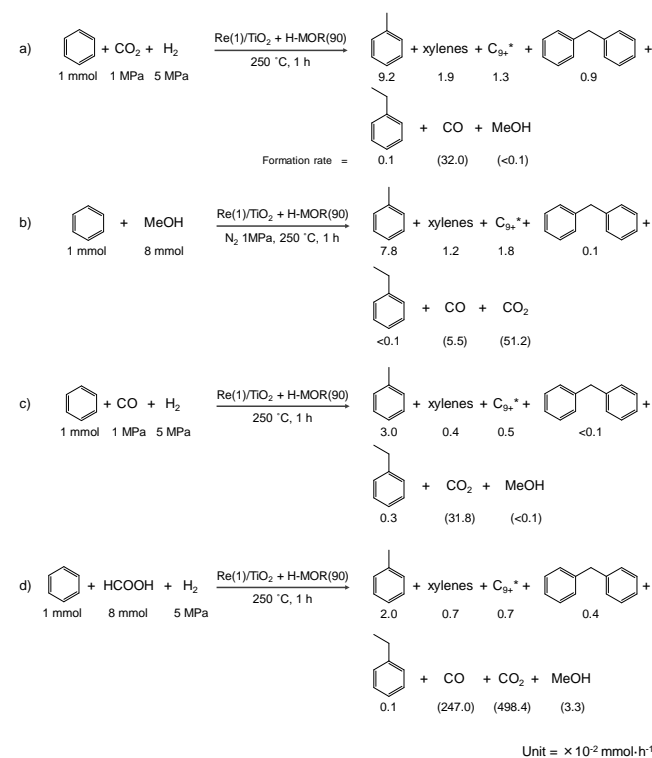


**Figure 4.** Time course plot for the methylation of benzene using  $\text{CO}_2$  and  $\text{H}_2$  catalyzed by  $\text{Re}(1)/\text{TiO}_2$  and H-MOR(90). Pre-treatment:  $500^\circ\text{C}$ , 0.5 h under a  $\text{H}_2$  flow ( $20\text{ mL min}^{-1}$ ); reaction conditions: 0.15 g of  $\text{Re}(1)/\text{TiO}_2$  and 0.10 g of H-MOR ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 90$ ), 1.0 mmol of benzene,  $\text{CO}_2$  (1 MPa),  $\text{H}_2$  (5 MPa),  $250^\circ\text{C}$ .

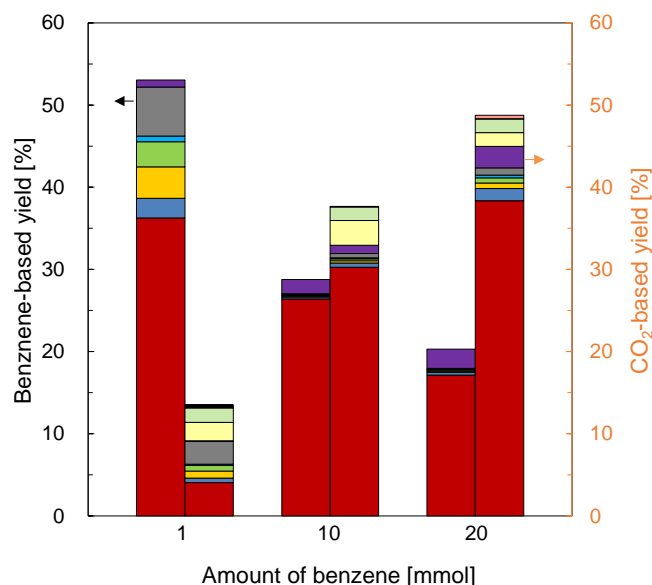
To gain more insights into the specifics of the reaction, methylation reactions employing various methylating agents, including MeOH, HCOOH and CO, were carried out under the comparable reaction conditions (**Scheme 1**). Note that each reaction was performed for just 1 h so as to observe the initial reaction rates. Both  $\text{CO}/\text{H}_2$  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  $\text{CO}_2/\text{H}_2$  (**Scheme 1, a**). On the other hand, the reaction proceeded efficiently when MeOH was used even in the absence of  $\text{CO}_2$  and  $\text{H}_2$ , suggesting that MeOH is a possible intermediate in this reaction system (**Scheme 1, b**). It is likely that MeOH is first produced from  $\text{CO}_2/\text{H}_2$  over the  $\text{Re}(1)/\text{TiO}_2$  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  $\text{CO}_2$ -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  $\text{CO}_2$ -to-methanol reaction at  $250^\circ\text{C}$  (theoretical methanol yield = 30%; see **Figure S1** for the equilibrium calculation). The results clearly proved that

one-pot methylation reaction using  $\text{CO}_2/\text{H}_2$  can achieve higher  $\text{CO}_2$  conversion in one pass compared to direct  $\text{CO}_2$ -to-methanol reaction. Recycling tests for our catalyst system were also attempted, and the results are shown in the supporting information (**Figure S5**).

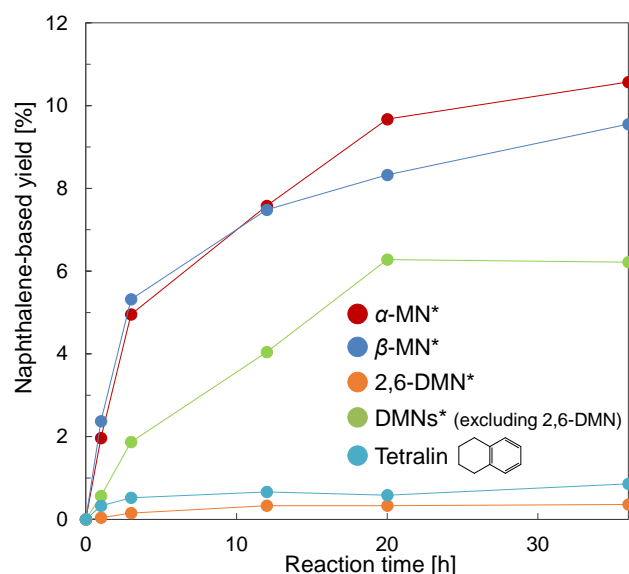


**Scheme 1.** Methylation of benzene catalyzed by  $\text{Re}(1)/\text{TiO}_2$  and H-MOR ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 90$ ) using a)  $\text{CO}_2$ , b) MeOH, c) CO and d) HCOOH as methylating agents. \*Includes  $\text{C}_9$  to  $\text{C}_{12}$  methylated benzenes.



**Figure 5.** Methylation of benzene using CO<sub>2</sub> and H<sub>2</sub> catalyzed by Re(1)/TiO<sub>2</sub> and H-MOR(90) with different initial amount of benzene as reactant. Pre-treatment: 500 °C, 0.5 h under a H<sub>2</sub> flow (20 mL min<sup>-1</sup>); reaction conditions: 0.15 g of Re(1)/TiO<sub>2</sub> and 0.10 g of H-MOR (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 90), CO<sub>2</sub> (1 MPa), H<sub>2</sub> (5 MPa), 250 °C, 20 h. Benzene-based yield is shown in left axis whereas CO<sub>2</sub>-based yield is shown in right axis. \*Includes C<sub>9</sub> to C<sub>12</sub> methylated benzenes. The same legend is used as in Figure 1.

The catalytic methylation of naphthalene using CO<sub>2</sub> and H<sub>2</sub> was also carried out to explore the applicability of our catalyst system. Instead of Re(1)/TiO<sub>2</sub> and H-MOR(90), which were identified to be the best catalysts for the methylation of benzene, the combination of Re(1)/TiO<sub>2</sub> 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 CO<sub>2</sub> and H<sub>2</sub> 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<sub>2</sub> and H<sub>2</sub> catalyzed by Re(1)/TiO<sub>2</sub> and H-BEA(40). Pre-treatment: 500 °C, 0.5 h under a H<sub>2</sub> flow (20 mL min<sup>-1</sup>); reaction conditions: 0.15 g of Re(1)/TiO<sub>2</sub> and 0.10 g of H-BEA(40), CO<sub>2</sub> (1 MPa), H<sub>2</sub> (5 MPa), 230 °C. \*MN = Methyl naphthalene, DMN = Dimethyl naphthalene.

In conclusion, one-pot synthesis of value-added products using a mixture of CO<sub>2</sub>/H<sub>2</sub> was demonstrated by employing a combination of CO<sub>2</sub> hydrogenation catalyst and zeolite catalyst. We developed a heterogeneous catalytic system for the methylation of benzene using CO<sub>2</sub> and H<sub>2</sub>. After a thorough catalyst screening process, the combination of Re(1)/TiO<sub>2</sub> 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<sub>2</sub> and H<sub>2</sub> was also carried out successfully using a similar catalyst system comprising Re(1)/TiO<sub>2</sub> 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<sub>2</sub> as the source of the methyl group.

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**Keywords:** CO<sub>2</sub> hydrogenation • C-methylation • Aromatics • One-pot synthesis

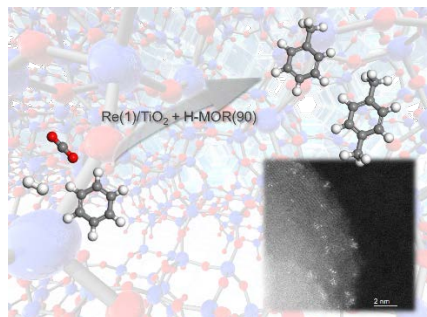
- [2] W. Zhou, K. Cheng, J. Kang, C. Zhou, V. Subramanian, Q. Zhang, Y. Wang, *Chem. Soc. Rev.* **2019**, *48*, 3193–3228.
  - [3] J. Bao, G. Yang, Y. Yoneyama, N. Tsubaki, *ACS Catal.* **2019**, *9*, 3026–3053.
  - [4] W. L. Vrijburg, E. Moiola, W. Chen, M. Zhang, B. J. P. Terlingen, B. Zijlstra, I. A. W. Filot, A. Züttel, E. A. Pidko, E. J. M. Hensen, *ACS Catal.* **2019**, *9*, 7823–7839.
  - [5] M. Ronda - Lloret, G. Rothenberg, N. R. Shiju, *ChemSusChem* **2019**, *12*, 3896–3914.
  - [6] K. Natte, H. Neumann, M. Beller, R. V. Jagadeesh, *Angew. Chem. Int. Ed.* **2017**, *56*, 6384–6394.
  - [7] J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow, W. Leitner, *Chem. Rev.* **2018**, *118*, 434–504.
  - [8] R. Gaikwad, A. Bansode, A. Urakawa, *J. Catal.* **2016**, *343*, 127–132.
  - [9] M. D. Porosoff, B. Yan, J. G. Chen, *Energy Environ. Sci.* **2016**, *9*, 62–73.
  - [10] C. A. Huff, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 18122–18125.
  - [11] S. Wesselbaum, T. Vom Stein, J. Klankermayer, W. Leitner, *Angew. Chem. Int. Ed.* **2012**, *51*, 7499–7502.
  - [12] K. W. Ting, T. Toyao, S. M. A. H. Siddiki, K. I. Shimizu, *ACS Catal.* **2019**, *9*, 3685–3693.
  - [13] S. Dabral, T. Schaub, *Adv. Synth. Catal.* **2019**, *361*, 223–246.
  - [14] K. Beydoun, T. Vom Stein, J. Klankermayer, W. Leitner, *Angew. Chem. Int. Ed.* **2013**, *52*, 9554–9557.
  - [15] X. Cui, X. Dai, Y. Zhang, Y. Deng, F. Shi, *Chem. Sci.* **2014**, *5*, 649–655.
  - [16] T. Toyao, S. M. A. H. Siddiki, K. Ishihara, K. Kon, W. Onodera, K. Shimizu, *Chem. Lett.* **2017**, *46*, 68–70.
  - [17] T. Toyao, S. M. A. H. Siddiki, Y. Morita, T. Kamachi, A. S. Touchy, W. Onodera, K. Kon, S. Furukawa, H. Ariga, K. Asakura, et al., *Chem. - Eur. J.* **2017**, *23*, 14848–14859.
  - [18] Y. Li, T. Yan, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2014**, *53*, 10476–10480.
  - [19] M. Volanti, D. Cespi, F. Passarini, E. Neri, F. Cavani, P. Mizsey, D. Fozar, *Green Chem.* **2019**, *21*, 885–896.
  - [20] S. Fujita, N. Hiyoshi, N. Takezawa, *Appl. Catal. A.* **1999**, *185*, 323–327.
  - [21] S. Lee, D. Kim, J. Lee, Y. Choi, Y. W. Suh, C. Lee, T. J. Kim, S. J. Lee, J. K. Lee, *Appl. Catal. A.* **2013**, *466*, 90–97.
  - [22] X. Zhao, F. Zeng, B. Zhao, H. Gu, *China Pet. Process. Petrochem. Technol.* **2015**, *17*, 31–38.
  - [23] Y. Bai, F. Yang, X. Liu, C. Liu, X. Zhu, *Catal. Lett.* **2018**, *148*, 3618–3627.
  - [24] C. Kuei, M. Lee, *Can. J. Chem. Eng.* **1991**, *69*, 347–354.
  - [25] Y. Ni, Z. Chen, Y. Fu, Y. Liu, W. Zhu, Z. Liu, *Nat. Commun.* **2018**, *9*, 3457.
  - [26] Y. Wang, L. Tan, M. Tan, P. Zhang, Y. Fang, Y. Yoneyama, G. Yang, N. Tsubaki, *ACS Catal.* **2019**, *9*, 895–901.
  - [27] X. Cui, P. Gao, S. Li, C. Yang, Z. Liu, H. Wang, L. Zhong, Y. Sun, *ACS Catal.* **2019**, *9*, 3866–3876.
  - [28] J. Zhang, M. Zhang, S. Chen, X. Wang, Z. Zhou, Y. Wu, T. Zhang, G. Yang, Y. Han, Y. Tan, *Chem. Commun.* **2019**, *55*, 973–976.
  - [29] Y. Xu, C. Shi, B. Liu, T. Wang, J. Zheng, W. Li, D. Liu, X. Liu, *Catal. Sci. Technol.* **2019**, *9*, 593–610.
  - [30] Z. Li, Y. Qu, J. Wang, H. Liu, M. Li, S. Miao, C. Li, *Joule* **2019**, *3*, 570–583.
  - [31] K. W. Ting, T. Toyao, S. M. A. H. Siddiki, K. Shimizu, *ACS Catal.* **2019**, *9*, 3685–3693.
  - [32] S. Sultana Poly, S. M. A. Hakim Siddiki, A. S. Touchy, S. Yasumura, T. Toyao, Z. Maeno, K. Shimizu, *J. Catal.* **2018**, *368*, 145–154.
  - [33] I. Hill, A. Malek, A. Bhan, *ACS Catal.* **2013**, *3*, 1992–2001.
  - [34] M. Deluca, P. Kravchenko, A. Hoffman, D. Hibbitts, *ACS Catal.* **2019**, *9*, 6444–6460.
  - [35] C. Xie, C. Chen, Y. Yu, J. Su, Y. Li, G. A. Somorjai, P. Yang, *Nano Lett.* **2017**, *17*, 3798–3802.
  - [36] W. Li, G. Zhang, X. Jiang, Y. Liu, J. Zhu, F. Ding, Z. Liu, X. Guo, C. Song, *ACS Catal.* **2019**, *9*, 2739–2751.
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Entry for the Table of Contents

## COMMUNICATION

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The catalytic methylation of benzene using  $\text{CO}_2$  and  $\text{H}_2$  was performed in conjunction with a catalyst system comprising  $\text{TiO}_2$ -supported Re ( $\text{Re}(1)/\text{TiO}_2$ ) and H-MOR ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 90$ ). 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  $\text{Re}(1)/\text{TiO}_2$  and H-BEA ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 40$ ).



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**Catalytic Methylation of Aromatic Hydrocarbons using  $\text{CO}_2/\text{H}_2$  over  $\text{Re}/\text{TiO}_2$  and H-MOR catalysts**