Selective methylation of toluene using CO₂ and H₂ to para-xylene

Jiachang Zuo, Weikun Chen, Jia Liu, Xinping Duan, Linmin Ye, Youzhu Yuan*

Toluene methylation with methanol to produce xylene has been widely investigated. A simultaneous side reaction of methanol-to-olefin over zeolites is hard to avoid, resulting in an unsatisfactory methylation efficiency. Here, CO₂ and H₂ replace methanol in toluene methylation over a class of ZnZrOₓ–ZSM-5 (ZZO-Z5) dual-functional catalysts. Results demonstrate that the reactive methylation species (H₂CO₂*; * represents a surface species) are generated more easily by CO₂ hydrogenation than by methanol dehydrogenation. Catalytic performance tests on a fixed-bed reactor show that 92.4% xylene selectivity in CO-free products and 70.8% para-xylene selectivity in xylene are obtained on each optimized catalyst. Isotope effects of H₂O₂ and CO₂/¹³CO₂ indicate that xylene product is substantially generated from toluene methylation rather than disproportionation. A mechanism involving generation of reactive methylation species on ZZO by CO₂ hydrogenation and migration of the methylation species to Z5 pore for the toluene methylation to form xylene is proposed.

INTRODUCTION

Para-xylene (PX), as a substantial value-added chemical feedstock, is in great demand with the rapid development of the downstream polyester industry (1, 2). Toluene methylation, an atomic economy process to synthesize PX, has attracted sustained interest in the last decades, and methanol has been widely researched to methylate toluene over zeolite catalysts in a cost-effective manner. However, the temperature of methanol-to-olefin (MTO) side reaction (typically at 400° to 500°C) is approximate to that of toluene/methanol methylation reaction (420° to 480°C) as well over zeolites, leading to the generation of unwanted gaseous hydrocarbon by-products (3–5). To restrain the side reactions, researchers modified zeolites with the oxides of Mg, P, Si, and so on (6–8) or performed the reaction at a high toluene/methanol molar ratio of 4:6, causing limited conversion of toluene. Furthermore, the intermediate species of MTO side reaction are prone to be transformed into coke and deposited onto the surface of zeolites, causing rapid deactivation (9, 10). Researchers usually add adequate amount of water to the reactants to retard the deactivation of catalyst (8). However, this leads to suppressing the methylation reaction of toluene and increasing the difficulty of industrial production. Once methanol is used as a methylation reagent over zeolites at approximately 450°C, MTO side reaction products are unavoidable and will decrease methanol usage for methylation. Therefore, new types of methylation reagents and catalysts that can work at a relative low temperature must be developed to avoid competing reactions.

The rate-determining step of toluene/methanol methylation is to overcome the high-energy barrier of converting methanol to surface methoxy species. An efficient methylation regent must rapidly generate surface methoxy. In recent years, syngas is used to methylate toluene over Cr₂O₃/ZnO and ZSM-5 (Z5) mixture catalyst (11). However, using greenhouse gaseous CO₂ combined with renewable H₂ as methyl source and nontoxic catalyst could be a better avenue. Recently, several types of oxide solid solution catalysts, such as ZnZrOₓ (ZZO), InZrOₓ, ZnAlOₓ, and ZnGaOₓ, have been investigated in CO₂ hydrogenated to methanol, olefins, or aromatics via the formate route with the methoxy intermediate (H₂CO₂*) (12–18). In tandem catalysts composed of oxides and zeolites, intermediates can migrate between the two components (19–24). Hydrogenation of CO₂ or CO can also directly produce aromatics (14–16, 22, 25, 26), but the production distribution is complex and the selectivity to xylene is usually less than 30%. On the basis of the cognizance above, CO₂ and H₂ are introduced as methylation reagents into toluene methylation reaction over ZZO-Z5 dual-functional catalysts. Multiple side reactions that may occur simultaneously need to be suppressed when CO₂ and H₂ are used in toluene methylation, such as xylene isomerization, toluene disproportionation, excessive methylation, and reversed water-gas shift reaction. Therefore, it is highly demanded to design a catalyst that can suppress the impacts of these side reactions as far as possible. In this research, zeolites are modified to inhibit xylene isomerization, toluene disproportionation, excessive methylation, and reversed water-gas shift reaction. The reaction temperature is reduced as possible to inhibit water-gas shift reaction, which is considered as an endothermic process.

The research highlights the potential for using alternative C₁ synthetic unit, greenhouse gaseous CO₂, associated with toluene more efficiently than conventional methanol, as a alternative avenue to synthesize featured xylene. Results show that a 70.8% selectivity to PX in xylene via CO₂ route over the optimized dual-functional ZZO-Z5 while only 32.7% to PX via methanol route over the optimized Z5 can be obtained (Fig. 1). As far as we are aware, there are no reports hitherto on the selective toluene methylation using CO₂ and H₂ to PX.

RESULTS AND DISCUSSION

Initially, the reaction temperature and zeolite Si/Al ratio of dual-functional ZZO-Z5 catalyst were optimized, and then 360°C and a Si/Al ratio of 85 were chosen in the following investigations (fig. S1). Notably, 1,2,4-trimethylbenzenes is the main by-product in outlet, but no any 1,2,3- and 1,3,5-trimethylbenzenes are detected. Thus, the
The deep-methylation reaction of PX and excessive pore size of zeolites lead to the generation of 1,2,4-trimethylbenzen. The mass ratio of ZZO to zeolites was decreased to reduce CO\textsubscript{2} hydrogenation reaction rates and inhibit the deep-methylation reaction. Tetraethyl orthosilicate was deposited on Z5 twice (the modified zeolite was labeled as 2SZ5; 2 represents the time of modification) to minimize the pore size of zeolites. Results show that xylene selectivity rises from 66.3 to 92.4%, with the ZZO mass percent decreased to 10% (Fig. 2A). At the same time, 4-ethyltoluene, a deep-methylation by-product with a smaller molecular diameter than 1,2,4-trimethylbenzen, increases compared with the result by unmodified Z5. This result indicates that the pore size of zeolites is effectively decreased, which conforms to the pore width distribution results in Fig. 3F. Controlled experiments that only toluene/N\textsubscript{2} flowed over zeolites were executed to eliminate the influence of toluene disproportionation side reaction. The results show that toluene conversions are only 0.2 and 0.5% for the Z5 and 2SZ5 catalysts, respectively, which indicate that toluene methylation reaction rather than toluene disproportionation is the dominant process that produces xylene.

Although xylene selectivity is improved to more than 90% by adjusting the molar ratio of ZZO and 2SZ5 components in the dual-functional catalyst, the selectivity to PX in xylene is unsatisfied and tends to the thermodynamic equilibrium distribution state (Fig. S2A). Moreover, increasing amount of ZZO benefits the CO\textsubscript{2} conversion and tends to the thermodynamic equilibrium distribution state (fig. S2A). Moreover, increasing amount of ZZO benefits the CO\textsubscript{2} conversion and tends to the thermodynamic equilibrium distribution state.

The ZZO-Z5 catalysts were characterized by several methods to indicate the relationship between PX selectivity and physiochemical properties of dual-functional catalysts. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images indicate the relationship between PX selectivity and physiochemical properties of dual-functional catalysts. TEM and SEM images show the distribution of ZZO and 2SZ5 in the catalyst, which explains the PX selectivity in xylene.

The ZZO-Z5 catalysts were characterized by several methods to indicate the relationship between PX selectivity and physiochemical properties of dual-functional catalysts. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images indicate the relationship between PX selectivity and physiochemical properties of dual-functional catalysts. TEM and SEM images show the distribution of ZZO and 2SZ5 in the catalyst, which explains the PX selectivity in xylene.
show that unmodified Z5 features a cube-like morphology and a clean surface. While Z5 was modified four times with TEOS and mixed with ZZO, zeolites show a tendency to become sphere, and small particles appear on the zeolite surface. Energy dispersive spectroscopy (EDS) line-scanning experiment indicates that the small particles are ZZO (Fig. 3, A to E). X-ray powder diffraction (XRD) pattern for ZZO shows a slight shift of ZrO2 diffraction peaks to a high angle, suggesting that the small Zn atoms are successfully doped into the ZrO2 crystal lattice to form ZZO solid solution structure (fig. S5A). Meanwhile, ZZO and Z5 are mixed at a mass ratio of 1:9, and the diffraction peaks of ZZO are difficult to recognize because the peaks of Z5 are too intense. The Brunauer-Emmett-Teller surface area of Z5 decreases from 360 to 253 m2 g⁻¹ as the number of modification times is increased. The decrement is mainly caused by the decrease of micropore area rather than external area based on the t-plot method (table S1). Meanwhile, pore size distribution curves show that the pore volume and the most probable pore size are reduced on the basis of the nonlocal density functional theory (NLDFT) (27, 28). The finding matches the result that 1,2,4-trimethylbenzen selectivity is decreased and 4-ethyltoluene selectivity is increased (Fig. 2A and fig. S1). The reductions in specific surface and pore size of Z5 after TEOS modification are essentially due to the changes of zeolite structure and crystallinity according to XRD results, although the molecular diameter of TEOS is larger than the pore size of intact Z5. Carbon dioxide temperature-programmed desorption (CO2-TPD) curves indicate that CO2 can be steadily adsorbed on ZZO until 550°C, but zeolites cannot adsorb CO2 (fig. S5B). Acid amounts and types of zeolites are decisive for PX selectivity in xylene. Thus, ammonia TPD (NH3-TPD) and pyridine Fourier transform infrared (Py-FTIR) spectroscopy are used to characterize acid properties. In the NH3-TPD curves (Fig. 3G), three main peaks at 100° to 250°C, 250° to 550°C, and 550° to 700°C belong to weak acid, medium strong acid, and strong acid sites, respectively (14). Weak and medium strong acid are mainly contributed by zeolites, and strong acid is contributed by ZZO. The modified Z5 catalysts show an extreme decrease in the amount of medium acid compared with no modification. The more modified times performed, the less medium acid amount obtained. However, weak acid and strong acid amounts are changed slightly. In the Py-FTIR spectra shown in fig. S5C, the peaks at 1543, 1491, and 1448 cm⁻¹ are attributed to pyridine adsorbed on Brønsted acid, surface hydroxyl, and Lewis acid sites, respectively. The quantity ratios of Brønsted acid to Lewis acid were calculated...
from their corresponding peak intensities, which firstly rises up to 0.83 of ZZO-4SZ5 and then declines, with the number of zeolite-modified times increased. This result matches well with the tendency of PX selectivity in xylene (fig. S3), indicating that the higher Bronsted acid ratio of zeolite, the higher PX selectivity obtained. AI magic angle spinning nuclear magnetic resonance (MAS NMR) profiles show that all AI atoms in Z5 are tetra-coordinate at the zeolite framework. While Z5 is modified with TEOS, some lattice AI atoms are replaced by Si and converted to hexa-coordinate extra-framework octahedral aluminum (29, 30). The signal-to-noise ratio of 4SZ5 is lower than that of Z5, which indicates that the content of Al decreases after zeolites are modified by TEOS (fig. SSD).

The $\text{H}_2/\text{D}_2$ kinetic isotope effect was obtained by fixed-bed reactor activity test to understand the reaction mechanism of toluene methylated with CO$_2$ and H$_2$ over ZZO-Z5 catalysts. While insetting D$_2$ instead of H$_2$ over ZZO-4SZ5 catalyst, toluene conversion increases from 14.5 to 18.2%, $k_\text{H}/k_\text{D} = 0.80$ (Fig. 4C). Such an inverse isotope effect indicates that the C—D bond is easier to form than the C—H bond, which may be related to the rate-determining step. Meanwhile, the outlet gas was injected into gas chromatography–mass spectrometry (GC-MS) to determine the substitution position by D atom.

When ZZO-4SZ5 is exposed to CO$_2$ + H$_2$, the species of HCOO$^*$ and CO$_2$ is detected (fig. S7A) (31–34). When the catalyst is exposed to C$_7$H$_8$ + CO$_2$ + H$_2$, no any peak of CO$_2$ is observed (Fig. 4A), which means that the introduction of toluene would accelerate CO$_2$ hydrogenation rate by consuming intermediate species. When H$_2$ is switched to D$_2$, the peaks at 2166 and 2120 cm$^{-1}$ appear, corresponding to the C—D asymmetric stretching and symmetric stretching vibrations for DCOO$^*$, respectively. The peaks at 2709 and 2662 cm$^{-1}$ are assigned to the O—D asymmetric stretching and symmetric stretching vibrations for OD$^*$, respectively. The peaks at 3080 and 3035 cm$^{-1}$ are assigned to the C—H stretching vibrations of benzene ring, and 2935 and 2884 cm$^{-1}$ are assigned to the C—H stretching vibrations of the methyl group (35, 36). In Fig. 4A, the peaks at 3080 and 3035 cm$^{-1}$ decrease because of the replacement of H on benzene ring by D. Since the H on methyl group is unsubstituted, there is no decrease in the peak of 2935 and 2884 cm$^{-1}$, which is consistent with GC-MS results. The HCOO$^*$ (DCOO$^*$) species increase after switching H$_2$ to D$_2$ in Fig. 4A and fig. S7A, indicating that the formation rate of DCOO$^*$ is higher than that of HCOO$^*$, because of the different zero-point energy for isotope. For CO$_2$/CO$_2^{13}$ isotope-switching studies, when reaction gases are switched from CO$_2$ + H$_2$ + C$_7$H$_8$ to CO$_2$ + H$_2$ + C$_7$H$_8^{13}$,
the O—C—O stretching vibration peak of HCOO* is shifted from 1584 to 1535 cm⁻¹ (Fig. 4B). Meanwhile, the enhancement of the C—C stretching vibration of benzene ring (1503 cm⁻¹) and C—H bending vibration of CH₃* species (1437 cm⁻¹) indicates that more toluene is adsorbed on the catalysts, which may be because the slower rate of breaking ¹³C—O than C—O bond reduces the methylation reaction rate. On the basis that HCOO* is the main species in DRIFTS, and the use of D₂ shows a higher reaction rate than H₂, the formation or hydrogenation of HCOO* is likely related to the rate-determining step. Combined with the DFT calculations in literature, the further hydrogenation of HCOO* to HCOOH* is suppressed by its reverse reaction, due to the high stability of HCOO*, which is consistent with in situ DRIFTS results above. The reverse reaction of HCOOH* to HCOO* is faster than not only HCOO* hydrogenation but also HCOOH* further hydrogenation (37–39). Thereby, we are more inclined to consider that the hydrogenation of HCOO* is the rate-determining step.

Reactive methylation species must migrate to the pore structure of zeolites to accomplish toluene methylation reaction. Therefore, the closer proximity of ZZO and zeolite, the higher U_methy could be obtained. To confirm the inference, different proximities of power-mixing, granule-mixing, and dual-bed mixed modes for ZZO and 4SZ5 were used, and the carbon usage of CO₂ was calculated. The power-mixing mode shows the highest U_methy up to 84.8%, whereas only 33.2% converted CO₂ participates in toluene methylation reaction under the dual-bed mode (Fig. 5A). The close proximity of the components in dual-functional catalysts could prominently accelerate the second step (toluene methylation) reaction rate in tandem reaction. With the consumption of reactive methylation species, the reaction equilibrium of CO₂ hydrogenation can be shifted to generate more reactive methylation species, which cause high U_methy. The stability test for ZZO-4SZ5 shows no obvious decline in toluene conversion and PX selectivity in xylene for more than 100 hours, but xylene selectivity decreases slightly and 4-ethyltolueneselectivity increases with time (Fig. 5B and fig. S8). Moreover, the catalyst that has been run for 100 hours is regenerated by a simple calcination in air and subjected to testing the performance to explore the reason of decrease in xylene selectivity. The results show that the xylene selectivity in initial stage is slightly lower than that over fresh catalyst, but it reaches to the same level after 40 hours on stream. The finding suggests that the decrease in xylene selectivity may not be caused by carbon deposition but is more likely that the changes of active and acidic sites of zeolite occurred in the process of reaction.

Fig. 4. H₂/D₂ or CO₂/¹³CO₂ isotope effect studies. In situ DRIFTS spectra over the ZZO-4SZ5 catalyst exposed to the stream of (A) C₇H₈ + CO₂ + H₂ and subsequently switched to C₇H₈ + CO₂ + D₂ and of (B) C₇H₈ + CO₂ + H₂ and subsequently switched to C₇H₈ + ¹³CO₂ + H₂. (C) H₂/D₂ kinetic isotope effect of toluene methylated to xylene using CO₂ and H₂(D₂) over ZZO-4SZ5 catalyst. Reaction conditions are the same as those in Fig. 2.

In conclusion, CO₂ and H₂ show great potential as methylation reagents for selectively methylating toluene to xylene over ZZO-Z5 dual-functional catalysts. Compared with methanol route, the reactive methylation species of H₃CO* entity is much easier obtained by the CO₂ hydrogenation route. Optimizing the mass ratio of ZZO

Zuo et al., Sci. Adv. 2020; 6 : eaba5433  21 August 2020
to modified Z5 results in a high selectivity to xylene of 92.4% in CO-free products. Moreover, PX selectivity in xylene reaches to 70.8% over ZZO-4SZ5 in CO2 route, while only 32.7% over 4SZ5 in methanol route. The reactive methylation species generated in CO2 route is dynamically reacted by the subsequent methylation step, which substantially depressed the reactions of deep methylation and MTH. In the stability test of ZZO-4SZ5, toluene conversion and PX selectivity in xylene do not change significantly. CO2 hydrogenation follows the formate route, and we tend to consider that the formation or hydrogenation of HCOO* is included in the rate-determining step. The proposed mechanism is that reactive methylation species are generated from ZZO by CO2 hydrogenation and migrated to the pore structure of Z5 and methylating toluene to xylene. This work demonstrates the virtue of CO2 hydrogenation coupled with toluene methylation over the dual-functional catalysts for PX production, which would inspire further explorations on other related systems.

MATERIALS AND METHODS

Catalyst preparation

ZZO was synthesized by a coprecipitation method based on the research of Li et al. (14). Zn(NO3)2·6H2O (0.60 g) and Zr(NO3)4·5H2O (5.80 g) were dissolved in 100 ml of deionized water labeled as solution A. (NH4)2CO3 (3.06 g) was dispersed into 100 ml of deionized water labeled as solution B. Then, solution B was dropwise added into solution A at the speed of approximately 3 ml min⁻¹ and continuously magnetically stirred for 2 hours at 70°C. After cooling down to ambient temperature and ageing for 2 hours, the precipitate was washed with deionized water, dried overnight, and calcined in air at 500°C for 3 hours. Z5 zeolites were purchased from the Nankai University Catalyst, and the method of using TEOs to modify Z5 was referred to the literature of Ni et al. (16). Typically, the steps to modify the Z5 once were to immerse 2.00 g of Z5 into the mix solution of 2.44 ml of TEOs and 1.00 ml of cyclohexane for 4 hours. Then, Z5 was dried at 110°C overnight and calcined in air at 550°C for 4 hours. While the above steps were repeated, a new symbol of nSZ5 (n means the number of repetitions) was used. Then, the dual-functional catalyst was obtained by the well mixing of ZZO and nSZ5 in an agate mortar. Before the performance in fixed-bed reactor system or the characterization of physicochemical properties, dual-functional catalysts were hydrogenated in 5% H2/Ar mixed gas flow at 450°C for 2 hours.

Catalyst evaluation

Catalytic performance was evaluated on a high-pressure fixed-bed reactor equipped with a quartz sample tube. Typically, 200-mg catalyst (40 to 60 mesh) and 800-mg quartz sand were mixed and loaded into reaction tube. Before testing, samples were reduced by 5% H2/Ar at 450°C for 2 hours. For the study of toluene methylated with CO2 and H2, a mixture gas of CO2/H2/N2 [24/72/4 (v/v/v)] was induced into a stainless container loaded with toluene at 90°C, and then toluene was carried into reaction tube with a constant concentration. Typically, the reaction was conducted at 360°C and 3.0 MPa, with a GHSV of 12,000 ml g⁻¹ hour⁻¹ and a toluene WHSV of 1 hour⁻¹, and the data were collected at the reaction time of 15 hours. For the contrast experiment of toluene methylated with methanol, a mixed solution of C7H8/CH3OH [2/1 (mol/mol)] was pumped into reaction tube with a toluene WHSV of 0.9 hour⁻¹ at 360° to 460°C and 0.1 and 3.0 MPa, while 12,000 ml g⁻¹ hour⁻¹ N2 or H2/N2 [72/28 (v/v)] was used as a carry gas simultaneously. Three GCs were used together equipped with PLOT-Q, WAX, and TDX-01 columns to analyze gaseous hydrocarbons, aromatics, and inorganic gases, respectively. CH4 was taken as a reference bridge between the three GCs.
Toluene conversion was calculated according to
\[
\text{Conv}_{\text{C6-H}} = \frac{\sum n \left( \frac{n}{n} C_n H_{\text{moul}} \right) - C_7 H_{\text{8outlet}}}{\sum n \left( \frac{n}{n} C_n H_{\text{moul}} \right)} \times 100\%
\]
where \( C_n H_{\text{moul}} \) \((n \geq 6)\) represents moles of aromatics at the outlet.

Product selectivity without CO for toluene methylated with CO2 and H2 was obtained according to
\[
\text{Sel}_{C_n H_m} = \frac{n C_n H_{\text{moul}}}{\sum n C_n H_{\text{moul}} - C_7 H_{\text{8outlet}}} \times 100\%
\]
where \( C_n H_{\text{moul}} \) \((n \geq 1)\) represents moles of hydrocarbons at the outlet.

Product selectivity for toluene methylated with methanol was obtained according to
\[
\text{Sel}_{C_n H_m} = \frac{n C_n H_{\text{moul}}}{\sum n C_n H_{\text{moul}} - \text{CH}_3 \text{OH}_{\text{outlet}}} \times 100\%
\]
where \( \text{CH}_3 \text{OH}_{\text{outlet}} \) represents the mole of methanol at the outlet.

CO2 carbon usages for methylation, C1-C5, and CO were obtained according to
\[
\begin{align*}
U_{\text{methy}} &= \frac{\sum n \left( \frac{n-2}{n} C_n H_{\text{moul}} \right) + \sum n C_n H_{\text{moul}} + \text{CO}_{\text{outlet}}}{\sum n \left( \frac{n-2}{n} C_n H_{\text{moul}} \right)} \times 100\% \\
U_{C_1-C_5} &= \frac{\sum n C_n H_{\text{moul}}}{\sum n \left( \frac{n-2}{n} C_n H_{\text{moul}} \right) + \sum n C_n H_{\text{moul}} + \text{CO}_{\text{outlet}}} \times 100\% \\
U_{\text{CO}} &= \frac{n C_n H_{\text{moul}}}{\sum n \left( \frac{n-2}{n} C_n H_{\text{moul}} \right) + \sum n C_n H_{\text{moul}} + \text{CO}_{\text{outlet}}} \times 100\%
\end{align*}
\]
where \( \text{CO}_{\text{outlet}} \) represents the mole of carbon monoxide at the outlet.

Methanol carbon usages for methylation, C1-C5, and DME were obtained according to
\[
\begin{align*}
U_{\text{methy}} &= \frac{\sum n \left( \frac{n-2}{n} C_n H_{\text{moul}} \right) + \sum n C_n H_{\text{moul}} + 2 \text{CH}_3 \text{OCH}_3_{\text{outlet}}}{\sum n \left( \frac{n-2}{n} C_n H_{\text{moul}} \right)} \times 100\% \\
U_{C_1-C_5} &= \frac{\sum n C_n H_{\text{moul}}}{\sum n \left( \frac{n-2}{n} C_n H_{\text{moul}} \right) + \sum n C_n H_{\text{moul}} + 2 \text{CH}_3 \text{OCH}_3_{\text{outlet}}} \times 100\% \\
U_{\text{DME}} &= \frac{\sum n C_n H_{\text{moul}}}{2 \text{CH}_3 \text{OCH}_3_{\text{outlet}}} \times 100\%
\end{align*}
\]
where \( \text{CH}_3 \text{OCH}_3_{\text{outlet}} \) represents the mole of dimethyl ether at the outlet.

**Catalyst characterization**

XRD patterns were performed on a SmartLab SE diffractometer equipped with a Cu-Kα radiation source \((\lambda = 1.5418 \text{ Å})\), operated at 40 kV and 40 mA, with a scan speed of 2°/min (20). Physical absorptions were carried out on a Micromeritics ASAP 2020 equipment. Initially, particle sample was degassed at 350°C under high vacuum for 3 hours to remove adsorbed moisture and organics. Then, measurements were executed, and Ar was used as adsorbate. Pore width distribution was obtained by NLDFT algorithm (27, 28, 40). NH3-TPD and CO2-TPD curves were carried out on a Micromeritics AutoChem 2920 apparatus with thermal conductivity detector, and a tandem online mass spectrometer was used to monitor outlet gases. Typically, a pretreatment process by 5% H2/Ar at 450°C for 1 hour over 50 mg catalysts was used before the above three types of temperature-programmed reactions. After the pretreatment process and cooling down to 50°C, 10% NH3/Ar or pure CO2 was inducted for 1 hour, and then the sample was exposed to Ar at 100°C for 2 hours until a stable baseline was obtained. Subsequently, the m/z signals of 16 for NH3 and 44 for CO2 were recorded by online mass spectrometer, with the temperature increased to 800°C at a heating rate of 10°C/min. MAS NMR profiles were obtained on a Bruker AVANCE III equipment. Py-FTIR spectroscopy experiment was carried out on the same instrument as DRIFTS. A pretreatment process was carried out that the sample was exposed to 5% H2/Ar at 450°C for 2 hours, and then inlet gas was changed into N2, with the temperature returned to 80°C. After the temperature kept stably, inlet gas was turned off and vacuum pump was opened to vent the filled gas. Subsequently, the switch that is connected with pyridine was opened to induce pyridine volatilized into sample chamber for 3 min. Last, the entrance of pyridine was cut off, and gaseous or physical adsorbed pyridine was vacuumed, and then spectra were recorded for 32 scans at the resolution ratio of 4 cm−1. In situ DRIFTS measurements were performed on a Nicolet 6700 instrument equipped with a mercury cadmium telluride (MCT) detector at ambient pressure. First, the catalyst of ZZO-4SZ (ZZO mass percent, 50%) was exposed to 5% H2/Ar at 450°C for 1 hour to obtain reduced state. Then, the inlet gas was changed into N2 flow cooling down to 360°C, and a background was recorded. Toluene steam was induced by inletting reaction gases into a Montegia washing bottle containing toluene at 80°C. All spectra were obtained by collecting 32 scans at the resolution ratio of 8 cm−1.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/6/34/eaba5433/DC1

**REFERENCES AND NOTES**

1. J. Zhou, Z. Liu, Y. Wang, D. Kong, Z. Xie, Shape selective catalysis in methylation of toluene: Development, challenges and perspectives. *Front. Chem. Sci. Eng.* **12**, 103–112 (2018).
2. J. H. Ahn, R. Kolvenbach, C. Neudeck, S. S. Al-Khattaf, A. Jentys, J. A. Lercher, Tailoring mesoskopically structured H-ZSM5 zeolites for toluene methylation. *J. Catal.* **311**, 271–280 (2014).
3. J. Zhou, Y. Wang, W. Zou, C. Wang, L. Li, Z. Liu, A. Zheng, D. Kong, W. Yang, Z. Xie, Mass transfer advantage of hierarchical zeolites promotes methanol converting into para-methyl group in toluene methylation. *Ind. Eng. Chem. Res.* **56**, 9310–9321 (2017).
4. J. H. Ahn, R. Kolvenbach, S. S. Al-Khattaf, A. Jentys, J. A. Lercher, Methanol usage in toluene methylation with medium and large pore zeolites. *ACS Catal.* **3**, 817–825 (2013).
5. Y. Bi, Y. Wang, Y. Wei, Y. He, Z. Yu, Z. Liu, L. Xu, Improved selectivity toward light olefins in the reaction of toluene with methanol over the modified HZSM-5 catalyst. *ChemCatChem* **6**, 713–718 (2014).
6. W. Tan, M. Liu, Y. Zhao, K. Hou, H. Wu, A. Zhang, H. Liu, Y. Wang, C. Song, X. Guo, Para-selective methylation of toluene with methanol over nano-sized ZSM-5 catalysts: Synergistic effects of surface modifications with SiO2, P2O5, and MgO. *Micropor. Mesopor. Mater.* **196**, 18–30 (2014).
7. J. Zhang, W. Qian, C. Kong, F. Wei, Increasing para-xylene selectivity in making aromatics from methanol with a surface-modified Zr/PI-ZSM-5 catalyst. *ACS Catal.* **5**, 2982–2988 (2015).
8. C. Wang, L. Zhang, X. Huang, Y. Zhu, G. Li, Q. Gu, J. Chen, L. Ma, X. Li, Q. He, J. Xu, Q. Sun, C. Song, M. Peng, J. Sun, D. Ma, Maximizing sinusoidal channels of HZSM-5 for high shape-selectivity to p-xylene. *Nat. Commun.* **10**, 4348 (2019).
shape-selective HZSM-5 catalysts for methylation of fluids.

58. C. Schild, A. Wokaun, A. Baiker, On the mechanism of CO and H\textsubscript{2} hydrogenation reactions on zirconia-supported catalysts: A diffuse reflectance FTIR study: Part II. surface se"ces on copper/zirconia catalysts: Implications for methanation synthesis selectivity. J. Mol. Catal. 63, 243–254 (1990).

59. W. Li, K. Wang, J. Huang, X. Liu, D. Fu, J. Huang, Q. Li, G. Zhan, Me\textsubscript{2}O\textsubscript{2}–ZrO\textsubscript{2} (M = Zn, Co, Cu) solid solutions derived from Schiff base-bridged UO\textsubscript{2}O\textsubscript{6} composites as high-performance catalysts for CO\textsubscript{2} hydrogenation. ACS Appl. Mater. Interfaces 11, 33265–33272 (2019).

60. K. Chen, H. Fang, S. Wu, X. Liu, J. Zheng, S. Zhou, X. Duan, Y. Zhuang, S. C. E. Tsang, Y. Yuan, CO\textsubscript{2} hydrogenation to methanol over Cu catalysts supported on La-modified SBA-15: The crucial role of Cu-LaO\textsubscript{2} interfaces. Appl. Catal. Environ. 251, 119–129 (2019).

61. K. Chen, X. Duan, H. Fang, X. Liang, Y. Yuan, Selective hydrogenation of CO\textsubscript{2} to methanol catalyzed by Cu supported on rod-like La\textsubscript{2}O\textsubscript{3}CO\textsubscript{3}. Catal. Sci. Technol. 8, 1062–1069 (2018).

62. G. Muller, T. Narashibehu, G. Mirth, J. A. Lercher, Infrared microscopic study of sorption and diffusion of toluene in ZSM-5. J. Phys. Chem. 98, 7436–7439 (1994).

63. O. I. El-Sabbagh, M. M. Baraka, S. M. Ibrahim, C. Panneconouque, G. Andrei, R. Snoeck, J. Balzarini, A. A. Rashad, Synthesis and anti-viral activity of new pyrazole and thiazole derivatives. Eur. J. Med. Chem. 44, 3746–3753 (2009).

64. M. Dou, M. Zhang, Y. Chen, Y. Yu, DFT study of In\textsubscript{2}O\textsubscript{3} catalyzed methanol synthesis from CO\textsubscript{2} and CO hydrogenation on the defective site. New J. Chem. 42, 3293–3300 (2018).

65. M. Dou, M. Zhang, Y. Chen, Y. Yu, Theoretical study of methanol synthesis from CO\textsubscript{2} and CO hydrogenation on the surface of ZrO\textsubscript{2} supported In\textsubscript{2}O\textsubscript{3} catalyst. Surf. Sci. 672–673, 7–12 (2018).

66. S. Kattel, B. Yan, Y. Yang, J. G. Chen, P. Liu, Optimizing binding energies of key intermediates for CO\textsubscript{2} hydrogenation to methanol over oxide-supported copper. J. Am. Chem. Soc. 138, 12440–12450 (2016).

67. A. S. Al-Dughailher, H. de Lasa, HZSM-5 zeolites with different SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios. Characterization and NH\textsubscript{3} desorption kinetics. Ind. Eng. Chem. Res. 53, 15303–15316 (2014).

Acknowledgments: Funding: This work was supported by the National Key Research and Development Program of China (2017YFA0206801), the National Natural Science Foundation of China (2017YFA0206801), and the Program for Innovative Research Team in Chinese Universities (IRT_14R13). Author contributions: J.Z. developed the sample synthesis approach and performed most of the experiments. W.C. provided help in the TEM measurements. J.L. helped to carry out the experiments in early stage. X.D. and L.Y. helped to analyze the data. J.Z. and Y.Y. wrote the manuscript. Y.Y. designed and guided the work. All the authors read and commented on the manuscript. Competing interests: Y.Y., J.Z., X.D. and L.Y. are the authors on a patent application related to this work (no. 201911149539.2, filed 21 November 2019). Y.Y., J.Z., X.D. and L.Y. are the authors on a second patent application related to this work (no. PCT/ CN2020/077412, filed 21 November 2019). The other authors declare no conflict of interest.

Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. The primary data that support the plots within this paper and other finding of this study are available from the corresponding author on reasonable request.

Submitted 15 December 2019
Accepted 9 July 2020
Published 21 August 2020
10.1126/sciadv.aba5433

Citation: J. Zuo, W. Chen, J. Liu, X. Duan, L. Ye, Y. Yuan, Selective methylation of toluene using CO\textsubscript{2} and H\textsubscript{2} para-xylene. Sci. Adv. 6, eaba5433 (2020).
Selective methylation of toluene using CO₂ and H₂ to para-xylene

Jiachang Zuo, Weikun Chen, Jia Liu, Xinping Duan, Linmin Ye and Youzhu Yuan

Sci Adv 6 (34), eaba5433.
DOI: 10.1126/sciadv.eaba5433