In$_2$O$_3$ Nanocrystals for CO$_2$ Fixation: Atomic-Level Insight into the Role of Grain Boundaries

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HIGHLIGHTS

We prepared In$_2$O$_3$ nanocrystals with high density of grain boundaries (HGB-In$_2$O$_3$)

HGB-In$_2$O$_3$ gained 82% yield of N,N-dimethylaniline in N-methylaniline methylation

The grain boundaries in In$_2$O$_3$ facilitated the adsorption and activation of CO$_2$

The grain boundaries in In$_2$O$_3$ enhanced the activation of N-H bond in amines

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In$_2$O$_3$ Nanocrystals for CO$_2$ Fixation: Atomic-Level Insight into the Role of Grain Boundaries

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SUMMARY

N-functionalization of amines with CO$_2$ and H$_2$ is one of the most important processes to make use of CO$_2$. Although noble metal-based catalysts with remarkable performance have been widely used in this process, developing efficient non-noble-metal-based catalysts remains a grand challenge. Herein, we report In$_2$O$_3$ nanocrystals with high density of grain boundaries (HGB-In$_2$O$_3$), which show excellent activity toward methylation of amines. Impressively, HGB-In$_2$O$_3$ achieved the optimal yield of 82.7% for N,N-dimethylaniline with a mass activity of 21.2 mmol $g^{-1} h^{-1}$ in methylation of N-methylaniline, comparable to noble-metal-based catalysts. As a bonus, HGB-In$_2$O$_3$ held noticeable stability, remarkable selectivity, and comprehensive applicability. Further mechanistic studies revealed that the presence of high density of grain boundaries not only facilitated the adsorption and activation of CO$_2$ to generate CH$_3$OH as the intermediate but also enhanced the activation of N-H bond in amines, contributing to the attractive activity of HGB-In$_2$O$_3$ toward methylation of amines.

INTRODUCTION

Owing to the superfluous consumption of fossil fuels, anthropogenic emissions of CO$_2$ to the atmosphere are rapidly increasing, which gives rise to global warming. In this case, reduction of CO$_2$ into fuels utilizing electric or solar energy was considered as an efficient approach to mitigate the environmental problem. Besides, converting CO$_2$ into high value-added fine chemicals by organic reaction is also an effective way to recycle CO$_2$, which has attracted intensive attention around the world. In particular, N-functionalization of amines with CO$_2$ and H$_2$ is one of the most important processes to make use of CO$_2$ efficiently. For instance, a homogeneous well-defined [Ru(triphos)(tmm)] catalyst was reported by Beydoun and coworkers. In the reductive methylation of amines by using CO$_2$ and H$_2$, the desired product was isolated with 83% yield. Another notable example is the ruthenium-pincer-type complexes, which were found to attain remarkable turnover numbers of up to 1,940,000. Cui et al. described an efficient procedure for the reductive amination of CO$_2$ using Pd/CuZrO$_x$ catalyst, which can be realized with up to 97% yield under relatively mild reaction conditions.

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Herein, we report a rational design of In$_2$O$_3$ nanocrystals with high density of grain boundaries (HGB-In$_2$O$_3$), which shows remarkable catalytic performance toward methylation of amines using CO$_2$ and H$_2$. During the methylation of N-methylaniline, HGB-In$_2$O$_3$ achieved an optimal yield of 82.7% for N,N-dimethylaniline, which is not inferior to noble metal-based catalysts. In addition, 84% of the original reaction activity for HGB-In$_2$O$_3$ was preserved after five rounds of reaction. Besides, HGB-In$_2$O$_3$ exhibited excellent applicability in the methylation of amines. Further mechanistic studies revealed that the presence of high density of grain boundaries not only facilitated the adsorption and activation of CO$_2$ to generate CH$_3$OH as the intermediate, but also enhanced the activation of N-H bond in amines, which led to the attractive catalytic activity of HGB-In$_2$O$_3$ toward methylation of amines.

RESULTS

Synthesis and Structural Characterizations of In$_2$O$_3$ Nanocrystals

To begin with, the metal-organic frameworks containing indium ions (In-MOFs) were synthesized in a Teflon-lined autoclave at 150°C for 20 h. Figure S1 shows representative scanning electron microscopic (SEM) images of the as-obtained In-MOFs, indicating the formation of stacked structure with single layer having thickness of ~1 μm. In-MOFs were then calcined into powder in a muffle furnace at 350°C and kept for 3 h. Figure 1A shows a high-angle annular dark-field scanning transmission electron microscopic (HAADF-STEM) image of the as-obtained powder. Most of the nanocrystals take a square morphology with an average size of about 14.4 nm (Table S1). The composition and crystalline structure of the as-synthesized nanocrystals were further characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). In particular, XRD patterns of HGB-In$_2$O$_3$, LGB-In$_2$O$_3$, and NGB-In$_2$O$_3$ nanocrystals are shown in Figure 1D, demonstrating the presence of characteristic diffraction peaks corresponding to the In$_2$O$_3$ phase. The XPS spectra of In 3d and O 1s core levels for the three types of nanocrystals are presented in Figure 1E and F, respectively, confirming the successful synthesis of In$_2$O$_3$ nanocrystals with different grain boundary structures.
Patterns of the recovered HGB-In2O3 were also indexed to a highly crystalline In2O3 phase (JCPDS#89-4595). Further observation of the high-resolution HAADF-STEM of In2O3 displays an individual nanocrystal, in which two sets of fringes with interplanar spacing of 2.41 Å and 2.83 Å are observed, relating to the (411) and (222) planes, respectively. Obviously, the individual nanocrystal is determined to be multiple grains instead of a single grain. As a result, there remains abundant grain boundaries highlighted by yellow dotted lines in Figures 1B and S2. This sample with high density of grain boundaries was named as HGB-In2O3. For analysis of the chemical compositions of the nanostructure, the STEM energy-dispersive X-ray elemental mapping images of nanocrystal are shown in Figure 1C, demonstrating the homogeneous distribution of both In and O throughout the nanocrystal. When conducting the synthetic procedure similar to that of the HGB-In2O3 except for changing the calcined temperature from 350 to 600°C, nanocrystals with an average size of about 22.2 nm containing grain boundaries were formed (Figure S3 and Table S1). Owing to lower density of grain boundaries compared with HGB-In2O3, this sample was named as LGB-In2O3. For comparison, In2O3 nanocrystals without grain boundaries (NGB-In2O3) were also prepared according to a previously reported method (Gao et al., 2017; Albani et al., 2017). These NGB-In2O3 nanocrystals have an average size of about 20.2 nm (Figure S4 and Table S1). Besides, the Brunauer-Emmett-Teller surface areas of all samples were also measured (Table S1), where no obvious difference was observed for HGB-In2O3, LGB-In2O3, and NGB-In2O3. In addition, we estimated the density of grain boundary (DGB) of the samples based on the Formulas 1 and 2 in Transparent Methods. Accordingly, the DGB for HGB-In2O3 and LGB-In2O3 were estimated to be 180,000 and 53,000 m/mg, respectively (Table S1). To characterize the electronic properties of the obtained samples, we conducted X-ray photoelectron spectroscopic (XPS) measurements of In2O3. The binding energies of In 3d5/2 and In 3d3/2 in HGB-In2O3 are 444.3 and 451.9 eV, which are same as that in LGB-In2O3 and 0.2 eV higher relative to that in NGB-In2O3, respectively (Figure 1E) (Gu et al., 2015; Xu et al., 2007). The O 1s XPS spectra of In2O3 nanocrystals exhibited three distinct peaks. The prominent peak at 529.7 eV was assigned to O species in internal In2O3 nanocrystals. Another binding energy of O 1s was 531.3 eV, corresponding to that of the species (such as O2 and CO2) adsorbed on the surface of samples. Besides, for HGB-In2O3 and LGB-In2O3, there existed peak at 530.4 eV, which was assigned to O species in In2O3 at grain boundaries (Figure 1F) (Ding et al., 2015).

**Catalytic Properties of HGB-In2O3 in CO2 Fixation**

The catalytic properties of the as-obtained In2O3 were evaluated in methylation of amines using CO2 and H2. The model substrate was N-methylaniline leading to N,N-dimethylaniline. Each reaction was performed under 70 bar of mixed gas (CO2/H2 = 1:3) at 180°C by using tetrahydrofuran as the solvent. A blank test was conducted without any catalyst, in which no product was observed. Figure 2A illustrates the product yields of adding 25 mg of In2O3 catalysts with different density of grain boundaries. When the reaction was catalyzed by HGB-In2O3, N,N-dimethylaniline was produced attaining an yield of 82.7% after 9 h. In comparison, the yields decreased to only 21.7% and 12.6% catalyzed by LGB-In2O3 and NGB-In2O3 under the same reaction condition, respectively. Thus HGB-In2O3 catalyst exhibits remarkable activity and selectivity, which was even comparable to the noble metal-based catalysts (Li et al., 2013a, 2013b; Beydoun et al., 2014; Kon et al., 2014; Cui et al., 2014a, 2014b). To further investigate the diversity of catalytic property, we calculated the mass activity for In2O3 catalysts at 180°C. As shown in Figure 2B, the mass activity of HGB-In2O3 is 21.2 mmol·g−1·h−1, which is almost 4 and 7 times as high as that of LGB-In2O3 and NGB-In2O3, respectively. We then plotted the profile of the mass activity versus DGB over different catalysts, where an almost linear correlation was observed (Figure S5). This indicated that grain boundaries played the dominant role in catalytic performance. In addition, the stability of HGB-In2O3 was also studied by performing successive rounds of reaction. As revealed in Figures 2C and S6, almost 84% of the original reaction activity was preserved after five rounds with product of N,N-dimethylaniline. In addition, the XRD patterns of the recovered HGB-In2O3 were also indexed to a highly crystalline In2O3 phase (JCPDS#89-4595) (Figure S7A). Although the morphology of the recovered HGB-In2O3 had a slight change, grain boundaries in HGB-In2O3 were still preserved after five cycles based on the high-resolution HAADF-STEM image (Figure S7B). Both XRD and HAADF-STEM results proved the high stability of HGB-In2O3, which is extremely important for potential applications in industrial processes by reducing the cost and pollution efficiently. Furthermore, hot filtration tests showed that the reaction was a heterogeneous catalysis (Figure S8). In the filtrate, only 0.29% of In element relative to HGB-In2O3 was leached determined by inductively coupled plasma atomic emission spectrometry. Figure 2D shows a systematic comparison of the methylation of various substituted anilines using HGB-In2O3 as catalyst under 70 bar mixed gas (CO2/H2 = 1:3) at 180°C for 24 h. When 4-chloroaniline was used as reactant, 4-chloro-N,N-dimethylaniline was 531.3 eV, corresponding to that of the species (such as O2 and CO2) adsorbed on the surface of samples. Besides, for HGB-In2O3 and LGB-In2O3, there existed peak at 530.4 eV, which was assigned to O species in In2O3 at grain boundaries (Figure 1F) (Ding et al., 2015).
was obtained in high yield of 94.2%. On the contrary, in the transformations of aniline and 2-fluoroaniline, the yields of N,N-dimethylaniline and N,N-dimethyl-2-fluoroaniline slightly dropped to 90.9% and 89.2%, respectively. In addition, 74.3% and 53.2% of indole and 2,4,6-trimethylaniline converted into N-methylin-dole and N,N,2,4,6-pentamethylaniline, respectively. Notably, when using octylamine as the substrate, 26.3% of conversion was achieved with 99% selectivity of N-methyloctan-1-amine. As a result, HGB-In$_2$O$_3$ exhibited excellent applicability in the methylation of amines.

Mechanistic Studies of Remarkable Catalytic Activity for HGB-In$_2$O$_3$ in CO$_2$ Fixation

To elucidate the role of grain boundary in catalytic reaction, we investigated the interaction between CO$_2$ and In$_2$O$_3$ catalysts. CO$_2$ temperature-programmed desorption (CO$_2$-TPD) measurements of In$_2$O$_3$ nanocrystals were implemented. Figure 3A illustrates CO$_2$-TPD spectra of In$_2$O$_3$ catalysts with different densities of grain boundaries. In the presence of HGB-In$_2$O$_3$, a prominent peak of desorption appeared at 448°C, which corresponds to the chemisorbed CO$_2$. For LGB-In$_2$O$_3$ and NGB-In$_2$O$_3$, two obscure desorption peaks emerging at 455°C and 457°C were in line with chemisorbed CO$_2$ and the other two weak peaks at around 70°C–80°C conformed to physisorbed CO$_2$. The adsorption capability was compared on the basis of the peak area lying on the premise of setting the equivalent mass of each sample to 30 mg. The area of chemisorption peak of HGB-In$_2$O$_3$ was almost 8 and 11 times larger than that of LGB-In$_2$O$_3$ and NGB-In$_2$O$_3$, respectively. To further gain insight into the interaction between CO$_2$ and In$_2$O$_3$ catalysts, we carried out in situ diffuse reflectance infrared Fourier transform (DRIFT) spectroscopic measurements. After treatment with CO$_2$ at 180°C for 30 min, the in situ DRIFT spectrum of HGB-In$_2$O$_3$ exhibited a peak at 1,455 cm$^{-1}$ assigned to CO$_2$ species and another one at 1,285 cm$^{-1}$ assigned to CO$_2$ species (Graciani et al., 2014). With regard to LGB-In$_2$O$_3$ and NGB-In$_2$O$_3$ after exposure to CO$_2$ at 180°C for 30 min, peaks at 2,360 cm$^{-1}$ appeared, corresponding to the frequency of physisorbed CO$_2$ species (Figure 3B) (Wang et al., 2009). As a result, grain boundaries are beneficial to the chemisorption of CO$_2$. To rationalize the remarkable function of grain boundary in activation of CO$_2$, we carried out density functional theory (DFT) calculations. One
atomic model for single-crystal In$_2$O$_3$ was established along the (111) facet, which was named as In$_2$O$_3$(111). Another model consisted of two grains formed along (110) and (111) facets, respectively (Figure S9). This model involving a grain boundary was named as In$_2$O$_3$(GB). First-principle simulations were performed to calculate the adsorption energies of CO$_2$ on In$_2$O$_3$(111) and In$_2$O$_3$(GB). The adsorption energy of CO$_2$ on In$_2$O$_3$(GB) was $-1.66$ eV, much higher than that on In$_2$O$_3$(111) with the value as low as $0.1$ eV. Figures 3C and 3D reveal the adsorption geometries of CO$_2$ on In$_2$O$_3$(GB) and In$_2$O$_3$(111). For In$_2$O$_3$(GB), there exist higher negative charge density of surface O atoms and lower positive charge density of C atoms on the surface than that for In$_2$O$_3$(111). Thus, CO$_2$ obtained more negative electrons when adsorbed in In$_2$O$_3$(GB), promoting the process of activation. Notably, the interatomic bond angles of CO$_2$ decreased from 180° to 176.9° and 123.5° on In$_2$O$_3$(111) and In$_2$O$_3$(GB), respectively. The greater reduction of the bond angle led by grain boundaries increases the internal energy of CO$_2$ molecule, further making it unstable and prone to reaction. Thus, grain boundaries encourage the adsorption and activation of CO$_2$. We also performed in situ DRIFT measurement to study the activation of H$_2$. Before recording the DRIFT spectrum, HGB-In$_2$O$_3$ was exposed to H$_2$ (1 bar) at 180°C for 1 h. As shown in DRIFT spectrum, the set of frequencies at 3,660–3,551 cm$^{-1}$ corresponding to the stretching vibration of O-H were observed (Figure S10). It was thus speculated that H$_2$ was dissociated after adsorbing on the oxygen atoms of In$_2$O$_3$.

Furthermore, the interaction between amines and In$_2$O$_3$ catalysts was also explored. Figure 4A shows the in situ DRIFT spectra of HGB-In$_2$O$_3$, LGB-In$_2$O$_3$, and NGB-In$_2$O$_3$ after treatment with N-methylaniline at 180°C for 30 min. With regard to HGB-In$_2$O$_3$, peaks at 692–750, 1,262, 1,506–1,603, 2,904–3,049, and 3,416 cm$^{-1}$ appeared, corresponding to the bending vibration of C-H, the stretching vibrations C-N, the vibration of benzene skeleton, the stretching vibrations of C-H, and the stretching vibration of N-H, respectively. Considering that the fracture of N-H plays a pivotal role in the methylation of amines, we focused on the distinction of peaks for the stretching vibration of N-H among In$_2$O$_3$ catalysts. In the spectra of LGB-In$_2$O$_3$ and NGB-In$_2$O$_3$, the peaks for the stretching vibration of N-H shifted to 3,422 and 3,443 cm$^{-1}$, respectively. Thus, HGB-In$_2$O$_3$ was found to illustrate the lowest wave number of the peaks among the three samples, indicating the largest length of N-H bond. Therefore, grain boundary benefits the activation of N-H bond in amines. DFT calculations were conducted on In$_2$O$_3$(GB) and In$_2$O$_3$(111) to further verify the function
of grain boundary in activating N-H bond. The adsorption energy of N-methylaniline on In$_2$O$_3$(GB) was $0.48$ eV, implying exothermic adsorption on In$_2$O$_3$(GB). In comparison, the adsorption energy of $0.33$ eV for In$_2$O$_3$(111) demonstrates that the adsorption of N-methylaniline on In$_2$O$_3$(111) was endothermic.

As shown in Figures 4B and 4C, the length of N-H bond was 1.029 Å when absorbed on In$_2$O$_3$(GB), whereas for In$_2$O$_3$(111), the length of N-H bond decreased to 1.023 Å. The elongation of bond length was able to induce red-shift of stretching vibration frequency for adsorbed N-methylaniline on In$_2$O$_3$(GB), well consistent with the observation in in situ DRIFT measurements.

For methylation of amines with CO$_2$ and H$_2$, the selectivity for product varies with the intermediate of the reaction. For instance, amide is generated when CO serves as the intermediate, whereas aniline is synthesized by forming CH$_3$OH intermediate (Li et al., 2013a, 2013b; Cui et al., 2014a, 2014b; Tlili et al., 2014; Dang et al., 2015; Tsarev et al., 2015; Ogata et al., 2018; Fernández-Alvarez et al., 2018; Goeppert et al., 2014; Liu et al., 2017; Zhang et al., 2019). To determine the intermediate for methylation of amines, 70 bars of CO$_2$/H$_2$ mixed gas (CO$_2$/H$_2$ = 1:3) was allowed to react at 180°C for 8 h with In$_2$O$_3$ catalysts. After completion of the
reaction, CH$_3$OH was detected as the main product except a spot of CO (Figure 4D). Therefore, CH$_3$OH is considered to be the intermediate, conducive to methylation of amines. In addition, HGB-In$_2$O$_3$ was endowed with the highest yield of CH$_3$OH with a value of 17.7 mmol; owing to this, grain boundary promoted the activation of CO$_2$ (Figure 4D). In situ DRIFT measurement was also employed to further explore the reaction intermediate. After exposing HGB-In$_2$O$_3$ to the mixed gas (CO$_2$:H$_2$ = 1:3, 1 bar) at 180°C for 1 h, the DRIFT spectrum was recorded. As shown in Figure S10, two sets of frequencies were observed. One set of frequency at 2,360 cm$^{-1}$ corresponded to the physisorbed CO$_2^*$ species. The other set of frequencies at 3,645–3,619, 2,968–2,863, 1,580, and 1,050 cm$^{-1}$ corresponded to the stretching vibration of O-H, the stretching vibration of C-H, the bending vibration of C-H, and the stretching vibration of C-O in CH$_3$OH$^*$ species, respectively. This result confirmed that methanol was the intermediate during the catalytic reaction, which was consistent with the previous results (Gao et al., 2017; Ye et al., 2013). Moreover, to rationalize the function of activating amines in the methylation reaction, we applied CH$_3$OH and N-methylaniline to react at 180°C catalyzed by In$_2$O$_3$ catalysts. As shown in Figure 4E, when catalyzed by HGB-In$_2$O$_3$, N,N-dimethylaniline was produced attaining the yield of 79.8% after 4 h, 1.2 and 2.8 times higher than those of LGB-In$_2$O$_3$ and NGB-In$_2$O$_3$, respectively. Thus the activation of amines can indeed control the activity of methylation reaction, which can be facilitated by grain boundaries. Taking the discussion above into account, we proposed the reaction pathway of methylation of amines as illustrated in Figure S11. Collectively, grain boundaries not only facilitated the adsorption and activation of CO$_2$ to generate CH$_3$OH as the intermediate (Equation 1, Figure S11) but also enhanced the activation of N-H bond in amines (Equation 3, Figure S11), which led to the attractive catalytic activity of HGB-In$_2$O$_3$ toward methylation of amines.

**DISCUSSION**

In conclusion, given the high cost of noble metal-based catalysts, we reported a rational design of HGB-In$_2$O$_3$ nanocrystals, which achieved remarkable catalytic performance toward methylation of amines with CO$_2$ and H$_2$. We designed a series of In$_2$O$_3$ nanocrystals with different density of grain boundaries, i.e., HGB-In$_2$O$_3$, LGB-In$_2$O$_3$, and NGB-In$_2$O$_3$. During the methylation of N-methylaniline, HGB-In$_2$O$_3$ achieved an optimal yield of 82.7% for N,N-dimethylaniline, 3.8 and 6.6 times as high as those of LGB-In$_2$O$_3$ and NGB-In$_2$O$_3$, respectively. Further mechanistic studies revealed that the presence of high density of grain boundaries not only facilitated the adsorption and activation of CO$_2$ to generate CH$_3$OH as the intermediate but also enhanced the activation of N-H bond in amines, which led to the attractive catalytic activity of HGB-In$_2$O$_3$ toward methylation of amines. This work not only develops a catalyst with high density of grain boundaries to achieve the methylation of amines but also opens up new possibilities for designing efficient non-noble-metal-based catalysts.

**Limitations of the Study**

Although HGB-In$_2$O$_3$ exhibited excellent catalytic performance in the methylation of aromatic amines, the activity was still unsatisfactory when using fatty amines as substrates.

**METHODS**

All methods can be found in the accompanying Transparent Methods supplemental file.

**SUPPLEMENTAL INFORMATION**

Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.06.005.

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**AUTHOR CONTRIBUTIONS**

Lirong Wang and J.C. equally contributed to this work. Lirong Wang, S.L., and Liangbing Wang designed the studies and wrote the paper. Lirong Wang and L.X. synthesized catalysts. Lirong Wang and S.Y. performed catalytic tests. X.Z., J.G., L.X., and Lirong Wang conducted XRD, TPD, and in situ DRIFT.
measurements. J.Z., X.Z., J.Y. and L.Z. conducted XPS measurements. J.C. conducted DFT calculations. All authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental Information

In$_2$O$_3$ Nanocrystals for CO$_2$ Fixation: Atomic-Level Insight into the Role of Grain Boundaries

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Supplemental Figures

Figure S1. (A, B) SEM images of In-MOFs nanocrystals, related to Figure 1.
Figure S2. HRTEM image of HGB-In$_2$O$_3$, related to Figure 1.
**Figure S3.** (A, B) High resolution HAADF-STEM images of individual In$_2$O$_3$ nanocystal with low density of grain boundaries, related to Figure 1.
**Figure S4.** (A, B) High resolution HAADF-STEM images of individual In$_2$O$_3$ nanocrystal without grain boundary, related to Figure 1.
**Figure S5.** The plotted profile of the mass activity *versus* $D_{GB}$ over different catalysts, related to Figure 2.
Figure S6. The methylation of N-methylaniline in a 5-cycle repetition, related to Figure 2.
Figure S7. The characterization of the recovered HGB-In$_2$O$_3$ by (A) XRD and (B) High resolution HAADF-STEM image, related to Figure 2.
Figure S8. The plotted profile of the yield of product versus reaction time and hot filtration experiment over HGB-In$_2$O$_3$. In the hot filtration experiment, the reactor was charged and discharged with 70 bar of mixed gas (CO$_2$/H$_2$ = 1:3) at room temperature for three times after the addition of 5 mmol of N-methylaniline, 0.5 mmol of bis(trifluoromethylsulfonyl)imide, 25 mg of HGB-In$_2$O$_3$ and 40 mL of tetrahydrofuran as solvent. After reacting for 4 h at 180 ˚C, the HGB-In$_2$O$_3$ was removed by centrifugation at room temperature. The yield of N,N-dimethylaniline was 34.8% analyzed by GC-MS with chlorobenzene as internal standard. The filtrate was then added to the reactor, followed by re-charging 70 bar of mixed gas (CO$_2$/H$_2$ = 1:3) at room temperature for three times. As expected, the yield of N,N-dimethylaniline was still maintained to 34.8% after another 4 h. Besides, 0.5 mL of filtrate was used to perform ICP experiment. For HGB-In$_2$O$_3$, only 0.29 % of the In element was leached in the filtrate. Based on the above analysis, the methylation of amines over HGB-In$_2$O$_3$ was a heterogeneous catalysis, related to Figure 2.
Figure S9. (A) Atomic model for single-crystal In$_2$O$_3$ along the (111) facet. (B) Atomic model for two grains formed along (110) and (111) facets, related to Figure 3 and Figure 4.
Figure S10. In situ DRIFT spectra of HGB-In$_2$O$_3$ after the treatment with H$_2$ (1 bar) and the mixed gas (CO$_2$:H$_2$ = 1:3, 1 bar) at 180 °C for 1 h, related to Figure 4.
Figure S11. Proposed reaction pathway towards methylation of N-methylaniline with CO$_2$ and H$_2$.

* represents as an active site, related to Figure 3 and Figure 4.
Table S1. The particle sizes, BET surface areas and D_{GB} of different catalysts, related to Figure 1.

| Catalyst   | Particle sizes (nm) | BET surface areas (m²/g) | D_{GB} (m/mg) |
|------------|---------------------|--------------------------|---------------|
| HGB-In₂O₃ | 14.4±2.7            | 68.13                    | 180,000       |
| LGB-In₂O₃ | 22.2±4.4            | 50.61                    | 53,000        |
| NGB-In₂O₃ | 20.2±3.5            | 42.61                    | 0             |
Transparent Methods

Chemicals and materials
Indium(III) acetate (In(OAc)₃, 99.9%), 4,4'-bipyridyl (98.0%), 2,2'-biphenyldicarboxylic acid (98.0%), N-methylaniline (98.0%), 4-chloroaniline (≥98.0%), 2,4,6-trimethylaniline (98.0%) and 2-fluoroaniline (99.0%) were obtained from Shanghai Macklin Biochemical Co., Ltd. Indium(III) nitrate 4.5hydrate (In(NO)₃·4.5H₂O, 99.0%), ammonia aqueous (25.0%-28.0%), tetrahydrofuran (99.5%), acetone (≥99.0%), ethanol (≥99.7%), methanol (≥99.5%), indole (99.0%) and aniline (99.5%) were obtained from Shanghai Hushi Laboratorial Equipment Co., Ltd. Bis(trifluoromethylsulfonyl)imide (99.0%) was obtained from Sigma-Aldrich. All chemical reagents were used as received without further purification. All aqueous solutions were prepared using deionized (DI) water with a resistivity of 18.2 MΩ·cm⁻¹.

Preparation of catalysts
HGB-In₂O₃ and LGB-In₂O₃: In-MOFs were synthesized by a previously reported method. Briefly, 3 mmol of indium acetate, 1.62 mmol of 4,4'-bipyridine and 3 mmol of 2,2'-biphenyldicarboxylic acid were dissolved in 45 mL deionized water, followed by stirring for 30 min at room temperature. The solution was transferred into a 50 mL Teflon-lined autoclave, followed by being sealed and heated at 150 °C for 20 h. After the mixture was cooled down to room temperature, collecting the precipitate by centrifugation, washing it three times with deionized water, ethanol and acetone respectively and then drying it at 60 °C for 12 h. In a typical synthesis of HGB-In₂O₃, the obtained In-MOFs were calcined in muffle furnace at 350 °C for 3 h. Further HAADF-STEM image of product determined that there existed high density of grain boundaries. The synthetic procedure of LGB-In₂O₃ was similar to that of HGB-In₂O₃ except for raising the calcined temperature to 600 °C.

NGB-In₂O₃: NGB-In₂O₃ was synthesized by a previously reported method (Albani et al., 2017). Briefly, 2 mmol of In(NO₃)₃·4.5H₂O was dissolved in a mixture of deionized water (4 mL) and ethanol (12 mL), followed by the addition of the mixture of ammonia (3 mL, 25.0%-28.0%) and ethanol (9 mL) at room temperature. The resulting slurry was stirred for 10 min at 80 °C, before collecting the precipitate by filtration and washing it three times with deionized water and ethanol. The obtaining solid was dried at 60 °C. Afterwards, the powder was placed into muffle furnace,
followed by calcining at 400 °C for 3 h.

**Estimation of the DGB for different catalysts**

The D\textsubscript{GB} was estimated according to the following formulas:

\[
D_{\text{GB}} = \frac{L_{\text{GB}}}{S_{\text{grain-surface}}} \times \frac{S_{\text{catalysts}}}{M_{\text{catalysts}}} \quad (1)
\]

\[
\frac{S_{\text{catalysts}}}{M_{\text{catalysts}}} = \frac{\text{total surface area of catalysts}}{\text{total mass of catalysts}} = \text{BET surface area} \quad (2)
\]

Where L\textsubscript{GB} and S\textsubscript{grain-surface} represent the length of GB and particle area determined by HRTEM and HAADF-STEM images, respectively. S\textsubscript{catalysts} and M\textsubscript{catalysts} represent the total surface area and the total mass of the catalysts, respectively.

**Catalytic tests**

The methylation of amines was performed in a 200 mL automatic constant pressure reactor (Anhui Kemi Machinery Technology Company). In a typical catalytic test, the reactor was charged and discharged with 70 bar of mixed gas (CO\textsubscript{2}/H\textsubscript{2} = 1:3) at room temperature for three times after the addition of 5 mmol of N-methylaniline, 0.5 mmol of bis(trifluoromethylsulfonyl)imide, 25 mg of catalysts and 40 mL of tetrahydrofuran as solvent. The reaction proceeded under stirring at 180 °C for 9 h. After the completion of the reaction, the liquid phase of the reaction mixture was collected by centrifugation at 12,000 r.p.m. for 5 min, and analyzed by GC–MS (QP2010 Ultra, Shimadzu Corporation, Kyoto, Japan) by using chlorobenzene as internal standard. To test the stability of the catalysts, we conducted successive reaction rounds. The catalytic reaction proceeded at 180 °C for 9 h. After one round, the products were detected, while the catalysts were collected by centrifugation and washed three times with alcohol, followed by re-adding to the reactor for the next round. In addition, 4-chloroaniline, aniline, 2-fluoroaniline, 2,4,6-trimethylaniline and indole participated in the methylation as the reactants in turn under 70 bar of mixed gas (CO\textsubscript{2}/H\textsubscript{2} = 1:3) at 180 °C for 24 h.

The reaction of CO\textsubscript{2} and H\textsubscript{2} was performed in a 200 mL automatic constant pressure reactor (Anhui Kemi Machinery Technology Company). In a typical catalytic test, the reactor was charged and discharged with 70 bar of mixed gas (CO\textsubscript{2}/H\textsubscript{2} = 1:3) at room temperature for three times after the addition of 25 mg of catalysts and 40 mL of tetrahydrofuran as solvent. The reaction proceeded
under stirring at 180 °C for 8 h. After the completion of the reaction, the gas phase was determined by gas chromatography (GC-2014C, Shimadzu Corporation, Kyoto, Japan) and a spot of CO were detected. The liquid phase of the reaction mixture was collected by centrifugation at 12,000 r.p.m. for 5 min. 1 mmol of N,N-dimethylformamide was introduced to 1 mL of the reaction mixture as an internal standard. 50 μL of the mixture was dissolved in 0.5 mL of DMSO-d6 to determine the liquid product by 1H NMR spectroscopy.

With regard to the reaction of N-methylaniline and methanol over In2O3 catalysts, 3.6 mmol of methanol and 3 mmol of N-methylaniline were mixed in a 200 mL automatic constant pressure reactor after the addition of 25 mg of catalysts and 40 mL of tetrahydrofuran as solvent, followed by being sealed and heated at 180 °C for 4 h. After the completion of the reaction, the liquid phase of the reaction mixture was collected by centrifugation at 12,000 r.p.m. for 5 min, and analyzed by GC–MS (QP2010 Ultra, Shimadzu Corporation, Kyoto, Japan).

The mass activities shown in Figure 2B were calculated according to the following formula:

\[ \text{The mass activity} = \frac{N_{N,N-Dimethylaniline}}{M_{\text{catalyst}} \times h} \]  

Where \( N_{\text{N,N-Dimethylaniline}} \), \( M_{\text{catalyst}} \) and \( h \) represent the consumed amount of N, N-Dimethylaniline, the mass of the used catalysts and the reaction time (8 h).

**In-situ DRIFT tests**

*In-situ* DRIFTS experiments were conducted in an elevated-pressure cell (Harrick DRK-4-BR4) with a Fourier transform infrared spectrometer (Bruker TENSOR II) at 180 °C. After flowing 1 atm of \( N_2 \) at the rate of 50 sccm at 180 °C for 0.5 h, the background spectra of the samples were acquired. Then, 1 atm of \( CO_2 \) was allowed to flow into cell at 180 °C for 0.5 h. Afterwards, 1 atm of \( N_2 \) was allowed to flow into the cell at the rate of 50 sccm for 0.5 h. *In situ* DRIFT spectra of the samples after the treatment with \( CO_2 \) were obtained. In addition, for the treatment of the samples with N-methylaniline, the background spectrum of the sample was acquired after flowing with 1 bar of \( N_2 \) for 0.5 h at 180 °C. Then the \( N_2 \) were allowed to bubble in N-methylaniline solution, followed by flowing into the cell at a rate of 50 sccm at 180 °C for 0.5 h, to bring the saturated N-methylaniline vapor into the cell. Afterwards, 1 atm of \( N_2 \) was allowed to flow into the cell at the rate of 50 sccm for 0.5 h. *In situ* DRIFT spectra of the samples after the treatment with N-methylaniline were obtained.

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DFT calculations
All density functional theory (DFT) calculations were carried out using CASTEP module as implemented in the Materials Studios package of Accelrys Inc (Clark et al., 2005). Generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional was employed for the electron exchange-correlation potential. The ultrasoft pseudopotentials was employed and the core electrons of atoms were treated using effective core potential (ECP). 400 eV kinetic energy cutoff was assigned to the plane-wave basis set. The Brillouin zone was sampled by 2 * 2 * 1 Monkhorst-Pack mesh k-points for surface calculations. The convergence tolerances were set to 5.0 * 10^-4 eV per atom for energy, 5.0 * 10^-4 Å for maximum displacement, and 0.01 eV Å^-1 for maximum force. The vacuum width is 12 Å between the slabs along the Z axis. All atoms were relaxed during the geometry optimizations. The grain boundary was consisted with (111) and (110) surface. The binding energy of adsorbate (CO_2 or C_7H_9N) on surfaces (E_{adsorbate*}) were calculated by \( E_{adsorbate*} = E_{adsorbate*+surface} - E_{surface} - E_{adsorbate} \). Here \( E_{adsorbate*+surface} \) is the total energy of a surface covered with the adsorbate. \( E_{surface} \) is the energy of a surface. \( E_{adsorbate} \) is the energy of the adsorbate in the gas phase (Nie et al., 2018).

Instruments
TEM, HAADF-STEM, and STEM-EDX images were collected on a JEOL ARM-200F field-emission transmission electron microscope operating at 200 kV accelerating voltage. X-ray diffraction (XRD) patterns were recorded by using a Philips X’Pert Pro Super diffractometer with Cu-Kα radiation (\( \lambda = 1.54178 \text{ Å} \)). The BET surface areas of the samples were measured on a Micromeritics ASAP 2460 adsorption apparatus. X-ray photoemission spectroscopy experiments were conducted at the Catalysis and Surface Science Endstation connected to the BL11U beamline in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. TPD profiles were recorded by a VDsorb-91i chemisorption analyser.
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