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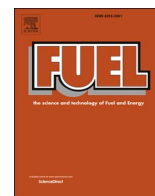
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Role of ZrO₂ and CeO₂ support on the In₂O₃ catalyst activity for CO₂ hydrogenation

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ABSTRACT

Methanol synthesis from CO₂ hydrogenation has drawn global attention as catalytic CO₂ hydrogenation is an attractive choice to mitigate CO₂ emissions and lessen dependency on fossil resources. In the present study, we have synthesized ZrO₂ and CeO₂-supported In₂O₃ catalysts for methanol synthesis from CO₂ hydrogenation and the catalytic performances of In_x/ZrO₂, and In_x/CeO₂ (x = 1 % and 13 %) were compared. Specifically, the effect of the ZrO₂ and CeO₂ supports on In₂O₃ catalyst during CO₂ hydrogenation was explored. This study reveals that ZrO₂ support increased the catalytic activity while the CeO₂ support decreased although both supports have almost the same indium loading and surface area. Various characterizations like XRD, DRIFT, CO₂-TPD, H₂-TPR and XPS analysis of catalysts provided insight into changes that arise after mixing the two oxides and during the reaction as well as after the reaction. The stabilities of In₂O₃, In₁₃/ZrO₂, and In₁₃/CeO₂ were tested for up to 50 h and we found In₁₃/ZrO₂ was stable during this time-on-stream, while In₁₃/CeO₂ lost activity after 2 h of reaction. XPS results of spent catalysts showed that In(OH)₃ was observed significantly over the spent In₁₃/CeO₂. OH groups were also verified by DRIFT experiments, however at low levels due to low CO₂ conversion at atmospheric pressure. XRD analysis confirmed the sintering of CeO₂ support during the reaction. Thus, the hydrophilic nature of CeO₂, redox properties of CeO₂ and sintering of CeO₂ support in the presence of water, were the main reasons for the early deactivation of In₁₃/CeO₂. A regeneration study was carried out to regenerate the catalyst and the results showed that partial regeneration of the In₁₃/CeO₂ catalyst is possible by Ar flushing. We, therefore, suggest that the build-up of OH groups deactivate the In₁₃/CeO₂ catalyst and some of these OH groups could be removed during flushing with inert gas, causing a partial regeneration. However, the decreased surface area is not reversible, and this results in a continuous decrease in the activity of the catalyst after repeated experiments, even if the catalyst is flushed with Ar between the experiments.

1. Introduction

The excessive use of fossil fuels increases the emissions of CO₂ into the atmosphere which contributes to global warming.[1,2] A combined process of CO₂ capture, storage and utilization is an important way to mitigate the surplus CO₂ and dependency on fossil fuels.[3,4] Thus, production of chemical feedstocks and transportation fuels from the utilization of CO₂ has attracted great attention recently.[5] Methanol is an important chemical feedstock which is used in various applications and can be further converted into other important chemicals such as chloromethane, methyl tert-butyl ether, formaldehyde, acetic acid, and fuels.[6,7] Methanol can be synthesized from various reactions where CO₂ hydrogenation is an environmentally important chemical reaction. It usually occurs with the following system of competing and series

reactions as shown in Scheme 1.

CH₃OH synthesis from CO₂ and CO hydrogenation are exothermic (Eq.1 and 2), whereas Eq. 3, the competitive reverse-water-gas-shift reaction (RWGS), is endothermic during the CO₂ hydrogenation.[6] Additionally, the conversion of methanol into hydrocarbons is also an attractive solution to provide alternative sustainable energy resources.[7]

Over the decades, Cu/ZnO/Al₂O₃ and Cu-ZnO catalysts have been used and studied for the synthesis of CH₃OH from syngas at industrial and laboratory scales, respectively. Similarly, a wide variety of heterogeneous catalysts are developed for the synthesis of CH₃OH from CO₂ hydrogenation [7] where transition metal catalysts like Cu, Pd, Ag, and Pt are used.[8] Recently, oxide-based catalysts like In₂O₃,[9,10] metal promoted In₂O₃,[11,12] and ZnO-ZrO₂[13] have been reported to have

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Scheme 1. Possible reactions for the synthesis of methanol.

excellent activity for methanol synthesis (Table S1, See supporting information).[14–16] The oxide-based catalysts have different active sites than traditional metal catalysts with different reaction mechanisms.[17] Martin et al. synthesized ZrO₂ supported In₂O₃ which rendered 100 % selectivity for CH₃OH synthesis and was found to be stable up to 1000 h on stream whereas the reference Cu-ZnO-Al₂O₃ catalyst lost 44 % of its activity in 100 h.[18] Recently, In_x/ZrO₂ (x = 0.1–5 wt%) catalysts were screened for CH₃OH synthesis under industrially relevant conditions and a highly tunable selectivity for CH₃OH from CO₂ hydrogenation was observed.[19] Loadings of 2.5–5 wt% In on catalysts have shown 70–80 % CH₃OH selectivity whereas 0.1 wt% loading of In exhibited a CO selectivity up to 80 %. In addition, the distribution of products was found to depend on the interfacial structure of ZrO₂ and In₂O₃. A composition of Cu-In-Zr-O was reported to act as a bifunctional catalyst, where In₂O₃ adsorbs CO₂ and the Cu-sites adsorb, and provide active hydrogen to adjacently adsorbed CO₂. [20]

Generally, high pressure and low temperature favor the synthesis of CH₃OH. However, a high reaction temperature aids CO₂ activation whereas a lower temperature is thermodynamically favorable for CH₃OH formation and this condition creates a kinetic limitation for the reaction.[21] At the reaction condition, other competing reactions occur in parallel in addition to the RWGS that can produce many side products like methane, formaldehyde, and formic acid.[22–25] The support materials play a significant role in heterogeneous catalysis.[8] In an interesting study by Hartadi et al., the authors have discussed the importance of support materials like Al₂O₃, ZnO, ZrO₂, and TiO₂ for CO₂ hydrogenation.[26] Due to the versatile properties and weak hydrophilic character of ZrO₂, over the past decades, substantial progress has been made over ZrO₂-supported catalysts.[27–30] It has been stated that ZrO₂ supports interact with metals and oxide-based catalysts and change various reaction parameters and environments which increased the activity of the catalysts.[31] Perez-Ramirez et al. studied the role of ZrO₂ as a support for In₂O₃ in CO₂ hydrogenation to methanol and suggested that the ZrO₂ support used its own oxygen vacancies to activate the CO₂. [32] The study was mainly focused on ZrO₂ whereas other supports like Al₂O₃ and CeO₂ were used for a comparison study. Gong et al. described the strong electronic interaction between In₂O₃ and ZrO₂ which was responsible for high selectivity towards methanol.[25] Previously, the promotional effect of CeO₂ on Ga₂O₃ was studied experimentally for the RWGS and it was observed that the CeO₂ increased the oxygen vacancies which increased the dissociation of adsorbed H₂ to react with adsorbed CO₂ and increase coverages of bicarbonate species.[33] Moreover, ceria can enhance the oxygen storage and release in oxidizing and reducing conditions, respectively.[34–36] In another study, In₂O₃/CeO₂ was studied for the RWGS and maximum CO₂ conversion of 20 % was reported when In₂O₃ and CeO₂ were mixed in a 1:1 weight ratio at 773 K. [37] However, this study has not discussed the formation of methanol over In₂O₃/CeO₂ catalysts. Thus, most studies have focused on CO formation over CeO₂ supported catalysts.

Although studies reported the positive effect of ZrO₂ as a support for methanol synthesis,[31] less attention has been paid to CeO₂ as a support which is also capable of promoting the formation of oxygen vacancies for CO₂ activation. Therefore, these studies intrigued us to explore more about CeO₂ as a support for CO₂ hydrogenation into methanol along with ZrO₂. Thus, a comparative study was carried out between In_x/ZrO₂ and In_x/CeO₂ to identify the influence of the catalyst support on catalyst activity, deactivation, and stability during CO₂ hydrogenation to methanol while having comparable quantities of oxygen

vacancies, In₂O₃ loadings and surface areas. To the best of our knowledge, there is no report where deactivation and regeneration studies of CeO₂-supported In₂O₃ were explored, which is the objective of the current study.

2. Experimental Section

2.1. Materials

In(NO₃)₃·xH₂O salt was purchased from Sigma-Aldrich. Supporting materials ZrO₂ (monoclinic phase, extrudates, SZ 31164, NORPRO), and CeO₂ powder (99.5 H.S.A 514, Rhône-Polenc, La Rochelle, France) were used. For activity tests in the reactor, the catalyst powders were pelletized into 250–500 μm particles using a hydraulic press after impregnation of indium oxide (In₂O₃) on zirconia (ZrO₂) and ceria (CeO₂).

2.2. Catalysts preparation

The catalysts (In_x/ZrO₂ & In_x/CeO₂, x = 1 and 13 wt% In loading) were prepared by incipient wetness impregnation using CeO₂ and ZrO₂ as supports for In₂O₃ loading (Figure S1). For that, the In(NO₃)₃·xH₂O salt was dissolved in a mixture of ethanol and MilliQ water and dropwise added directly to the powder support to form a slurry. Further, the slurry was dried at 373 K and then the powder was calcined at 573 K in a furnace for 3 h. A similar procedure was used for the preparation of In_x/CeO₂. Note that to determine the role of the supports, unsupported bulk In₂O₃ was prepared using a calcination process where the Indium salt was calcined at 573 K in the furnace for 3 h. Further, catalytic CO₂ hydrogenation was conducted in a continuous reactor setup. Prior to the reaction, a thermal treatment was done in which the catalyst was heated in pure Ar (30 mL min⁻¹) at 573 K and 0.5 MPa for 1 h.

2.3. Characterization

To determine the crystalline nature of the catalysts, powder X-Ray diffraction (XRD) measurements were performed in a SIEMENS diffractometer D5000 using Cu Kα radiation (λ = 1.5418 Å) with a tube current and voltage of 40 mA and 45 kV, respectively. Diffraction patterns were collected with 2θ ranging from 20° to 70° using a step size of 0.02.

In-situ FTIR spectroscopy experiments were performed in diffusive reflectance (DRIFT) mode with a BRUKER Vertex 70 spectrometer equipped with a nitrogen-cooled MCT detector and a high-temperature stainless steel reaction cell (Harrick Praying Mantis™) with KBr windows. To measure the temperature of the sample, a K-type thermocouple was fitted into the sample holder and controlled by a PID regulator (Eurotherm). The total flow of gases into the reaction cell was fixed at 100 ml min⁻¹ in all experiments by feeding the gases via individual mass flow controllers. Spectra were recorded by accumulating 265 scans in the range of 4000–600 cm⁻¹ with a resolution of 4 cm⁻¹ for the temperature range of 493–553 K at atmospheric pressure. Time-resolved spectra were recorded every 60 s to obtain phase-resolved spectra.

The specific surface area of the catalysts was determined by nitrogen sorption at 77 K (Micromeritics Tristar 3000) using the Brunauer–Emmett–Teller (BET) method. The samples were dried in N₂ flow at 500 K for 3 h prior to the measurements.

X-ray photoelectron spectroscopy (XPS) was conducted using a Physical Electronics (PHI) 5000 VersaProbe III Scanning XPS Microprobe featuring focused monochromatic Al-Kα radiation with the X-ray (E = 1486.6 eV) beam size around 100 μm. The X-ray was generated via the electron beam bombardment onto the Al anode which was operating at 15 kV and 25 W. A hemispherical capacitor electron-energy analyzer was used equipped with a 32-channel plate and a position-sensitive detector. The samples were adhered onto double-sided tapes, fastened to the sample plate, and then introduced into the spectrometer after a

prolonged pre-pumping process in the introduction chamber. Due to the poor-conducting/insulating nature of the powder samples, charge compensation was conducted under the operation of both the electron neutralizer and ion gun. The measurements were run under a UHV environment around $1.0\text{-}3.0 \times 10^{-6}$ Pa. The take-off angle of the emitted photoelectron is 45° and the analyzer was operated in the constant pass energy mode (Survey: 280 eV; Regional/Narrow scan: 26 eV).

X-ray fluorescence (XRF) spectroscopy was carried out using a WDXRF (Wavelength Dispersive X-ray Fluorescence) spectrometer equipped with a Rh source operated at 60 kV and 125 mA.

TEM measurements were performed on a Titan 80-300 system (FEI Company) operated at 300 kV. The sample was crushed between two glass slides and distributed over a perforated carbon Cu grid to prepare the sample for TEM analysis.

CO_2 temperature-programmed desorption (CO_2 -TPD) and H_2 temperature-programmed reduction (H_2 -TPR) were studied using a digital scanning calorimeter (Sensys DSC, Setaram) coupled with a mass spectrometer (HPR-20 QUI, Hiden). For CO_2 -TPD, 50 mg of powder catalyst was loaded into a microreactor and then pretreated with Ar at 573 K for 30 min. Thereafter, the microreactor was cooled to 313 K and exposed to a flow of 5000 ppm CO_2/Ar for 90 min. Further, the catalyst was purged with Ar for 60 min. Then, the CO_2 desorption behavior was studied in Ar by increasing the temperature from 313 K to 973 K with a ramp rate of 10 K/min. The concentration of CO_2 was monitored using the mass number of $m/z = 44$. For H_2 -TPR measurements, the catalyst (30 mg) was pretreated in Ar at 573 K for 30 min and then cooled to 298 K. The H_2 flow (20 NmL/min, 1 vol% H_2/Ar) was introduced at 298 K for 20 min and then the temperature was ramped up to 1073 K (10 K/min) and maintained for 30 min at this temperature. The concentration of H_2 was monitored using the mass number of $m/z = 2$.

2.4. Catalytic activity test

The CO_2 hydrogenation reaction was evaluated in a continuous high-pressure fixed bed vertically positioned tubular stainless-steel reactor (0.85 cm diameter and 21.45 cm length) supplied by Vinci Technologies, France. The reactor was loaded with 0.5 g of catalyst sample. Reaction conditions were as follows: $\text{H}_2/\text{CO}_2 = 3$ (molar ratio), $\text{GHSV} = 12000 \text{ h}^{-1}$, $T = 493\text{-}573 \text{ K}$ and $P=3.0 \text{ MPa}$. The packing of the reactor consisted first of a bottom layer of 10.3 cm of pure SiC, above which was placed a layer of pure catalyst of (ca. 0.7 cm), which was placed between two thin layers of quartz wool. Finally, the remaining upstream part of the reactor (ca. 10.5 cm) was filled with SiC. A thermocouple was positioned in the reactor with its tip in contact with the catalyst sample for measuring the actual catalyst temperature during the reaction. Prior to the reaction, the catalysts were pre-treated with pure Ar (30 NmL min^{-1}) at 573 K for 1 h under 0.5 MPa pressure. After that, the catalysts were cooled down to reaction temperature in pure Ar, and then the reactant gases (CO_2 and H_2 with a molar ratio of 1:3) were introduced into the reactor at a gas hourly space velocity (GHSV) of 12000 h^{-1} and the pressure was raised to 3.0 MPa. Catalytic activity was measured at temperatures ranging from 493 to 573 K. The Ar flow was resumed after each day of measurements and maintained overnight. The catalyst bed remained in a temperature range from the desired reaction temperature to room temperature. Measurements were recorded when the reaction reached a steady state. The concentrations of the gaseous products in the outlet streams were measured by an on-line gas chromatograph (GC, SCION 456) equipped with a flame ionized detector (FID), and a thermal conductivity detector (TCD). The TCD detector was connected to an HS-Q column whereas the FID was connected to a mild-polar aluminum oxide packed column (Agilent Technologies, Inc., HP-Al/S, $30^*0.53 \text{ mm}$, $15 \mu\text{m}$) for product separation.

The CO_2 conversion (X_{CO_2}), selectivities for CH_3OH ($S_{\text{CH}_3\text{OH}}$), CO (S_{CO}), and CH_4 (S_{CH_4}), and space-time-yield (STY) were calculated according to the following equations:

$$X_{\text{CO}_2} = \frac{F_{\text{CO}_2, \text{in}} - F_{\text{CO}_2, \text{out}}}{F_{\text{CO}_2, \text{in}}} \times 100 \% \quad (4)$$

$$S_{\text{CH}_3\text{OH}} = \frac{F_{\text{CH}_3\text{OH}, \text{out}}}{F_{\text{CO}_2, \text{in}} - F_{\text{CO}_2, \text{out}}} \times 100 \% \quad (5)$$

$$S_{\text{CO}} = \frac{F_{\text{CO}, \text{out}}}{F_{\text{CO}_2, \text{in}} - F_{\text{CO}_2, \text{out}}} \times 100 \% \quad (6)$$

$$S_{\text{CH}_4} = \frac{F_{\text{CH}_4, \text{out}}}{F_{\text{CO}_2, \text{in}} - F_{\text{CO}_2, \text{out}}} \times 100 \% \quad (7)$$

$$\text{STY} = \frac{F_{\text{CH}_3\text{OH}} * M}{W_{\text{cat}}} \quad (8)$$

where F_i is the molar flow rate of component i , M is the molar mass of methanol and W is the weight of the catalyst sample.

3. Results

3.1. Catalyst characterization

Table 1 shows the In contents of four catalysts from XRF measurements. The In loadings were close to the targeted values of 1 and 13 wt %. A similar loading of In for each pair of catalysts using different supports ZrO_2 and CeO_2 allows for comparing the properties and the activity of the samples.

The crystallinity of CeO_2 and ZrO_2 -supported In_2O_3 catalysts were studied using XRD analysis (Figure 1). The patterns of the unsupported bulk In_2O_3 showed four main reflections at $2\theta = 30.5^\circ$, 35.4° , 50.9° and 60.5° , which are assigned to the diffractions from the (2 2 2), (4 0 0), (4 4 0) and (6 2 2) planes. The XRD patterns of the freshly prepared $\text{In}_{13}/\text{ZrO}_2$ showed the characteristic diffractions of cubic In_2O_3 and monoclinic ZrO_2 . [38] It should be noted that a small shift in the diffraction peaks corresponding to In_2O_3 was observed, for example, the reflection of (2 2 2) was shifted from 30.5° to 30.9° (Figure S2a). These results suggest some changes in the coordination of In-O-In (Figure 2a). It has been reported that the ZrO_2 support helps to make In_2O_3 electronically rich which is favourable for methanol formation. [39] Previous studies have discussed such interactions between the support and catalyst. [25,32] In the pattern of $\text{In}_{13}/\text{CeO}_2$, the diffraction peaks of the CeO_2 support were observed at $2\theta = 28.6^\circ$, 33.1° , 47.5° and 56.3° , which corresponds to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of CeO_2 . [40] However, it should be noted that the intensity of the diffractions of In_2O_3 is low for the $\text{In}_{13}/\text{CeO}_2$ sample, making the interpretation difficult. This is likely due to that the In_2O_3 is well dispersed and does not form large In_2O_3 crystallites. These results are supported by the STEM images, where the particles were not as clear as for the $\text{In}_{13}/\text{ZrO}_2$ sample. This will be further discussed in connection to Figure 3. The peaks of In_2O_3 on ZrO_2 support, on the other hand, are significantly stronger, suggesting larger crystallinity of In_2O_3 on the ZrO_2 support than on the CeO_2 support. The crystallite size of the bulk In_2O_3 was 19.5 nm for the (222) plane ($2\theta = 30.5^\circ$), whereas it was only 9.1 nm for $\text{In}_{13}/\text{ZrO}_2$. The crystallite size of In_2O_3 on CeO_2 , was not possible to determine with accuracy because the diffraction peak was so small. The

Table 1
Porous and compositional properties of In_x/ZrO_2 and In_x/CeO_2 .

| Catalysts | In content | | Porous properties ^b | |
|-------------------------------|----------------|------------------------------|--|--|
| | Nominal (wt %) | Measured ^a (wt %) | A_{BET} (m^2/g) | V_{pore} (cm^3/g) |
| $\text{In}_{13}/\text{ZrO}_2$ | 13 | 11.9 | 60.0 | 0.21 |
| $\text{In}_{13}/\text{CeO}_2$ | 13 | 13.5 | 66.6 | 0.13 |
| In_1/ZrO_2 | 1 | 0.7 | 69.9 | 0.27 |
| In_1/CeO_2 | 1 | 0.8 | 80.8 | 0.16 |
| Bulk In_2O_3 | - | - | 5.0 | 0.02 |

^aDetermined by XRF. ^bMeasured by N_2 adsorption.

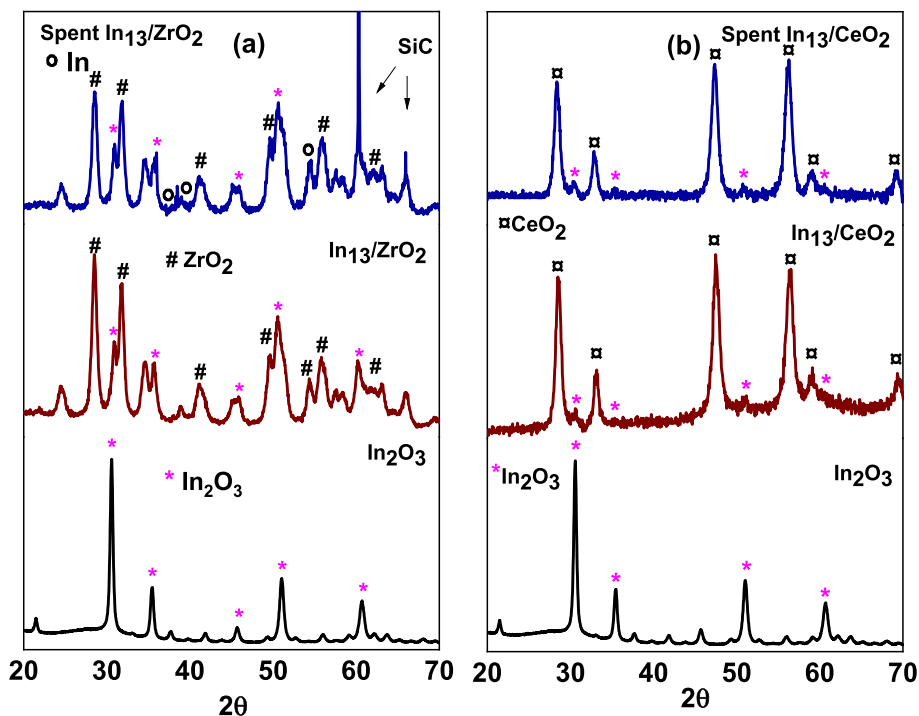


Figure 1. XRD patterns of (a) bulk In_2O_3 (black), $\text{In}_{13}/\text{ZrO}_2$ (red) and spent $\text{In}_{13}/\text{ZrO}_2$ (blue) and (b) bulk In_2O_3 (black), $\text{In}_{13}/\text{CeO}_2$ (red) and spent $\text{In}_{13}/\text{CeO}_2$ (blue) catalyst.

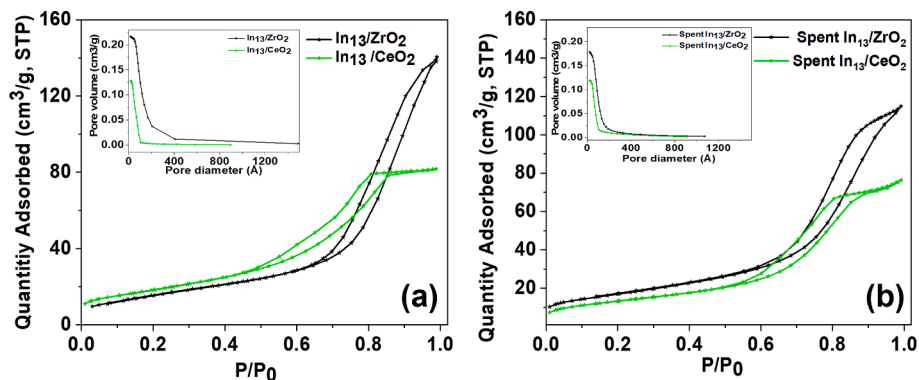


Figure 2. N_2 adsorption/desorption of $\text{In}_{13}/\text{ZrO}_2$ and $\text{In}_{13}/\text{CeO}_2$ for a) Degreened and b) Spent catalyst. The pore size distribution of the catalysts is presented in the inset.

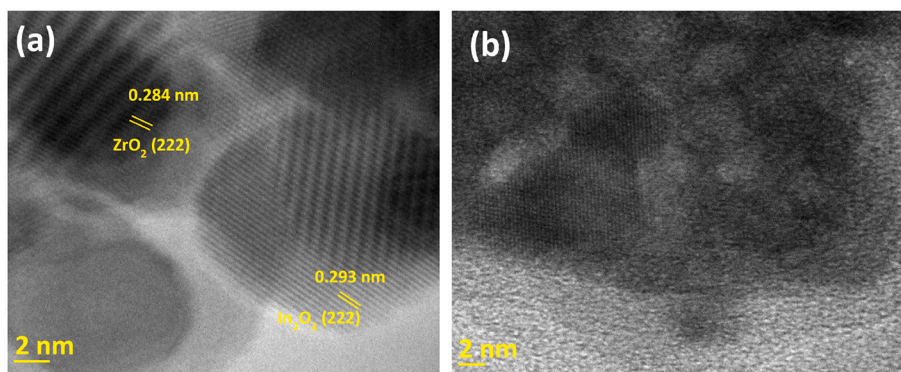


Figure 3. TEM analysis of (a) $\text{In}_{13}/\text{ZrO}_2$ and (b) $\text{In}_{13}/\text{CeO}_2$.

results are in line with earlier reported studies where the size of In_2O_3 particles decreased after impregnation on CeO_2 and ZrO_2 . [37] XRD patterns with negligible In_2O_3 peak intensities were found with 1 wt% loading of In on both supports (Figure S3).

The diffraction patterns of SiC were observed in the XRD in the case of the spent $\text{In}_{13}/\text{ZrO}_2$ catalyst since it was used as a filler while packing the reactor. [41,42] There was no change in the diffraction of In_2O_3 and ZrO_2 for the spent $\text{In}_{13}/\text{ZrO}_2$ which indicates no change in the crystalline structure of the catalyst after the reaction. However, small intensity peaks of In metal ($2\theta = 36.7^\circ, 39.1^\circ, 54.4^\circ$, PDF#04-010-6206) were observed which was also detected in the XPS analysis of the spent $\text{In}_{13}/\text{ZrO}_2$ catalysts. [43]

The porosity of $\text{In}_{13}/\text{ZrO}_2$ and $\text{In}_{13}/\text{CeO}_2$ was measured using N_2 physisorption and the data is summarized in Table 1. The surface areas of $\text{In}_{13}/\text{ZrO}_2$ and $\text{In}_{13}/\text{CeO}_2$ were found to be $60.0 \text{ m}^2/\text{g}$ and $66.6 \text{ m}^2/\text{g}$, respectively, whereas the surface area of the unsupported bulk In_2O_3 catalyst was only about $5 \text{ m}^2/\text{g}$. The surface area and pore volume increased when the In loading was decreased from 13 % to 1 % over ZrO_2 and CeO_2 (Table 1 and Figure 2 and Figure S4). The pore volume of the ZrO_2 -supported catalysts was found to be larger than that of CeO_2 -supported catalysts while the opposite was true for surface areas. It was observed that the surface area and pore volume decreased after loading of In on both supports. The results indicate that the loading of In_2O_3 blocks some of the pores of the support. It is also noted that the average pore width was larger for ZrO_2 than for the CeO_2 support. A larger pore size of ZrO_2 than CeO_2 could explain the larger crystallite size of $\text{In}_{13}/\text{ZrO}_2$ than $\text{In}_{13}/\text{CeO}_2$.

Type IVa N_2 -Isotherms were observed for all catalysts (Figure 2), which is characteristic of mesoporous materials. [44] The CeO_2 -supported In_2O_3 catalysts show a hysteresis loop of type H1 which is associated with porous materials exhibiting a narrow distribution of relatively uniform pores while a type H3 loop was observed for ZrO_2 -supported In_2O_3 catalysts [44]. The surface area and In contents of all the supported catalysts are similar which is favorable to compare their catalytic performance. Only the bulk In_2O_3 sample had a far lower surface area and pore volume.

The surface area of spent $\text{In}_{13}/\text{ZrO}_2$ and $\text{In}_{13}/\text{CeO}_2$ were also measured, and it was found that the surface area of $\text{In}_{13}/\text{CeO}_2$ was reduced from 66.6 to $48.0 \text{ m}^2/\text{g}$, whereas no change was observed in the surface area of $\text{In}_{13}/\text{ZrO}_2$ (Figure 2b). The pore volumes decreased of

both spent $\text{In}_{13}/\text{ZrO}_2$ (from 0.21 to $0.17 \text{ cm}^3/\text{g}$) and $\text{In}_{13}/\text{CeO}_2$ (from 0.13 to $0.11 \text{ cm}^3/\text{g}$) which indicates blockage of pores.

TEM imaging of $\text{In}_{13}/\text{ZrO}_2$ and $\text{In}_{13}/\text{CeO}_2$ are shown in Figure 3. It demonstrates that the crystalline In_2O_3 particles are well distributed on the surface of the crystalline ZrO_2 (Figure 3a). While on the CeO_2 support, In_2O_3 particles might be embedded between CeO_2 layers that cover the crystalline planes of In_2O_3 . Thus, the crystalline planes for In_2O_3 were difficult to distinguish. These results are consistent with the XRD patterns where the diffraction of indium was very weak (Figure 1b). The uniform distribution of In_2O_3 over CeO_2 and ZrO_2 was observed in EDX mapping of both catalysts (Figure S5)

To examine the chemical state of the elements, XPS analyses of In_2O_3 , $\text{In}_{13}/\text{ZrO}_2$, and $\text{In}_{13}/\text{CeO}_2$ were carried out (Figure 4-5, Figure S6). Before each analysis, all samples were *ex situ* pretreated in Ar at 573 K for 1 h. The O 1s core level of the unsupported In_2O_3 catalyst was deconvoluted into three peaks at $531.7, 530.9$ and 529.2 eV which were assigned to surface OH, defect (vacancy), and lattice (In-O-In), respectively (Figure 4a). [45] For the supported catalyst, it is more complicated to make the deconvolution because each component of the core O 1s is also contributed by the support. Moreover, the interaction between In_2O_3 and the support can cause a change in the electron density around O, which possibly makes a shift in the position of the peaks. $\text{In}_{13}/\text{ZrO}_2$ revealed three pronounced O 1s peaks at $533.0, 531.0$, and 529.7 eV (Figure 4a). The peaks at about 529.7 and 533.0 eV correspond to $\text{O}_{\text{lattice}}$ and OH, respectively, while that at 531.0 eV is related to the oxygen defects. [46] In the case of the $\text{In}_{13}/\text{CeO}_2$ catalyst, four peaks of O 1s at $528.8, 530.2, 531.3$, and 533.0 eV are assigned to the binding energies of $\text{Ce}^{4+}\text{-O}$, oxygen defects ($\text{Ce}^{3+}\text{-O}$), In-O-In and OH, respectively (Figure 4b).

It is seemingly difficult to identify the contribution of support material in the total amount of oxygen defects as peaks are overlapped after deconvolution. To better understand the contribution of the support, the core level of Zr 3d and Ce 3d were deconvoluted and the data are summarized in Figure 5. As shown in Figure 5a, the Zr 3d core level was deconvoluted into three doublets at $181.8, 183.3$, and 185.2 eV . The binding energies at 181.8 and 183.3 eV were assigned to ZrO_2 and Zr (OH)₄, respectively [47], while the higher binding energy at 185.2 eV could be from changed forms of ZrO_2 due to synergic interaction with In_2O_3 (In-O-Zr, Figure 5a). [25,48,49] The spectrum of Ce 3d core level was deconvoluted into two series of bands u and v, corresponding to the

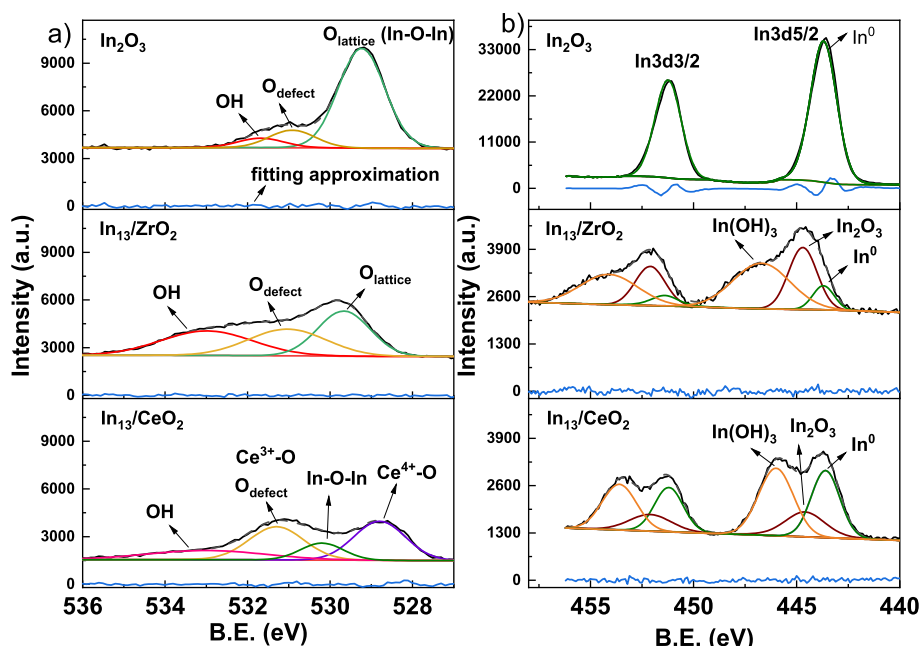


Figure 4. XPS analysis of (a) O 1s of In_2O_3 , $\text{In}_{13}/\text{ZrO}_2$ and $\text{In}_{13}/\text{CeO}_2$ and, (b) In 3d of In_2O_3 , $\text{In}_{13}/\text{ZrO}_2$ and $\text{In}_{13}/\text{CeO}_2$.

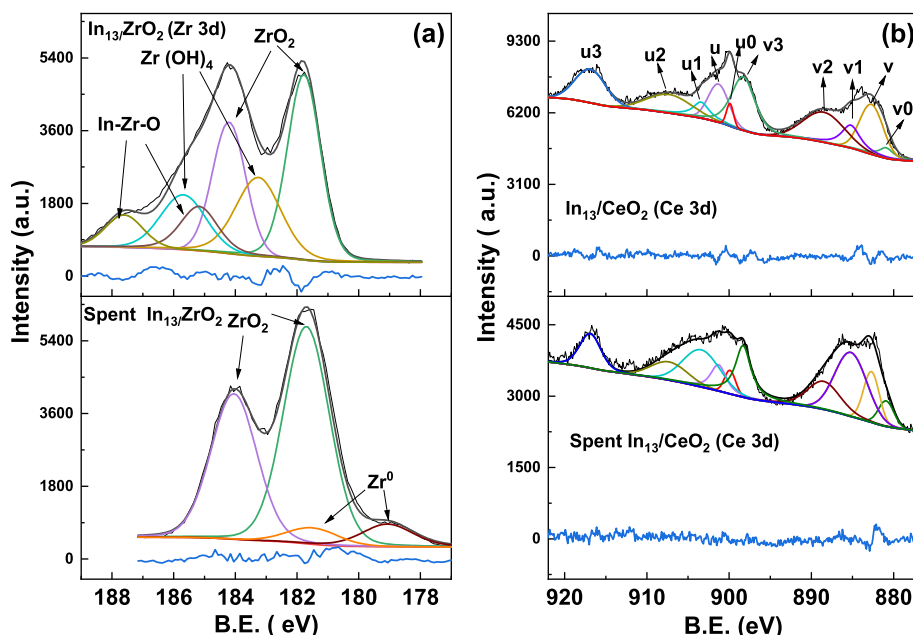


Figure 5. XPS analysis of (a) Zr 3d of $\text{In}_{13}/\text{ZrO}_2$ and spent $\text{In}_{13}/\text{ZrO}_2$, (b) Ce 3d of $\text{In}_{13}/\text{CeO}_2$ and spent $\text{In}_{13}/\text{CeO}_2$.

3d3/2 and 3d5/2 spin-orbits, respectively (Figure 5b). The group of six peaks denoted as v, v2, v3, u, u2, and u3 was assigned for the oxidation state of +4 (Ce^{4+}) whereas the group of four peaks labeled as v0, v1, u0, and u1 was characteristic of the oxidation state of +3 (Ce^{3+}). [50] The oxidation state of +4 (Ce^{4+}) is dominant (82 %) in the $\text{In}_{13}/\text{CeO}_2$. [51,52 53]

Figure 4b shows the binding energy of In3d core levels of In_2O_3 , $\text{In}_{13}/\text{ZrO}_2$ and $\text{In}_{13}/\text{CeO}_2$ catalysts. Two peaks located at 443.6 and 451.3 eV were observed in the XPS spectra for the unsupported bulk In_2O_3 , which can be attributed to the characteristic spin-orbit splits 3d5/2 and 3d3/2 of In 3d core level. [48,49] Both peaks are associated with indium as the catalyst was prepared by thermal composition and was unsupported. The binding energy of 3d5/2 at 443.7 eV is rarely reported in the literature for oxide forms of indium. Instead, the peak at 443.7 eV and 444.8 eV have been usually reported for In^0 and In^{3+} , respectively. [54] Therefore, the unusual characteristics of the 3d5/2 binding energy of the unsupported In_2O_3 catalyst could be related to the nature of the material prepared by the decomposition of $\text{In}(\text{NO}_3)_3$ precursor. It can be noted that metallic In was not detected by the XRD analysis (Figure 1). The metallic indium could either have been formed during heating of the salt in the preparation, and/or possibly by reduction of the surface under the ultra-high vacuum environment of the XPS instrument. In addition, XPS is a surface analysis technique, whereas XRD measures bulk properties. So metallic In is apparently only present on the surface of the materials. For the supported catalysts, the In 3d spectrum was deconvoluted into three doublets assigning to metallic In, In_2O_3 , and $\text{In}(\text{OH})_3$ (Figure 4b). The percentage of surface In_2O_3 was slightly higher on $\text{In}_{13}/\text{ZrO}_2$ (36.2 %) than $\text{In}_{13}/\text{CeO}_2$ (31.1 %). A core level of 3d5/2 of In3d was observed in both supported catalysts at 446.0 eV for $\text{In}_{13}/\text{CeO}_2$ and 446.7 eV for $\text{In}_{13}/\text{ZrO}_2$ (Figure 4b), which are due to $\text{In}(\text{OH})_3$. [55] This peak was higher in the case of $\text{In}_{13}/\text{ZrO}_2$ (53.3 %) than $\text{In}_{13}/\text{CeO}_2$ (41.3 %). These results indicate that the amount of $\text{In}(\text{OH})_3$ is higher over fresh $\text{In}_{13}/\text{ZrO}_2$ than $\text{In}_{13}/\text{CeO}_2$ which is also the same trend as the percentage of the OH fraction from the O 1s core level data. The metallic species of In with the binding energy of 3d5/2 at 443.7 eV were also observed in both supported catalysts and their percentage were 27.5 % and 10.5 % over $\text{In}_{13}/\text{CeO}_2$ and $\text{In}_{13}/\text{ZrO}_2$, respectively.

Deconvolutions of the XPS spectra of spent catalysts were carried out to interpret the changes in the chemical state of In and supports after the reaction (Figure S6 and Table 2). For that, the spent catalysts were

Table 2

XPS analysis of $\text{In}_{13}/\text{ZrO}_2$, $\text{In}_{13}/\text{CeO}_2$, spent $\text{In}_{13}/\text{ZrO}_2$ and spent $\text{In}_{13}/\text{CeO}_2$.

| Chemical state | ZrO ₂ (%) from Zr 3d | Oxygen defects (%) from O 1s | In (OH) ₃ (%) from In 3d | Ce ³⁺ state (%) from Ce 3d |
|-------------------------------------|---------------------------------|------------------------------|-------------------------------------|---------------------------------------|
| $\text{In}_{13}/\text{ZrO}_2$ | 60 | 31 | 53.3 | - |
| Spent $\text{In}_{13}/\text{ZrO}_2$ | 90 | 19 | 0 | - |
| $\text{In}_{13}/\text{CeO}_2$ | - | 33 | 41.3 | 18 |
| Spent $\text{In}_{13}/\text{CeO}_2$ | - | 39 | 30.8 | 45 |

flushed with Ar during the cooling down of the catalyst bed after the reaction and thereafter exposed to air at room temperature before the XPS measurements. XPS analysis showed 31 % oxygen vacancies over fresh $\text{In}_{13}/\text{ZrO}_2$ whereas it was 34 % over $\text{In}_{13}/\text{CeO}_2$. Further, the percentage of oxygen vacancies increased from 34 to 39 % over the spent $\text{In}_{13}/\text{CeO}_2$ while it dropped from 31 to 19 % in the case of $\text{In}_{13}/\text{ZrO}_2$. The chemical state and amount of metal hydroxide were also examined in spent and fresh catalysts, and it was found that the amount over ZrO_2 also increased from 60 to 90 % in the spent $\text{In}_{13}/\text{ZrO}_2$ (Figure 5a). A smaller peak, with a binding energy of around 179 eV was also observed in the spent $\text{In}_{13}/\text{ZrO}_2$ (Figure 5a), which could be associated with Zr 3d5/2 for metallic Zr [47] The amount of Ce^{3+} ion increased from 18 to 45 % in the spent $\text{In}_{13}/\text{CeO}_2$ (Figure 5b). This result indicates that the CeO_2 support creates more oxygen vacancies in an H_2 environment. Moreover, the percentage of $\text{In}(\text{OH})_3$ (determined from the In3d core level) was reduced from 41.3 to 30.8 % over the spent $\text{In}_{13}/\text{CeO}_2$ whereas it became zero from 53.3 % over the spent $\text{In}_{13}/\text{ZrO}_2$ (Figure S6, Table 2). We also observed a change in the ratio of $\text{In}^0/\text{In}_2\text{O}_3$ after the reaction. It increased from 0.29 to 0.65 for the $\text{In}_{13}/\text{ZrO}_2$ whereas it decreased from 0.88 to 0.34 for the $\text{In}_{13}/\text{CeO}_2$. The data suggest that during the reaction, the oxidation states changed not only for the active phase ($\text{In}^0/\text{In}_2\text{O}_3$) but also for the supports.

3.2. Characterization of the interaction of gas-phase species with the catalyst surface

In-situ DRIFT spectroscopy was conducted to study the adsorption behavior of CO_2 and identify the adsorbed species during the interaction of CO_2 with H_2 over $\text{In}_{13}/\text{ZrO}_2$, and $\text{In}_{13}/\text{CeO}_2$ (Figures 6-7). Prior to each

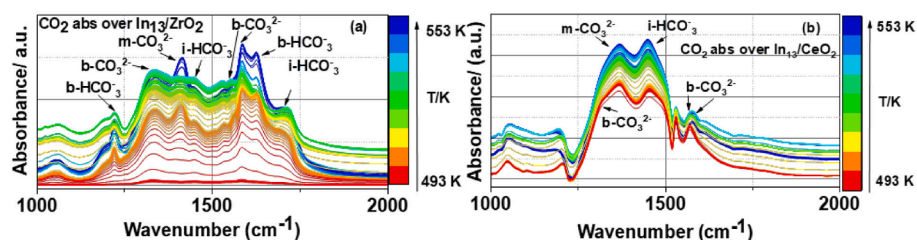


Figure 6. CO₂ adsorption study over (a) In₁₃/ZrO₂ and, (b) In₁₃/CeO₂.

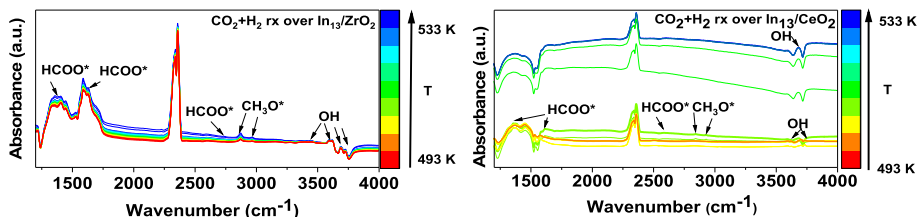


Figure 7. CO₂+H₂ reaction study over (a) In₁₃/ZrO₂ and, (b) In₁₃/CeO₂.

experiment, the catalysts were pre-treated at 573 K in Ar for 1 h. After pretreatment, the catalyst was cooled down in Ar to the desired temperature where the background spectrum was collected at 493 K. The catalyst was thereafter exposed to a steady gas flow of 0.03 vol.% CO₂ in Ar at 493 K and the adsorption behavior of CO₂ for In₁₃/CeO₂ and In₁₃/ZrO₂ catalysts are shown in Figure 6. Bands related to ionic bicarbonate (i-HCO₃⁻) [56] as well as bridged bicarbonate (b-HCO₃⁻) [56] were observed on the surface of In₁₃/ZrO₂. The bands related to b-HCO₃⁻ appeared at 1620 and 1225 cm⁻¹ while for i-HCO₃⁻ the bands were found at 1695 and 1435 cm⁻¹ (Figure 6a). [57] Bands related to carbonates were also observed at 1585, 1555 and 1335 cm⁻¹ for b-CO₃²⁻ and 1375 cm⁻¹ for monodentate carbonate (m-CO₃²⁻). [57] The peak intensity of b-HCO₃⁻ species was higher than those of i-HCO₃⁻ at 553 K for In₁₃/ZrO₂. Additionally, the b-CO₃²⁻ and m-CO₃²⁻ species bands were more intense than the bicarbonate bands at this temperature. Thus, the features for carbonate species are much stronger than those for bicarbonate species at higher adsorption temperatures. [56] The CO₂ absorption bands observed on In₁₃/CeO₂ at 1575 and 1315 cm⁻¹ suggest the presence of b-CO₃²⁻ at 493 K. When the temperature increased from 493 to 553 K, the b-CO₃²⁻ species began to disappear or their intensity decreased on the surface of In₁₃/CeO₂, whereas the m-CO₃²⁻ and i-HCO₃⁻ species at 1375, and 1448 cm⁻¹, were detected at 553 K (Figure 6b). [32]

In addition, time and temperature resolved spectra were collected during the introduction of 0.09 vol.% H₂ in Ar together with 0.03 vol.% CO₂ to maintain a 1:3 molar ratio and to study the CO₂ and H₂ interactions on the surface of In₁₃/ZrO₂ and In₁₃/CeO₂. When the sample was exposed to the H₂ atmosphere, new peaks related to methoxy groups around 2850 and 2937 cm⁻¹ appeared at 493 K over In₁₃/ZrO₂ (more intense) and In₁₃/CeO₂ (less intense) along with carbonate and bicarbonate species (Figure 7). [58,59] The large peak around 2334-2364 cm⁻¹ is due to the presence of gas-phase CO₂. The formate species were also observed at 1620, 1380, and 2740 cm⁻¹ on the surface of In₁₃/ZrO₂ and In₁₃/CeO₂. [58,59] The intensity of formate peaks was higher over In₁₃/ZrO₂ than In₁₃/CeO₂. The peaks disappeared in the case of In₁₃/CeO₂ while they became more intense over In₁₃/ZrO₂ when the temperature was increased from 493 to 553 K (Figure 6). [60] In addition to this, various types of O-H bands between 3400-3700 cm⁻¹, which are related to bridge as well as hydrogen-bonded OH groups, were observed over In₁₃/ZrO₂ (Figure 7a). While over In₁₃/CeO₂, only two OH bands related to bridged species on Ce³⁺ and Ce⁴⁺ appeared at low temperatures which further disappeared at higher temperatures and only one OH band remained over the catalyst surface which is assigned to hydrogen-bonded OH groups (Figure 7b). In the DRIFT experiments, the OH

bands are weak and the reason for this is likely that DRIFT experiments are run at atmospheric pressure. It is well known that CO₂ hydrogenation requires higher pressure to increase the yield. The low conversion of CO₂ and thereby the low formation of water could explain why the OH bands are small. Anyhow, OH bands are visible, and it is likely that these species would be significantly larger at real operating conditions with high pressure hydrogen. It is therefore possible that at higher H₂ pressure the O-H groups could cover the surface of In₁₃/CeO₂, which could result in low CO₂ conversion and methanol selectivity. This hypothesis is supported by the XPS data where 30.8 % metal hydroxides was found over the spent

In₁₃/CeO₂ catalyst.

The CO₂ adsorption and desorption were studied in TPD experiments for In₂O₃, In₁₃/ZrO₂ and In₁₃/CeO₂ (Figure 8). A common desorption peak was below 550 K which was due to physisorbed CO₂. [19] The peak above 550 K could be attributed to chemisorption of CO₂ from thermally induced oxygen vacancies. [18] It was difficult to distinguish the boundary between physio- and chemisorbed CO₂ peaks in the case of In₁₃/CeO₂. The total CO₂ desorbed values were 30, 181, and 191 μmol/g for In₂O₃, In₁₃/ZrO₂ and In₁₃/CeO₂, respectively. A significantly lower amount of CO₂ adsorption was found on the unsupported In₂O₃ compared to the supported catalysts, which was probably related to its substantially lower specific surface area. The total amount of CO₂ desorbed was higher on In₁₃/CeO₂ than In₁₃/ZrO₂, which might be due to more oxygen defects on In₁₃/CeO₂, which is in-line with the XPS analysis (Figure 8a). [12,61]

H₂-TPR measurements were used to study the reduction behavior of the catalysts (Figure 8b). The H₂-TPR profile of the unsupported bulk In₂O₃ exhibited two main stages of H₂ consumption. The first one was at approximately 531 K due to the reduction of the surface species while the second one started from around 798 K and the reduction was not complete even when it was prolonged at 1073 K for 30 min. This is a typical behavior of In₂O₃ as reported in the literature [62]. The H₂-TPR profile of the In₁₃/ZrO₂ sample showed two hydrogen consumption peaks at 513 and 943 K. We note that the ZrO₂ support consumed only a negligible amount of H₂ at around 943 K (data not shown). Therefore, the reduction of the In₂O₃ component accounted mainly for the hydrogen consumption of the In₁₃/ZrO₂ catalyst. However, the first peak was shifted to a lower temperature than that of the unsupported bulk In₂O₃, suggesting that the reduction of In₂O₃ was enhanced. Furthermore, the total area of the peaks was significantly smaller than that of the bulk In₂O₃ because the In₁₃/ZrO₂ contained a lower amount of In₂O₃ than the unsupported catalyst. In₁₃/CeO₂ showed two H₂ uptakes at 531

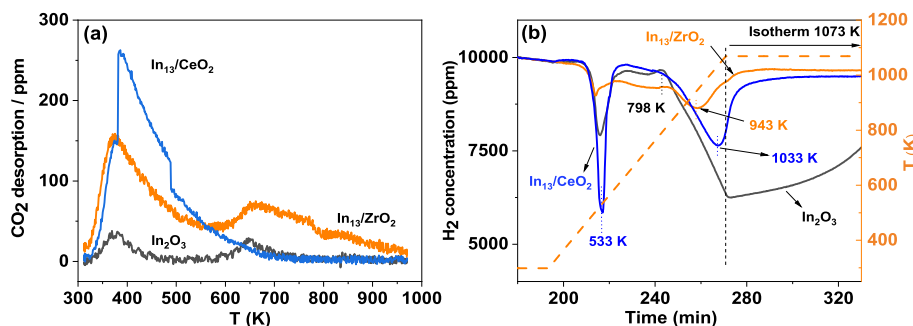


Figure 8. CO₂ TPD (a) of bulk In₂O₃, In₁₃/ZrO₂ and In₁₃/CeO₂, and H₂-TPR (b) of bulk In₂O₃, In₁₃/ZrO₂ and In₁₃/CeO₂ at atmospheric pressure.

K and 1033 K. The total area of the two peaks was significantly higher than that of the In₁₃/ZrO₂. Because both catalysts had a similar loading of In₂O₃, this suggests that CeO₂ contributed to the hydrogen consumption of the In₁₃/CeO₂ catalyst. Indeed, the CeO₂ support exhibited two peaks of hydrogen consumption. The first one started around 593 K and peaked at 843 K due to the reduction of surface CeO₂ while the second one began at approximately 953 K due to the reduction of bulk CeO₂ and it was not completed even at 1073 K for 30 min (data not shown). It should be noted that the first reduction peak (at 533 K) of the In₁₃/CeO₂ was substantially larger than that on both unsupported In₂O₃ and In₁₃/ZrO₂. This suggested that CeO₂ enhanced the reduction of In₂O₃. The quantification of H₂ consumption was not performed because the reduction was not completed for all three catalysts in the measured temperature range.

3.3. Catalytic activity

The catalytic performance of the Indium supported (In_x) on CeO₂ and ZrO₂ was assessed, where Indium loading (x) was kept at 1 % and 13 %. The In₁₃/ZrO₂ catalyst was tested at various temperatures from 493 to 573 at 3.0 MPa to examine the effect of reaction conditions on methanol synthesis (Figure 9). It was observed that the CO₂ conversion and CO selectivity increased with increasing temperature while the selectivity for CH₃OH decreased because of the competition of the RWGS reaction at high temperatures, which is in line with previous studies. [18] The In₁₃/ZrO₂ catalyst exhibited 100 % CH₃OH selectivity with 0.6 % CO₂ conversion at 493 K. Increasing the temperature to 573 K, resulted in the CO₂ conversion increasing to 12.7 %, while the CH₃OH selectivity dropped to 57.3 % and the CO selectivity was 42.3% (Figure 9). In

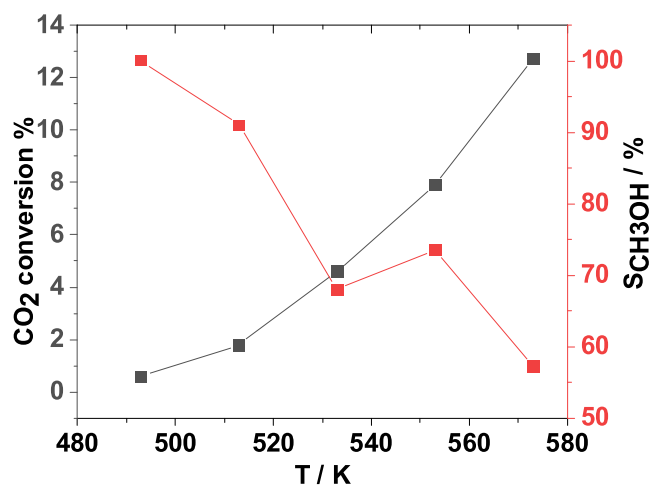


Figure 9. CO₂ hydrogenation over In₁₃/ZrO₂ at various temperatures, Reaction conditions: Catalyst= 0.5 g, feed gas molar ratio (H₂ : CO₂) = 3:1; GHSV = 12000 h⁻¹ and P = 3.0 MPa.

addition, the CH₄ selectivity also increased from 0 to 0.21 % with increasing temperature from 493 to 573 K.

Figure 10 shows that the combination of In₂O₃ and ZrO₂ improved significantly the CO₂ conversion as compared to its individual components. Activity measurements for each catalyst were performed at 493, 553 and 573 K. After the temperature reached the set value, the reaction was prolonged at this temperature for about 1 h while the outlet gas was continuously analyzed. We report the data near the end of this period. At 553 K, the CO₂ conversions over the unsupported bulk In₂O₃ and ZrO₂ support were negligible while it significantly increased from 0.6 % (over bulk In₂O₃) to 7.9 % over In₁₃/ZrO₂. Both samples of CeO₂-supported In catalysts showed lower conversion of CO₂ than the unsupported bulk In₂O₃ but higher than the CeO₂ support. The CO₂ conversion increased with increasing temperature over In₂O₃, ZrO₂, In_x/ZrO₂ and In_x/CeO₂. Surprisingly, the conversion decreased over CeO₂ when increasing the temperature, however, it should be noted that the conversions over CeO₂ were very low over the entire temperature span investigated. The change in CO₂ conversion over In_x/CeO₂ with increasing temperature was more moderate compared to that with In_x/ZrO₂. The low increment in the conversion of CO₂ with increasing temperature for the CeO₂-based catalysts raises some suspicion that there is a factor that makes these catalysts unstable under the operating conditions of the reaction and this will be further discussed in Section 3.8. The CO₂ conversion increased with increasing In loading from 1 % to 13 % over both supports. Thus, the further characterizations were carried out with 13 % In loading catalysts and are discussed here in detail.

The CH₃OH selectivity decreased with increasing temperature from 493 to 573 K over all catalysts due to the competition of the RWGS reaction at high temperatures. Notably, methanol was the main product when the In loading was 13 % while CO was the main product with 1 % In loading at 573 K for both the supported catalysts. At 493 K, the selectivity for CH₃OH increased from 68 % to 85 % as the loading of In increased from 1 % to 13 %. Wang et al. found that the activity of bulk ZrO₂ was negligible, with only 0.18 % CO₂ conversion at 573 K. [13] The CH₄ selectivity also increased with increasing temperature over all catalysts from 493 to 573 K. Additionally, In_x/CeO₂ exhibited higher selectivity towards CH₄ than In_x/ZrO₂ for both In loadings. The CeO₂ exhibited negligible conversion. After loading In over CeO₂, it became active toward methanol synthesis. Further, the CH₃OH selectivity decreased, and the CO selectivity increased over In_x/CeO₂, when the temperature increased from 493 to 573 K. The change in selectivity for CH₃OH and CO was much less when In loading was 13 %. The In_x/CeO₂ showed higher methanol selectivity as compared to In_x/ZrO₂ with both levels of In loading at 553 and 573 K. However, the maximum methanol STY at 553 K and 3.0 MPa was 0.17 and 0.007 g_{MeOH} h⁻¹ g_{cat}⁻¹ over In₁₃/ZrO₂ and In₁₃/CeO₂, respectively.

3.4. Catalyst stability

Stability is a key factor to determine the use of catalysts for CH₃OH synthesis from CO₂ hydrogenation on an industrial scale. The stability

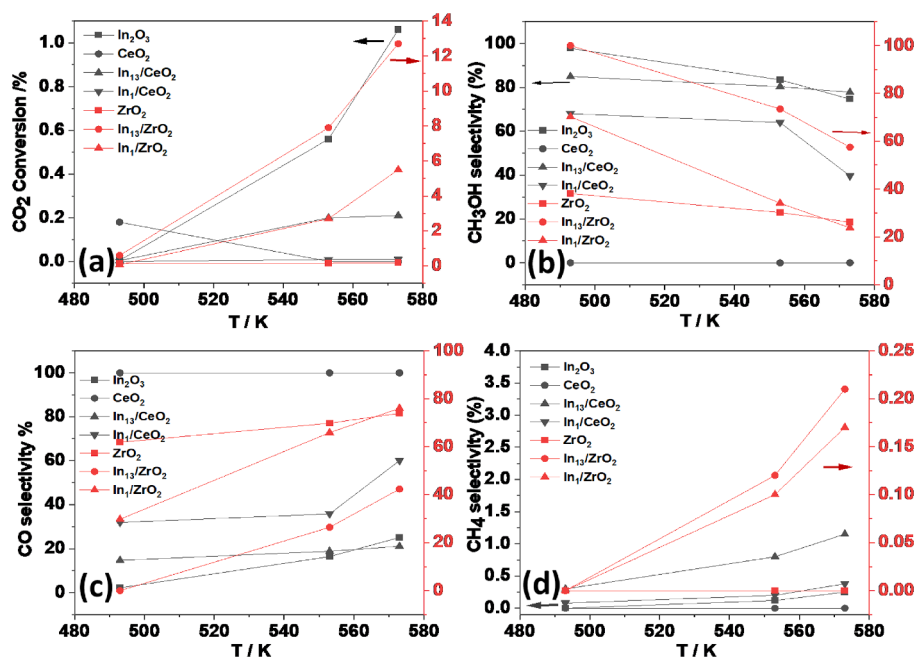


Figure 10. CO₂ hydrogenation over In₂O₃, In₁₃/ZrO₂, In₁₃/CeO₂, In₁/ZrO₂, In₁/CeO₂, ZrO₂ and CeO₂ (a) CO₂ conversion and (b) CH₃OH selectivity, (c) CO selectivity and, (d) CH₄ selectivity, Reaction conditions: Catalyst= 0.5 g, feed gas ratio (H₂ : CO₂)=3:1, P = 3.0 MPa and, GHSV = 12000 h⁻¹.

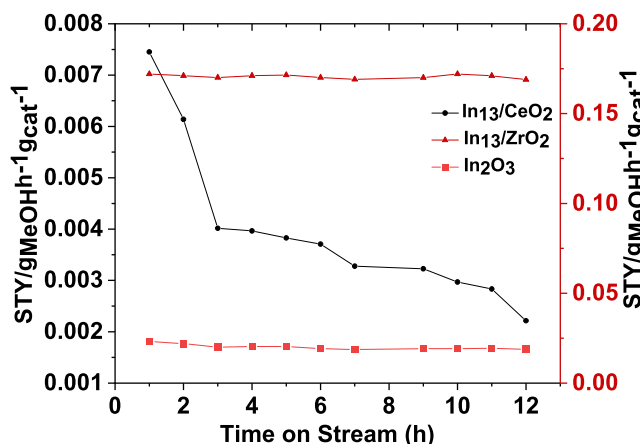


Figure 11. Evolution of the methanol STY with time on stream (TOS) over In₁₃/ZrO₂ and In₁₃/CeO₂. Reaction conditions: Catalyst= 0.5 g, feed molar gas ratio (H₂ : CO₂)=3:1, P = 3.0 MPa and, GHSV = 12000 h⁻¹, T = 553 K.

test of bulk In₂O₃, In₁₃/ZrO₂ and In₁₃/CeO₂ was performed at 553 K and 3.0 MPa because the catalysts exhibited the best STY of methanol at this condition. Figure 11 compares the methanol STY versus the time-on-stream over bulk In₂O₃, In₁₃/ZrO₂ and In₁₃/CeO₂. The In₁₃/ZrO₂ and bulk In₂O₃ catalysts were found to be stable for the entire duration of 12 h, whereas methanol STY of In₁₃/CeO₂ decreased dramatically from the beginning to 2 h of time-on-stream and then dropped steadily till the end of the test at 12 h. Further, the stability test for In₁₃/ZrO₂ was prolonged and the methanol STY was stable up to 50 h of time-on-stream (Figure S7). The deactivation will be discussed in Section 4.

4. Discussion

The selectivity for CH₃OH was higher for In₁₃/CeO₂ than In₁₃/ZrO₂ at 553 K while the STY for CH₃OH was higher over In₁₃/ZrO₂ than In₁₃/CeO₂. The positive effect of CeO₂ in CO₂ hydrogenation has been reported in terms of CH₃OH selectivity when ZrO₂ was partially replaced

by CeO₂. [63] In the DRIFT study, more bi-carbonates, formates, and methoxy species were observed over In₁₃/ZrO₂. The higher activity of In₁₃/ZrO₂ than our unsupported bulk In₂O₃ is likely due to the significantly higher surface area. In addition, we observed an interaction between ZrO₂ and In₂O₃ in XRD and it has been reported that this interaction increased the stability of various intermediates like *CO₂, *CO, *HCO, and *H₂CO which could give a higher activity of In₁₃/ZrO₂. [25,64]

During the reaction period, the STY of CH₃OH was constant for In₁₃/ZrO₂ while it approached zero for In₁₃/CeO₂ with time. These results show that the In₁₃/CeO₂ catalyst deactivated after 12 h on stream. Similar deactivation has been observed in the case of a Pd/CeO₂ catalyst for CO₂ hydrogenation. [65] To further understand the deactivation of In₁₃/CeO₂, we have characterized the catalyst before and after reaction (spent catalyst) using XRD, N₂ physisorption and XPS. The XRD measurements (Figure 1) revealed that the crystallite size of the ceria support increased in the spent catalyst, which is a sign of sintering of the support material. Moreover, the specific surface area also decreased from 66 to 48 m²/g which also suggests that the support sintered during the reaction. Interestingly, the XPS data also revealed that the In(OH)₃ species were still present over spent In₁₃/CeO₂ while they disappeared in the spent In₁₃/ZrO₂ (Figure S6a). Moreover, the In⁰/In₂O₃ ratio also changed significantly differently between In₁₃/ZrO₂ and In₁₃/CeO₂ after the reaction. The ratio of In⁰/In₂O₃ increased 2.2-fold for In₁₃/ZrO₂ whereas it decreased by 2.6-fold for In₁₃/CeO₂. This suggested that In₂O₃ in In₁₃/ZrO₂ was reduced further while metallic In in In₁₃/CeO₂ was partially oxidized after the reaction. Furthermore, it was also noted that more Ce³⁺ was present in the spent In₁₃/CeO₂ while a small fraction of Zr⁰ was also detected for the spent In₁₃/ZrO₂. This indicated that the supports (CeO₂ and ZrO₂) were partially reduced after the hydrogenation reaction; however, the reduction of CeO₂ is easier than ZrO₂ to some extent as also observed from H₂-TPR. A redox pair of Ce³⁺/Ce⁴⁺ and In⁰/In³⁺ may explain an increase in the amount of Ce³⁺ and a decrease in the amount of In⁰ in the In₁₃/CeO₂ after the reaction, and this is in line with the H₂-TPR data. Also, from DRIFTS measurements OH groups were visible although at low levels, likely due to low conversion and low water formation in the DRIFT experiments since they were performed at atmospheric pressure. Here, water should play a crucial role in the

deactivation of the catalyst as it is a side product of CO₂ hydrogenation. Therefore it might be possible that the produced water can deactivate the active sites of the catalyst.[65] It has been reported and confirmed that CeO₂ is a good adsorbent for water molecules due to its hydrophilic nature and a very stable configuration of water has been observed on the surface of CeO₂. [37]

It was also observed in the DRIFT study that the bands related to methoxy, formate and carbonate species disappeared at higher temperature over In₁₃/CeO₂, indicating less adsorption of CO₂ molecules over CeO₂ at higher temperature. [66,67] However, the presence of water molecules around the In surface could create a physical hindrance for the CO₂ molecules and also cause sintering of In. [18]

To summarize, In₁₃/CeO₂ has a high initial selectivity for methanol production, but it rapidly deactivates with time on stream. In₁₃/ZrO₂ on the other hand exhibited a stable methanol production during the 50 h long experiment. The deactivation of In₁₃/CeO₂ is likely linked to a sintering of support which caused lower surface area and the redox property of CeO₂ which induced the oxidation of metallic In.

4.1. Regeneration of In/CeO₂

In₁₃/ZrO₂ catalysts were found to be stable at 533 K and 3.0 MPa whereas the In₁₃/CeO₂ catalyst showed severe deactivation after only a few hours of time on stream. A regeneration study of In₁₃/CeO₂ was therefore carried out at 533 K and 3.0 MPa to determine the type of deactivation (Figure 12). After the reaction, the catalyst was flushed with Ar (50 Nml/min), while the reactor was cooled from reaction temperature to room temperature and further maintained in Ar flow overnight. The next day, the Ar flow was switched to reactant feed and the temperature was increased from room temperature to reaction temperature. It was observed that the STY for methanol decreased during the first day under reaction conditions. Further, the catalyst bed was flushed and tested again on the second day at the same reaction conditions. The STY was partially recovered from the previous day but again started to decrease with time. This process was again repeated on the third day and a similar phenomenon was observed, although at significantly lower STY levels. It can be stated that some part of deactivation is reversible as the STY increased after flushing with Ar. Thus, due to the strong hydrophilic character of the CeO₂ carrier, significant amounts of water form and assemble on the catalyst during the reaction. The water could inhibit CO₂ hydrogenation, and we suggest that it could be partly removed after Ar flushing from the CeO₂ surface and thereby increasing the CO₂ adsorption and methanol formation. However, the decreased surface area is not reversible, and the catalyst could therefore not gain the original state back, which could be the reason behind the continuous overall deactivation of the catalyst over the three days observed in Figure 12.

5. Conclusions

To uncover the effect of ZrO₂ and CeO₂ supports on In₂O₃ activity in the hydrogenation of CO₂ to methanol, In₂O₃ supported on ZrO₂ and CeO₂ catalysts were prepared. The selectivity for CH₃OH was higher for In₁₃/CeO₂ than In₁₃/ZrO₂ at 553 K, but the CH₃OH yield was higher over In₁₃/ZrO₂. For the In₁₃/ZrO₂ the CO₂ conversion and CO selectivity increased with increasing temperature while the selectivity for CH₃OH decreased. In addition, some methane was formed, which increased with temperature. A large drawback with the In₁₃/CeO₂ sample was that it deactivated severely with time on stream and already after 2 h a significant deactivation was observed. In₁₃/ZrO₂, on the other hand, exhibited a stable behavior during 50 h on stream. The spent catalysts were characterized to understand the different behavior of In₁₃/CeO₂ than In₁₃/ZrO₂ during the time on stream. The XPS results revealed that during the reaction the ratio of In⁰/In₂O₃ increased from 0.29 to 0.65 for the In₁₃/ZrO₂ whereas it decreased from 0.88 to 0.34 for the In₁₃/CeO₂. The data suggest that the redox property of CeO₂ (Ce³⁺ ion increased

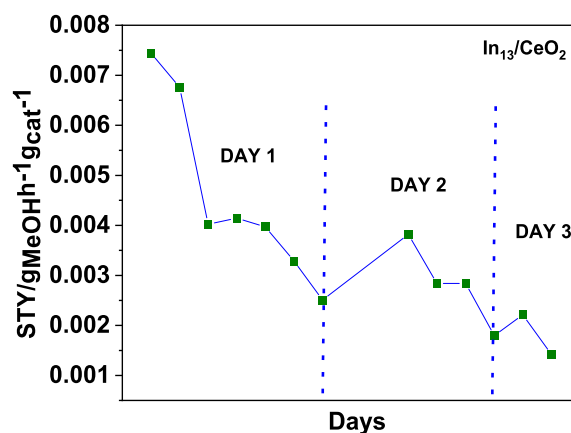


Figure 12. Regeneration study of In₁₃/CeO₂. Reaction conditions: Catalyst= 0.5 g, feed gas ratio (H₂ : CO₂) = 3:1, P = 3.0 MPa and, GHSV = 12000 h⁻¹, T = 553 K. Between each day the catalyst was flushed and cooled in Ar and then kept in Ar flow over night.

from 18 to 45 % in the spent In₁₃/CeO₂) induced the oxidation of metallic In and increased the amount of In₂O₃. Moreover, the percentage of In(OH)₃ was 30.8 % over the spent In₁₃/CeO₂ whereas it became zero over the spent In₁₃/ZrO₂. In addition, OH groups were found during DRIFT experiments, although at low levels likely due to that the experiments were performed at atmospheric pressure, resulting in low conversion and thereby low water production. We, therefore, propose that the water produced during reaction results in the formation of hydroxyls on the In₁₃/CeO₂, which was one of the deactivating factors. However, this is not the main reason for the deactivation, because XRD experiments showed that the sintering of CeO₂ support (larger crystallite size) for the spent In₁₃/CeO₂ catalyst. In addition, the specific surface area also decreased due to sintering, while it remained the same for In₁₃/ZrO₂. Thus, the structural changes, presence of more OH groups (hydrophilic nature) and the decreased surface area of spent In₁₃/CeO₂ after the reaction are the reasons for the decreased activity. Further, a regeneration study of In₁₃/CeO₂ was conducted and that revealed that the catalyst can be regenerated to some extent by flushing the catalyst with Ar. However, repeated reaction-regeneration cycles revealed that the conversion continued to decrease after the regeneration and was even lower after subsequent cycles. To conclude, the water adsorption on In₁₃/CeO₂ is partly reversible and the catalyst can therefore gain back some activity after Ar flushing, but the structural changes are not reversible and cause a continuous deactivation. In₁₃/ZrO₂, on the other hand, exhibited a stable behavior during the reaction conditions used in this study.

CRedit authorship contribution statement

Poonam Sharma: Conceptualization, Data curation, Formal analysis, Investigation, Visualization, Writing – original draft, Methodology. **Fuoc Hoang Ho:** Data curation, Formal analysis, Methodology, Validation, Visualization, Writing – review & editing. **Jieling Shao:** Data curation, Formal analysis, Validation. **Derek Creaser:** Conceptualization, Formal analysis, Methodology, Supervision, Writing – review & editing. **Louise Olsson:** Formal analysis, Funding acquisition, Methodology, Project administration, Supervision, Writing – review & editing.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2022.125878>.

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