Ni–In Synergy in CO₂ Hydrogenation to Methanol

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ABSTRACT: Indium oxide (In₂O₃) is a promising catalyst for selective CH₃OH synthesis from CO₂ but displays insufficient activity at low reaction temperatures. By screening a range of promoters (Co, Ni, Cu, and Pd) in combination with In₂O₃ using flame spray pyrolysis (FSP) synthesis, Ni is identified as the most suitable first-row transition-metal promoter with similar performance as Pd−In₂O₃. NiO−In₂O₃ was optimized by varying the Ni/In ratio using FSP. The resulting catalysts including In₂O₃ and NiO end members have similar high specific surface areas and morphology. The main products of CO₂ hydrogenation are CH₃OH and CO with CH₄ being only observed at high NiO loading (≥75 wt %). The highest CH₃OH rate (~0.25 gMeOH/(gcat h), 250 °C, and 30 bar) is obtained for a NiO loading of 6 wt %. Characterization of the as-prepared catalysts reveals a strong interaction between Ni cations and In₂O₃ at low NiO loading (≤6 wt %). H₂-TPR points to a higher surface density of oxygen vacancy (Oᵥ) due to Ni substitution. X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and electron paramagnetic resonance analysis of the used catalysts suggest that Ni cations can be reduced to Ni as single atoms and very small clusters during CO₂ hydrogenation. Supportive density functional theory calculations indicate that Ni promotion of CH₃OH synthesis from CO₂ is mainly due to low-barrier H₂ dissociation on the reduced Ni surface species, facilitating hydrogenation of adsorbed CO₂ on Oᵥ.

KEYWORDS: CO₂ hydrogenation, CH₃OH, flame spray pyrolysis, Ni promotion, Ni−In synergy

1. INTRODUCTION

The large amounts of CO₂ released into the atmosphere, mainly by the combustion of fossil fuels, constitute a significant threat to human well-being because it can lead to severe climate changes including global warming, sea-level rise, and ocean acidification.¹⁻³ A promising solution is to capture CO₂ from combustion processes or directly from air for reuse in fuels and chemicals. This can for instance be achieved by catalytic hydrogenation of CO₂ with H₂ generated from renewable energy sources such as solar and wind.⁴⁻⁷ This carbon capture and use (CCU) approach has the advantage over carbon capture and storage (CCS) that carbon is used in a circular manner, eventually leading to the replacement of fossil fuels by renewable resources for covering the energy demand. Besides sustainable energy carriers, hydrogenation of CO₂ can be used to obtain important intermediates for the chemical industry. Methanol is particularly attractive in the overall context of sustainability because it can be directly used as a fuel or be converted to a wide range of chemicals such as formaldehyde, dimethyl ether, olefins, hydrocarbon fuels, etc.⁸⁻¹⁰

The Cu/ZnO/Al₂O₃ catalysts used in the current commercial methanol synthesis process were pioneered by Imperial Chemical Industries in the 1960s.¹¹⁻¹² These catalysts are optimized for the conversion of synthesis gas (a mixture of mainly CO/H₂). Challenges arise however in the hydrogenation of CO₂ to CH₃OH. The high activity of the Cu–ZnO-based catalysts in the reverse water gas shift (rWGS) reaction decreases the CH₃OH selectivity.¹³ Moreover, deactivation of the Cu–ZnO-based catalysts is accelerated by the large amounts of water byproduct formed during CO₂ hydrogenation.¹⁴⁻¹⁶ Many efforts have been made to optimize Cu-based catalysts for selective CO₂ hydrogenation to CH₃OH.⁵,¹⁷ An important corollary of these studies is that tuning Cu–support interactions using other supports than alumina can mitigate some of these drawbacks. For example, zirconia (ZrO₂) has been widely investigated as a support with improved catalytic performance over alumina-supported catalysts.¹⁸⁻²¹

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Exploring completely new catalytic formulations is another approach to develop practical catalysts for CO2 hydrogenation to CH3OH. Several promising materials have been reported, for instance, mixed oxides (ZnO–ZrO2 and MnO2/CoO)22,23, molybdenum carbides,24,25 molybdenum phosphides,26 and intermetallic compounds (GaP2 and Ni3Ga)27,28. In recent years, oxygen-defective In2O3 has been proposed as an alternative catalyst for efficient CH3OH synthesis from CO2.29 The role of oxygen vacancies in the In2O3 surface has been emphasized for the adsorption and hydrogenation of CO2.29,30 Furthermore, ZrO2 has been extensively studied as a support for In2O3 due to the synergistic interactions between these two components.31-34 Perez-Ramirez’s group reported that nanosizing In2O3 by dispersion over ZrO2 can substantially enhance CH3OH synthesis from CO2.35 Addition of Pd was also found to significantly promote In2O3 for CO2 hydrogenation to CH3OH.36-38 It was proposed that low-nuclearity Pd clusters stabilized by a Pd-In interaction can enhance H2 activation and, therefore, CH3OH productivity.39

Given its price, it would be advantageous to replace Pd by a more earth-abundant metal. Earlier investigations have shown that the activity of In2O3 for CO2-to-CH3OH conversion can be promoted by Co and Cu.40-44 The replacement of Pd by Ni, a typical methanation catalyst, has been studied as well. Richard and Fan, for instance, found that NiInAl/SiO2 catalysts derived from phyllosilicate precursors can catalyze CO2 hydrogenation to CH3OH at ambient pressure although with low selectivity (<4%).45 In another study, Snider et al. suggested that the higher activity of bimetallic Ni–In catalysts for CH3OH synthesis from CO2 in comparison to In2O3 is related to the synergistic interactions between a Ni–In alloy and In2O3.46 Using wet chemical reduction with sodium borohydride, Jia et al. observed a similar promoting effect of Ni on In2O3 for CO2 hydrogenation to CH3OH. They suggested that the Ni promotion is associated with highly dispersed Ni species in strong interaction with In2O3.47 In a recent report, Frei et al. studied Ni-promoted In2O3 in detail for CO2 hydrogenation, highlighting the formation of highly dispersed InNi3 layers on In2O3.48

In the present study, a series of NiO–In2O3 catalysts were investigated to further understand the Ni promotion on In2O3 for CO2 hydrogenation to CH3OH. For this purpose, a one-step FSP method49,50 was used to synthesize well-defined NiO-In2O3 catalysts with controlled Ni–In interactions. Catalytic activity measurements at 250 °C and 30 bar point to a significant synergy between Ni and In2O3 for CH3OH synthesis from CO2: small amounts of Ni lead to substantially increased CH3OH formation rates, while high Ni loadings result in CH4 formation. To elucidate the Ni–In synergy, various techniques including N2 physisorption, transmission electron microscopy (TEM), X-ray diffraction (XRD), electron paramagnetic resonance (EPR), H2-TPR, X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS) were employed to characterize the as-prepared and used NiO-In2O3 catalysts, and density functional theory calculations were carried out to unravel the role of different Ni species in H2 activation.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. A series of metal (M = Co, Cu, Ni, and Pd with loading of 5 wt %)-promoted In2O3 catalysts were prepared by a one-step FSP method using a Tethis

NSP10 setup. Typically, a precursor solution was prepared by dissolving appropriate amounts of In(NO3)3·3H2O (99%, Alfa Aesar) and metal precursor (Co(NO3)2·6H2O (98%, Sigma Aldrich), Cu(NO3)2·3H2O (99.5%, Sigma Aldrich), Ni(NO3)2·6H2O (98.5%, Sigma Aldrich), and Pd(OOCCH3)2 (98%, Sigma Aldrich)) in a 1:1 (vol %) solvent mixture of ethanol (HPLC, Sigma Aldrich) and 2-ethylhexanoic acid (99%, Sigma Aldrich) at room temperature to a total metal concentration (In + M) of 0.15 M. The catalyst preparation was started by injecting the precursor solution into the nozzle of the flame synthesis setup at a flow rate of 5 mL/min. The flame was fed with a 1.5 L/min methane and 3.0 L/min oxygen flow with an additional 5.0 L/min oxygen dispersion flow around it. The catalyst powder was collected from the quartz filter placed downstream of the flame region. The as-prepared catalysts are denoted M-In2O3. Another series of catalysts were prepared using the same procedure to study the Ni promoter in detail. The as-prepared Ni–In catalysts are denoted In2O3, NiO(x)–In2O3, and NiO, where x stands for NiO loading in the catalysts (wt %).

2.2. Catalyst Characterization. 2.2.1. N2 Physisorption. The textural properties of the as-prepared and used catalysts were studied by N2 physisorption at −196 °C using a Micrometrics TriStar II 3020 instrument. For this purpose, approximately 100 mg of samples was transferred into glass sample tubes and pretreated at 120 °C under a nitrogen flow overnight before the measurements. The Brunauer—Emmett—Teller (BET) method was used to calculate the specific surface area of the catalysts.

2.2.2. Transmission Electron Microscopy (TEM). The morphology of the as-prepared and used catalysts was studied by TEM using a FEI Tecnai (type Sphera) instrument operating at an acceleration voltage of 200 kV. For sample preparation, appropriate amounts of samples were dispersed in ethanol under ultrasonic exposure and deposited on holey Cu grids.

2.2.3. X-ray Diffraction (XRD). The crystal structure of the as-prepared catalysts was analyzed using a Bruker D2 Phaser diffractometer with Cu Kα radiation (1.5406 Å). The XRD patterns were recorded between 15 and 80° with a step size of 0.05° at a 1.0 s/step scan rate.

2.2.4. Electron Paramagnetic Resonance (EPR) Spectroscopy. In situ EPR spectra of selected NiO-In2O3 catalysts during CO2 hydrogenation were measured at ambient pressure using an X-band EPR EMX CW-micro spectrometer (Bruker) with a microwave power of Ca 6.9 mW and modulation frequency and amplitude of 100 kHz and 5 G, respectively, while ex situ EPR spectra were recorded on an X-band EPR EMX CW-micro spectrometer (Bruker). For monitoring the EPR spectra at low temperature, the EPR spectrometer was equipped with a temperature controller and liquid N2 cryostat. The effective g values (g_{eff}) were calculated using eq 1, where h and β denote Planck’s constant and the Bohr magneton constant, respectively, and ν and B0 represent, respectively, the frequency and the magnetic resonance field.

$$\nu = g_{\text{eff}} \beta B_0$$  

(1)

2.2.5. Temperature-Programmed Reduction (H2-TPR). The reducibility of the as-prepared catalysts was analyzed by H2-TPR using a Micromeritics AutoChem II setup. Typically, about 50 mg of sample was loaded into a quartz U-tube between two quartz wool layers. The sample was pretreated at 200 °C for 1 h in a 5 vol % O2 in a He flow of 50 mL/min
before the measurements. The TPR profile was recorded by heating the sample from 40 to 700 °C at the rate of 10 °C/min in a 4 vol % H2 in He flow of 50 mL/min. The H2 consumption was monitored by a thermal conductivity detector (TCD) and calibrated against a reference Cu/SiO2 sample.

2.2.6. X-ray Photoelectron Spectroscopy (XPS). The surface chemical properties of the as-prepared and used catalysts after CO2 hydrogenation were studied using a K-Alpha XPS instrument (Thermo Scientific) with a monochromatic small-spot X-ray source and a 180° double-focusing hemispherical analyzer. For the analysis of used catalysts, a quasi-in situ approach was adopted. Specifically, the samples were placed on a double-sided carbon tape in a glovebox and transferred to the spectrometer via an airtight transfer holder. The sample preparation of the as-prepared catalysts was carried out at ambient conditions. Spectra were collected using an aluminum anode (Al Ka = 1486.68 eV) operating at 72 W and a spot size of 400 µm. Survey scans were measured at a constant pass energy of 200 eV and region scans at 50 eV. The spectra were analyzed using CasaXPS software (version 3.2.2.3), and energy calibration was performed again the C 1s peak of adventitious carbon at a binding energy of 284.6 eV.

2.2.7. X-ray Absorption Spectroscopy (XAS). Extended X-ray absorption fine structure (EXAFS) measurements at the Ni K-edge and In K-edge were performed at beamline B18 of the Diamond Light Source (Didcot, UK). EXAFS measurements of the as-prepared and used catalysts were performed in the fluorescence mode with a 36-element Ge detector. Notably, the used samples were prepared and sealed using Kapton tapes in a glovebox, and the as-prepared samples were prepared at ambient conditions. The NiO reference was measured in the transmission mode with a 36-element Ge detector. Metallic Ni and In foils were measured simultaneously with each sample in the transmission mode for energy calibration. Si(111) and Si(311) monochromators were used at Ni and In K-edges, respectively. EXAFS data reduction includes energy calibration, background subtraction, and normalization, and EXAFS fitting analysis was carried out using the Demeter package (Athena/Artemis software). Scattering paths were calculated using the FEFF6 code based on crystal structures of NiO, Ni metal, and In2O3. A Ni–In single scattering path was also included for the EXAFS fitting. In a typical fitting procedure, the energy shift (E0), distance change (ΔR), coordination number (CN), and Debye–Waller factor (σ2) were fitted, whereas the amplitude reduction factors (S02) were determined from the EXAFS fitting of the NiO reference and the as-prepared In2O3 sample. The amplitude reduction factors were fixed while fitting other parameters. The plotted Fourier transformed EXAFS results weighted by k3 have not been phase-corrected.

2.3. Catalytic Activity Measurements. The catalytic performance of the as-prepared catalysts in CO2 hydrogenation was evaluated at 250 °C and 30 bar using a down-flow stainless steel reactor (ID = 4 mm). Typically, about 50 mg of sieved catalyst (125–250 µm), diluted with 200 mg of SiC, was loaded into the reactor and pretreated at 250 °C (rate = 5 °C/min) and 1 bar for 1 h in a N2 flow of 10 mL/min. After the pretreatment, the catalyst was exposed to a reaction mixture flow (CO2/H2/N2 = 10:30:10 mL/min), and the pressure in the reactor was increased to 30 bar using a back-pressure regulator. The effluent gas mixture was continuously analyzed by an online gas chromatograph (Interscience, CompactGC) equipped with Rtx-1 (FID), Rt-QBond and Molsieve 5A (TCD), and Rt-QBond (TCD) columns. Catalytic measurements typically lasted for ca. 12 h until steady-state was reached. CO2 conversion (X), product selectivity (S), and product formation rate (r) were calculated using the following equations:

$$\frac{F(\text{CO}_2)_{\text{in}} + F(\text{CH}_3\text{OH})_{\text{in}} + F(\text{CH}_4)_{\text{in}}}{F(\text{CO}_2)_{\text{out}} + F(\text{CO})_{\text{out}} + F(\text{CH}_3\text{OH})_{\text{out}} + F(\text{CH}_4)_{\text{out}}}$$

$$\frac{F(\text{product})_{\text{in}}}{F(\text{CO}_2)_{\text{out}} + F(\text{CH}_3\text{OH})_{\text{out}} + F(\text{CH}_4)_{\text{out}}}$$

$$\frac{F(\text{product})_{\text{out}}}{V_m \times n_{\text{cat}}}$$

where F stands for the volumetric flow rate calculated based on the N2 internal standard using calibrated response factors and Vm is the molar volume of ideal gas at standard conditions. For the XPS and XAS analyses of the used catalysts, the catalysts after catalytic tests were transferred without air exposure: the reactor was depressurized at 250 °C, cooled to room temperature in a N2 flow of 10 mL/min, sealed with two three-way valves, and transferred to a glovebox for sample storage and preparation.

2.4. Density Functional Theory Calculations. All density functional theory (DFT) calculations were conducted using the projector augmented wave (PAW) method and the Perdew–Burke–Ernzerhof (PBE) functional as implemented in the Vienna ab initio simulation package (VASP) code. Solutions of the Kohn–Sham equations were calculated using a plane-wave basis set with a cutoff energy of 400 eV. The semicore 5s and 5p states of In were treated explicitly as valence states within the scalar-relativistic PAW approach. The Brillouin zone was sampled using a 3 × 3 × 1 Monkhorst–Pack grid. Electron smearing was employed using Gaussian smearing with a smoothing width (σ) of 0.1 eV. The stoichiometric In2O3(111) surface was modeled as a two-dimensional slab with periodic boundary conditions. A 20 Å vacuum region was used in the c-direction to avoid spurious interactions of adsorbed species between neighboring supercells. It was verified that the electron density approached zero at the edges of the periodic supercell in the c-direction. The supercell has a dimension of 14.57 Å × 14.57 Å × 26.01 Å. The In2O3(111) slab consists of 96 O atoms and 64 In atoms, distributed in four atomic layers. Three different Ni-containing models were constructed and optimized by DFT: (i) a Ni atom doped into In2O3(111) replacing an In atom, (ii) a Ni atom adsorbed on the In2O3(111) surface, and (iii) a Ni4 cluster adsorbed on the In2O3(111) surface. The activation of H2 on these surface models was investigated, and transition states were determined using the climbing-image nudged elastic band (CI-NEB) method. A frequency analysis was performed to confirm that all transition geometries corresponded to a first-order saddle point on the potential energy surface with an imaginary frequency in the direction of the reaction coordinate. The Hessian matrix was constructed using a finite difference approach with a step size of 0.0015 Å for displacement of individual atoms along each Cartesian coordinate. The corresponding normal-mode vibrations were

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used to determine the zero-point energy corrections and the vibrational partition functions.

3. RESULTS AND DISCUSSION

3.1. Screening of Metal Promotion. Using the one-step FSP approach, we prepared three In$_2$O$_3$-based catalysts promoted by base metals (Co, Ni, and Cu) together with Pd-promoted and unpromoted In$_2$O$_3$ catalysts. The loading of a metal promoter in these catalysts was kept at 5 wt %. XRD analysis (Figure S1) shows that all of the diffraction peaks belong to the cubic In$_2$O$_3$ phase (PDF # 00-006-0416). The average crystallite size of the samples (estimated by the Scherrer equation) was ~9 nm, irrespective of the metal promoter. No diffraction peaks related to any promoter in metallic or oxidic forms were observed, suggesting that all of the promoter metals are highly dispersed or amorphous in the as-prepared catalysts. The M-In$_2$O$_3$ and In$_2$O$_3$ catalysts were evaluated for CO$_2$ hydrogenation under the conditions of 250 °C and 30 bar. The complete catalytic results are listed in Table S1. A comparison of CH$_3$OH formation rates is presented in Figure 1. The Co-In$_2$O$_3$ and Cu-In$_2$O$_3$ displayed lower CH$_3$OH rates than In$_2$O$_3$ while Ni and Pd additions gave rise to similar promotion in CH$_3$OH formation. Note, however, that due to a lower activity in the rWGS reaction, the Co-In$_2$O$_3$ displayed a higher CH$_3$OH selectivity in comparison to Ni-In$_2$O$_3$ (72 vs 53%). As Pd is a relatively expensive precious metal, which has already been extensively investigated to promote In$_2$O$_3$ for CO$_2$ hydrogenation to CH$_3$OH, we focused in this work on the development of practical In$_2$O$_3$-based catalysts for CH$_3$OH synthesis from CO$_2$ using Ni as a promoter.

3.2. Basic Characterization. The specific surface areas of the as-prepared NiO-In$_2$O$_3$ catalysts were determined by N$_2$ physisorption (Table 1). Clearly, all of the samples display high specific surface areas. The values of In$_2$O$_3$ and NiO samples are 123 and 137 m$^2$/g, respectively. The binary NiO-In$_2$O$_3$ samples have slightly lower surface areas in the range of 98–114 m$^2$/g. The morphology and particle size distribution of these catalysts were studied by TEM. Figure 2 shows that all of the samples display a similar morphology consisting of homogeneously distributed globular nanoparticles, irrespective of the vast difference in chemical composition. The as-prepared NiO-In$_2$O$_3$ catalysts have comparable average particle size, ranging from 6.5 to 7.5 nm, as estimated from the TEM measurements.

XRD patterns of the as-prepared NiO-In$_2$O$_3$ catalysts are shown in Figure 3. Samples with a NiO loading up to 6 wt % have the cubic crystal structure of In$_2$O$_3$ (PDF # 00-006-0416). In addition, the In$_2$O$_3$ lattice constant estimated from the Rietveld refinement decreases with increasing NiO loading (Table 1), implying the substitution of Ni cations for the larger In cations in In$_2$O$_3$. It should be noted however that the changes in the lattice constant are very small. The sample with an intermediate NiO loading of 25 wt % displays new diffraction peaks, which are likely due to a NiIn$_2$O$_4$ spinel phase. Samples with NiO loading of 50 wt % and higher mainly consist of the NiO phase (PDF # 00-047-1049). The significant broadening of all of the diffraction peaks points to the nanocrystalline nature of the as-prepared NiO-In$_2$O$_3$ catalysts, in line with the previous N$_2$ physisorption and TEM results.

3.3. Catalytic Activity Measurements. The CO$_2$ hydrogenation performance of the as-prepared NiO-In$_2$O$_3$ catalysts was determined at 250 °C and 30 bar. Figure 4a shows that addition of a small amount of NiO (x = 1 and 6) leads to a substantial increase of CO$_2$ conversion. Nevertheless, the product distribution remains nearly unchanged with CH$_3$OH and CO as the main products, implying that the active sites for CO$_2$ activation in these catalysts (x = 1 and 6) are barely affected by Ni addition. Notably, only very small amounts of methane were formed on NiO(x)−In$_2$O$_3$ (x = 1 and 6), which is unusual for Ni-based catalysts. Methanation of CO$_2$ on Ni is a structure-sensitive reaction, and we infer that the suppression of CH$_4$ formation on NiO(x)−In$_2$O$_3$ (x = 1 and 6) catalysts might be due to the absence of step-edge Ni sites because of the high dispersion of Ni in the reduced catalysts (see below). The following trends were observed when the NiO loading was increased beyond 6 wt %: (i) CO$_2$ conversion decreased as compared to NiO(6)−In$_2$O$_3$ and (ii) CO and CH$_4$ selectivity increased at the expense of CH$_3$OH selectivity. Based on these observations and the XRD results, it becomes clear that the In$_2$O$_3$ phase plays a pivotal role in the selective CH$_3$OH synthesis from CO$_2$, in agreement with earlier reports. The formation of CH$_4$ at high NiO loading (x = 75 and 100) can be explained by the formation of metallic Ni particles, which are known to catalyze CO$_2$ methanation. Figure 4b further shows that the CH$_3$OH formation rate first increased and then decreased with respect to NiO loading, pointing to a clear Ni-In synergy in CO$_2$ hydrogenation to CH$_3$OH. At the optimum NiO loading (6 wt %), the CH$_3$OH rate is nearly 4 times higher than that of the unpromoted In$_2$O$_3$. The time-on-stream (TOS) catalytic performances of In$_2$O$_3$, NiO(1)-In$_2$O$_3$, and NiO(6)-In$_2$O$_3$ are presented in Figure 4c,d, showing that CO$_2$ conversion and CH$_3$OH selectivity were stable during the whole test of ~12 h.

Table 1. Specific Surface Area and In$_2$O$_3$ Lattice Constant of the As-Prepared NiO-In$_2$O$_3$ Catalysts

| catalyst | $S_{BET}$ (m$^2$/g) | In$_2$O$_3$ lattice constant a (Å) |
|----------|-----------------|----------------------------------|
| In$_2$O$_3$ | 123 | 10.118 |
| NiO(1)-In$_2$O$_3$ | 110 | 10.112 |
| NiO(6)-In$_2$O$_3$ | 98 | 10.110 |
| NiO(25)-In$_2$O$_3$ | 104 | n.a. |
| NiO(50)-In$_2$O$_3$ | 110 | n.a. |
| NiO(75)-In$_2$O$_3$ | 114 | n.a. |
| NiO | 137 | n.a. |
3.4. Characterization of Ni–In Synergy. N$_2$ physisorption (Table S2) and TEM (Figure S3) measurements were carried out on used In$_2$O$_3$, NiO(1)–In$_2$O$_3$, and NiO(6)–In$_2$O$_3$ catalysts. In comparison with the as-prepared catalysts, the average particle size of the used catalysts is the same after the reaction. This observation demonstrates that the difference in catalyst surface area cannot explain the observed Ni–In synergy.

EPR spectroscopy can be used to study defects and states with unpaired electrons in nickel oxides. The ex situ EPR spectra of the as-prepared samples measured at −173 °C are shown in Figure 5. The NiO bulk reference sample (NiO-ref) does not show an EPR signal. The antiferromagnetic state of bulk stoichiometric NiO can be explained by the very low contribution of disordered surface states. The NiO sample prepared by FSP shows a strong anisotropic EPR signal, which is due to the much smaller crystallite size (ca. 6.7 nm according to TEM). The ferromagnetic nature of NiO crystals with a size smaller than 10 nm has been described. The NiO(x)–In$_2$O$_3$ (x ≥ 25) samples show similar broad anisotropic ferromagnetic signals as the FSP-prepared NiO sample, however with different line shapes and intensities. This suggests that these materials contain also small NiO nanoparticles having different sizes and shapes with different anisotropic contributions. The decreasing EPR signal can be attributed to the dilution of NiO with In$_2$O$_3$. The two samples with low NiO loadings, i.e., NiO(1)–In$_2$O$_3$ and NiO(6)–In$_2$O$_3$, show only very weak signals. This implies that Ni is present in a different configuration than in small NiO particles. As it is unlikely that Ni is present as NiO particles at such low NiO loading, we speculate that Ni is present as atomically dispersed 3+ ions in In$_2$O$_3$ or at the In$_2$O$_3$ surface. This was supported by the appearance of a very weak signal (Figure S4), which might be attributed to the presence of isolated Ni$_{3+}$ ions in NiO(1)–In$_2$O$_3$. The presence of Ni$_{3+}$ ions was also suggested by the XPS and XAS results (see below).

Figure 6 shows Ni 2p$_{3/2}$ and In 3d$_{5/2}$ XP spectra of the as-prepared NiO–In$_2$O$_3$ catalysts. Interpretation of the 2p core level of transition-metal oxides with unfilled d-orbitals is complex because of the main line multiplet contributions as well as satellite peaks. The Ni 2p$_{3/2}$ spectrum of the as-prepared NiO is similar to that of polycrystalline NiO with the main lines at binding energies (BEs) of 853.0 and 854.9 eV and a main shake-up feature at 860.1 eV. The spectrum of NiO(75)–In$_2$O$_3$ contains similar lines as NiO, although the contribution around 854.9 eV is less intense. The NiO loading (x ≤ 50) leads to a strong decrease of the intensity of the peak at 853.0 eV, indicating the disappearance of NiO particles in these samples. The main peaks at ca. 855.1 eV of NiO(1)–In$_2$O$_3$ and NiO(6)–In$_2$O$_3$ can have different origins. This feature has been linked to Ni$_{3+}$, but this assignment is not unequivocal. Similar XP spectra with a main contribution at 855.5 eV (note that BE of C 1s set at 285.0 eV) were also reported for Ni/TiO$_2$ and Ni/CeO$_2$ samples and
could be explained by the presence of very small NiO patches stabilized by strong interactions with the oxide supports. The XP spectra of the In 3d region of NiO(1)-In2O3 and NiO(6)-In2O3 show a significant shift of the In 3d5/2 core line to lower BE in comparison to the spectrum of In2O3, which can be associated with Ni substitution in the In2O3 lattice. Such a shift is absent in the NiO(x)-In2O3 (x ≥ 25) samples, suggesting an electronic structure similar to the In2O3 sample. Normalized XANES spectra at the Ni K-edge are presented in Figure 7. The half-edge energies for NiO(1)-In2O3 and NiO(6)-In2O3 are, respectively, located at 8344.2 and 8343.9 eV. These values are substantially higher than the half-edge energy of 8342.5 eV observed for NiO, indicating that Ni is in the 3+ state. EXAFS analysis was also used to investigate Ni-In interactions in these two samples. Figure 8a shows that NiO(1)-In2O3 and NiO(6)-In2O3 samples contain a Ni-In shell due to the Ni-O-In path. The fit results of the Ni K-edge EXAFS data (Table 2) show that the CN of the Ni-In (oxidic) shells are 6.3 and 5.3 for the samples with 1 and 6 wt % NiO, respectively. The lower CN of the Ni-In (oxidic) shell for NiO(6)-In2O3 goes together with the appearance of a Ni-Ni (oxidic) shell (CN = 7.5) due to the Ni-O-Ni path in NiO. The coordination environment of In atoms does not change profoundly among the as-prepared In2O3, NiO(1)-In2O3, and NiO(6)-In2O3 samples (Figure 8b), which is to be expected due to the high In2O3 content in these samples. The fit results of the In K-edge EXAFS data (Table S3) also confirm that the bulk of In2O3 does not change significantly after adding small amounts of NiO (x ≤ 6).

The Ni species in the NiO(x)-In2O3 (x = 1 and 6) samples were also studied by H2-TPR (Figure 9a). The profile of NiO(1)-In2O3 contains a single reduction feature at ~300 °C. This feature can be attributed to the reduction of Ni cations substituted in the In2O3 lattice. The H2/Ni ratio corresponding to this feature is ~0.7, indicating that likely only a part of substituted Ni can be reduced. This may be explained by the fact that a part of Ni cations resides in the bulk of In2O3. The profile of NiO(6)-In2O3 contains more reduction features than NiO(1)-In2O3 after 300 °C. This observation points to the more heterogeneous speciation of Ni in the former sample, which is in line with the earlier EXAFS analysis. Oxygen vacancy (Ov) formation in In2O3 was also studied by H2-TPR measurements. The Ov formation in the as-prepared In2O3 sample is characterized by a reduction peak around 200 °C. For the NiO(1)-In2O3 and NiO(6)-In2O3 samples, we observed that this reduction feature is broadened compared to In2O3, with two distinct peaks being resolved for NiO(1)-In2O3. These differences can be due to Ni substitution in the In2O3 lattice, resulting in a more heterogeneous reduction process.
behavior of the In$_2$O$_3$ surface. Quantification of these reduction peaks indicates that the O$_v$ densities are 54 and 52 $\mu$mol/gcat for NiO(1)-In$_2$O$_3$ and NiO(6)-In$_2$O$_3$, respectively. These values are slightly higher than the value of 42 $\mu$mol/gcat for In$_2$O$_3$. The corresponding surface-area-normalized O$_v$ densities are 0.34, 0.49, and 0.53 $\mu$mol/m$^2$ for In$_2$O$_3$, NiO(1)-In$_2$O$_3$, and NiO(6)-In$_2$O$_3$, respectively. Although one may expect a lower O$_v$ density upon Ni substitution because of the stronger Ni$-$O bond (346 kJ/mol),$^{68}$ the presence of smaller Ni cations in In$_2$O$_3$ may distort the In$_2$O$_3$ lattice and weaken the In$-$O bonds. We also studied the In$_2$O$_3$ surface O$_v$ density from the O 1s XP spectra of the used catalysts (Figure 9b). The peaks at BE of 529.3 and 531.2 eV can be related to lattice O in In$_2$O$_3$ (O$_{lattice}$) and O close to oxygen vacancies (O$_{vacancy}$), respectively.$^{40}$ Peak deconvolution indicates that addition of Ni leads to a slight increase of surface O$_v$ density, in agreement with the H$_2$-TPR analysis.

We next compare the Ni 2p$_{3/2}$ XP spectra and Ni K-edge XAS data of the as-prepared and used NiO(1)-In$_2$O$_3$ and NiO(6)-In$_2$O$_3$ catalysts to gain insights into the evolution of Ni species under CO$_2$ hydrogenation conditions. Ni reduction is obvious as appreciated from the strong decrease of the Ni component at 855.1 eV and the appearance of a reduced Ni component at 851.9 eV (Figure 10a). Although a large part of Ni is reduced after CO$_2$ hydrogenation, some Ni cations remain in the used catalysts. The Ni reduction also follows from the decrease of the half-edge energies from $\sim$8344.0 to $\sim$8341.5 eV in these two samples as shown in Figure 7. The Ni k-edge EXAFS data (Figure 10b and Table 2) show that the Ni$-$O, Ni$-$O$-$Ni, and Ni$-$O$-$In contributions strongly decrease after CO$_2$ hydrogenation reactions. For the NiO(1)-In$_2$O$_3$ sample, a strong decrease in the Ni$-$O and Ni$-$In (oxidic) shells with final CNs of 1.7 and 2.3 goes
together with the appearance of a Ni-Ni shell with a CN of 7.4. These observations suggest that a substantial fraction of Ni cations in the as-prepared NiO(6)-In2O3 (x ≤ 6) samples were reduced into Ni single atoms (SAs) and/or Ni clusters under the reducing reaction conditions.

Finally, in situ EPR spectra confirmed the presence of reduced Ni species and Ov in In2O3 during CO2 hydrogenation at 250 °C (Figure 11). The weak EPR signal at g = 2.007 in NiO(1)-In2O3 and NiO(6)-In2O3 can be assigned to electrons trapped in anion vacancies of reducible oxides.70,71 The NiO(6)-In2O3 sample also showed a broad signal at g = 2.273. We attribute this to small ferromagnetic Ni clusters72 rather than paramagnetic Ni3+ since this signal disappeared at −153 °C (Figure S6), most probably due to reoxidation by trace

Table 2. Fit Parameters of the k3-Weighted EXAFS Spectra at the Ni K-Edge

| path                      | r(Å) [±] | CN [±] | δ2 (Å²) [±] | r²  |
|---------------------------|----------|--------|-------------|-----|
| as-prepared NiO(1)-In2O3  | Ni−O     | 2.04 [0.02] | 6.0 [1.2] | 0.007 [0.004] | 0.054 |
|                           | Ni−In (oxidic) | 3.34 [0.05] | 6.3 [2.2] | 0.016 [0.008] |  
| used NiO(1)-In2O3         | Ni−O     | 1.97 [0.06] | 1.7 [set] | 0.001 [0.003] | 0.017 |
|                           | Ni−Ni (metallic) | 2.37 [0.06] | 7.4 [4.0] | 0.032 [0.010] |  
|                           | Ni−In (oxidic) | 3.33 [0.05] | 2.3 [set] | 0.007 [0.005] |  
| as-prepared NiO(6)-In2O3  | Ni−O     | 2.09 [0.03] | 6.4 [1.9] | 0.007 [0.006] | 0.030 |
|                           | Ni−Ni (oxidic) | 3.01 [0.03] | 7.5 [5.2] | 0.008 [0.007] |  
|                           | Ni−In (oxidic) | 3.33 [0.28] | 5.3 [set] | 0.032 [0.037] |  

“No proper fit can be obtained.

Figure 9. (a) H2-TPR profiles of the as-prepared In2O3, NiO(1)-In2O3, and NiO(6)-In2O3 catalysts. (b) O 1s XP spectra of the used In2O3, NiO(1)-In2O3, and NiO(6)-In2O3 catalysts.

Figure 10. (a) Ni 2p½ XP spectra and (b) Ni K-edge k3-weighted R-space plots of the as-prepared and used NiO(x)-In2O3 (x = 1 and 6) catalysts.
oxygen or water during purging. Figure S6 also shows that both NiO(1)-In2O3 and NiO(6)-In2O3 samples after CO2 hydrogenation contain a signal at $g = 2.005$ due to the presence of Ov. Notably, the EPR spectra recorded at $-153^\circ C$ for the catalysts after CO2 hydrogenation are similar to those after subsequent H2 reduction at 300 °C.

3.5. Discussion. Based on the EPR, XPS, XAS, and H2-TPR results, we found that NiO(1)-In2O3 contains highly dispersed and possibly isolated Ni cations, which mostly substitute for In in the In2O3 lattice. The NiO(6)-In2O3 sample contains additional small Ni-oxide patches stabilized by the In2O3 support. Although XPS and XANES provide indications for the presence of Ni3+ in these two samples, this is only confirmed for NiO(1)-In2O3 by EPR, probably due to the strong spin exchange between Ni3+ centers at higher Ni loading.73 Moreover, the H2-TPR and O 1s XPS results indicate that introduction of Ni cations in the In2O3 lattice leads to a higher surface Ov density in comparison to In2O3. As oxygen vacancies in In2O3 are known to be involved in CO2 hydrogenation to CH3OH,29,30,32 the higher Ov density due to Ni addition can contribute to the improved CH3OH rate. Nevertheless, we also found that the increase in the CH3OH rate is much larger (In2O3:NiO(1)-In2O3:NiO(6)-In2O3 ≈ 1:2:4) than the increase in the estimated weight-based Ov density from H2-TPR (In2O3:NiO(1)-In2O3:NiO(6)-In2O3 ≈ 1:1.3:1.2). This observation suggests that the change in surface Ov density due to Ni addition is not the major reason for the observed Ni–In synergy. H2 activation is another important aspect of CO2 hydrogenation over In2O3-based catalysts. It has been demonstrated that heterolytic H2 dissociation on unpromoted In2O3 requires overcoming a high activation barrier of 0.95 eV (≈91 kJ/mol).32 Slow H2 dissociation is also in line with the strong dependence of the CH3OH formation rate on the H2 partial pressure32,43,74. Our characterization of the used NiO(x)-In2O3 catalysts (x ≤ 6) demonstrates that a part of oxidic Ni species in the as-prepared catalysts, present as Ni cations substituted in the In2O3 lattice and Ni-oxide patches on the In2O3 surface, will be in situ-reduced during the CO2 hydrogenation reaction.

We carried out DFT calculations to determine the influence of difference Ni species on the activation of H2. Four different model systems were considered, corresponding to (i) the stoichiometric In2O3(111) surface, (ii) a Ni single atom doped in the In2O3(111) surface, (iii) a Ni single atom located on the In2O3(111) surface, and (iv) a Ni8 cluster on the In2O3(111). The potential energy diagrams corresponding to H2 activation for these models are shown in Figure 12. For the stoichiometric In2O3 surface and the substituted Ni atom, H2 dissociation results in two OH groups, indicative of homolytic dissociation. The reaction over the stoichiometric surface is activated by 105 kJ/mol with an energy of $\Delta E_{\text{ads}} = 250$ kJ/mol. These values are in line with an earlier DFT study of H2 dissociation on the (111) surface of In2O3.43 Doping of a Ni single atom in this surface results in a small decrease of the

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**Figure 11.** In situ EPR spectra of (a) NiO(1)-In2O3 and (b) NiO(6)-In2O3 during CO2 hydrogenation reaction at 250 °C (1 bar and H2/CO2 = 3).

**Figure 12.** Potential energy diagrams for H2 activation on different (Ni)-In2O3 catalyst models with the forward barrier (kJ/mol) of H2 activation (left) and calculated (Ni)-In2O3 catalyst models (right). (O atoms in red, In atoms in brown, and Ni atoms in green.)
The activation barrier to H2 dissociation was 79 kJ/mol. The lower barrier goes together with a more exothermic reaction energy (ΔE_ads = -300 kJ/mol) for model ii. For model iii, H2 activation involves the single Ni atom adsorbed on top of the In2O3(111) surface. One of the H atoms remains at the Ni atom, while the other migrates to a neighboring O atom, resulting in, respectively, Ni−H and OH fragments. The barrier associated with H2 dissociation on this model is only 11 kJ/mol. Similar results have been reported by Frei et al. for a single-atom Ni−In2O3 model catalyst.50 H2 activation over the supported Ni8 cluster of model iv proceeds in two steps. After adsorption of molecular H2 with ΔE_ads = -90 kJ/mol, H−H bond scission results in two H atoms adsorbed in a bridged configuration. With respect to the gas phase, the process of H2 activation is barrierless. This elementary reaction step is exothermic by 5 kJ/mol. Dissociative H2 adsorption on extended Ni surfaces has been well investigated. Yang et al. reported barrierless activation of H2 on Ni(111) with an overall exothermicity of 92 kJ/mol.75 Similar results were reported for different Ni surface terminations as well.76 Thus, the results for the In2O3-supported Ni8 cluster are in good agreement with those obtained for metallic Ni surfaces.

To rationalize the influence of different Ni species on H2 dissociation, we studied the electron density differences as a function of the reaction coordinate of H2 dissociation for the different surface models. While the final state (FS) of H2 dissociation on In2O3(111) is indicative of homolytic H2 dissociation, the electron density difference analysis of the transition state (TS) shows electron depletion around one H atom and electron accumulation around the other one (Figure 13a). This is also reflected in the Bader charges, amounting to +0.45e for Hα and −0.23e for Hβ respectively. Thus, H2 dissociation involves heterolytic cleavage of the H−H bond, where the positively charged H atom already starts interacting with a surface O atom of the In2O3 surface. The relatively high activation energy can then be explained by considering that the negative charge around the other H atom is not well compensated by the oxygen-terminated surface, giving rise to a strong Coulombic repulsion. The two H atoms in the FS have positive charges of +0.61e and +0.63e, respectively, as expected for surface OH groups. For the Ni single atom doped inside the In2O3 surface (model ii), the same analysis of the TS (Figure 13b) indicates electron accumulation around both H atoms. Bader charge analysis shows that one of the H atoms is nearly neutral (Hα with −0.01e), while the other one (Hβ) has a positive charge of +0.22e. Although the charge on Hα is lower, the radical character of this fragment still results in Coulombic repulsion with the surface, explaining the relatively high activation energies. The final product of the H2 dissociation reaction is again that of homolytic dissociation. For the Ni atom adsorbed on the In2O3 surface (Figure 13c), H2 dissociates heterolytically with the two H fragments having opposite charges in the TS (Hα with +0.31e and Hβ with −0.24e). The positively charged Hα interacts with one surface O atom of In2O3, while the negatively charged Hβ interacts with the Ni atom. The charge of the Ni atom before interaction with H2 is +0.66e, which slightly decreases to +0.59e in the TS and +0.56e in the FS. The favorable electrostatic interactions for both H atoms with the surface in the TS can explain the much lower activation barrier for H2 dissociation on model iii. The FS of H2 dissociation is the product of heterolytic dissociation, with Hα acquiring a positive charge (+0.64e), indicative of the formation of an OH group. The Hβ atom has a slightly negative charge (−0.02e), indicative of the formation of a surface hydride adsorbed on the slightly positively charged Ni atom (+0.56e). For model iv (Figure 13d), areas of electron accumulation are observed around the Hα and Hβ atoms in both the TS and FS. This is also reflected by the negative charges on both H atoms in the TS (−0.1e for Hα and Hβ) and the FS (−0.19e for Hα and −0.22e for Hβ). Accordingly, we can conclude that the dissociation mechanism of H2 is homolytic. Compared with model iii, the Ni8 cluster stabilizes both H atoms through formation of Ni−H bonds, thus further decreasing the overall H2 dissociation barrier.

These DFT calculations point at the significantly positive influence of reduced Ni species on H2 activation due to the stabilization of hydride species. While H2 dissociation on a single Ni atom adsorbed on the In2O3 surface would follow a heterolytic dissociation mechanism resulting in Ni−H and OH species, a Ni8 cluster would result in classical metal-catalyzed homolytic H2 dissociation. The barriers for these cases are
much lower than those where the surface is terminated by O anions that cannot stabilize the negatively charged H atom during heterolytic dissociation. While our characterization data suggest that part of the Ni atoms may still be doped in the In₂O₃ surface during CO₂ hydrogenation, their role in H₂ activation appears to be limited. Therefore, we conclude that the observed Ni–In synergy can be mainly linked to in situ-reduced Ni species in the form of single atoms or very small clusters. These reduced Ni species can significantly facilitate the dissociative adsorption of H₂, which otherwise requires a high activation barrier on the unpromoted In₂O₃ surface. A similar mechanism of metal promotion was reported for other metal-promoted In₂O₃ catalysts. As shown in Table S4, the In₂O₃ catalyst in this study is compared to other Ni-promoted In₂O₃ catalysts. For example, a detailed study from Perez-Ramirez’s group emphasized the role of finely dispersed Pd clusters in the H₂ activation and the role of H atoms in the following hydrogenation steps of adsorbed CO₂. We also briefly discuss here our results in comparison to those recently reported by Frei et al., who prepared Ni/In₂O₃ catalysts by dry impregnation. In line with our work, Ni promotes CH₃OH formation at low Ni loading, whereas higher Ni loading leads to CO and CH₄ formation. In the work of Frei et al., evidence was found for the formation of an NiIn₃ phase by synchrotron XRD measurements. Our characterization data, however, do not provide strong evidence for the formation of such an alloy.

We next compare the FSP-prepared NiO-In₂O₃ catalysts in this study to other metal-promoted In₂O₃ catalysts. Using the FSP method, well-defined In₂O₃-based catalysts with tunable chemical composition can be prepared. The obtained catalysts have similar surface areas. These aspects render FSP an efficient method to study the influence of promoters on In₂O₃-based catalysts. We also found that metal promoters are better dispersed in In₂O₃ by FSP preparation in comparison with conventional preparation methods. This leads, among others, to Ni substitution in the In₂O₃ lattice, which is less likely to take place during impregnation. The high Ni dispersion in the oxide precursor also leads to a stronger Ni–In synergy in CO₂ hydrogenation to methanol. Specifically, the activity of the optimum NiO-In₂O₃ catalyst in this study is about 4 times higher than that of the In₂O₃ reference catalyst, while the synergetic effect is less pronounced in other studies of Ni-promoted In₂O₃ catalysts. As shown in Table S4, the NiO(6)−In₂O₃ catalyst in this study is compared to other Ni-promoted In₂O₃ catalysts with respect to their performance in CO₂ hydrogenation. To make such a comparison, we also performed additional catalytic tests at higher temperatures (275 and 300 °C) using the NiO(6)−In₂O₃ catalyst. In comparison to the work by Jia et al., our NiO−In₂O₃ catalyst shows a slightly higher methanol rate at 250 °C (0.26 vs 0.21 mmol gₐₗₜ⁻¹ h⁻¹), while the rates at higher temperatures of 275 and 300 °C are a bit lower. In addition, the methanol rate of our NiO−In₂O₃ catalyst at 275 °C (0.36 mmol gₐₗₜ⁻¹ h⁻¹) is similar to the rates reported in the literature for other Ni-promoted In₂O₃ catalysts (0.36 mmol gₐₗₜ⁻¹ h⁻¹ at 270 °C and 0.34 mmol gₐₗₜ⁻¹ h⁻¹ at 280 °C). The methanol selectivity of our NiO−In₂O₃ catalyst is somewhat lower than the reported values, which can be explained by the lower reaction pressure used in our catalytic tests (30 vs 50 bar in the cited literature).

4. CONCLUSIONS

Aiming at improving the performance of In₂O₃ in the hydrogenation of CO₂ to CH₃OH, a bimetallic Ni–In system was identified as a potential replacement for Pd−In₂O₃, outperforming Co−In₂O₃ and Cu−In₂O₃. FSP-prepared NiO−In₂O₃ catalysts are made up from small (~7 nm) particles with a high surface area. Strong Ni−In synergy is noted for CH₃OH synthesis from CO₂ with an optimal NiO loading of 6 wt %, whereas higher NiO loading (≥ 50 wt %) is mainly present as bulk NiO particles. H₂−TPR points to a higher surface O₃ density for the NiO(x)−In₂O₃ (x = 1 and 6) catalysts in comparison to the unpromoted In₂O₃, indicating that Ni substitution can destabilize the In₂O₃ lattice to some extent. XPS, XAS, and EPR data demonstrate that the use of NiO(x)−In₂O₃ (x = 1 and 6) catalysts in CO₂ hydrogenation leads to the reduction of Ni cations and the formation of Ni SAs and/or Ni clusters. In addition to a higher surface O₃ density relevant to CO₂ adsorption, DFT calculations suggest that the observed Ni−In synergy in CH₃OH synthesis from CO₂ is mainly originated from the formation of reduced Ni species on the In₂O₃ surface, which enhances the rate of H₂ dissociation and following hydrogenation of CO₂ adsorbed on O₃.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c03170.

Additional characterization (XRD and H₂-TPR) and catalytic results of the M−In₂O₃ catalysts (Figures S1 and S2 and Table S1); N₂ physisorption and TEM results of the used NiO−In₂O₃ catalysts (Figure S3 and Table S2); zoom-in of the ex situ EPR spectrum of NiO(1)−In₂O₃ (Figure S4); EXAFS data at the In K-edge with corresponding fit parameters (Figure S5 and Table S3); EPR spectra recorded after CO₂ hydrogenation and subsequent H₂ reduction (Figure S6); and comparison of CO₂ hydrogenation performance over different indium-based catalysts (Table S4) (PDF)

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