Mechanism and microkinetics of methanol synthesis *via* CO_2 hydrogenation on indium oxide

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ABSTRACT

Indium oxide has emerged as a highly effective catalyst for methanol synthesis by direct CO_2 hydrogenation. Aiming at gathering a deeper fundamental understanding, mechanistic and (micro)kinetic aspects of this catalytic system were investigated. Steady-state evaluation at 5 MPa and variable temperature indicated a lower apparent activation energy for CO_2 hydrogenation than for the reverse watergas shift reaction (103 *versus* 117 kJ mol^{-1}), which is in line with the high methanol selectivity observed. Upon changing the partial pressure of reactants and products, apparent reaction orders of -0.1, 0.5, -0.2, and -0.9 were determined for CO_2, H_2, methanol, and water, respectively, which highlight a strong inhibition by the latter. Co-feeding of H_2O led to catalyst deactivation by sintering for partial pressures exceeding 0.125 MPa, while addition of the byproduct CO to the gas stream could be favorable at a total pressure below 4 MPa but was detrimental at higher pressures. Density Functional Theory simulations conducted on $In_2O_3(1\,1\,1)$, which was experimentally and theoretically shown to be the most exposed surface termination, indicated that oxygen vacancies surrounded by three indium atoms enable the activation of CO_2 and split hydrogen heterolytically, stabilizing the polarized species formed. The most energetically favored path to methanol comprises three consecutive additions of hydrides and protons and features CH_2OOH and $CH_2(OH)_2$ as intermediates. Microkinetic modeling based on the DFT results provided values for temperature and concentration-dependent parameters, which are in good agreement with the empirically obtained data. These results are expected to drive further optimization of In_2O_3-based materials and serve as a solid basis for reactor and process design, thus fostering advances towards a potential large-scale methanol synthesis from CO_2.

1. Introduction

Aiming at mitigating global warming, the utilization of CO_2 captured either from the atmosphere or from localized emission points as a feedstock for the production of fuels and chemicals has taken centrer stage in catalysis research in the last decade [1,2]. Among the routes investigated for the conversion of this rather inert molecule, hydrogenation to methanol has attracted particular attention owing to the extreme relevance of this alcohol for the chemical industry and the energy sector [3]. At present, the industrial synthesis of methanol is carried out from syngas, which is predominantly derived from steam reforming of fossil fuels, in the presence of small amounts (3 vol%) of CO_2 over Cu-ZnO-Al_2O_3

catalysts [4]. When CO_2 is the only carbon-containing source ($CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O$), these catalysts exhibit limited activity, selectivity, and stability. Particularly, the production of methanol is suppressed by the competitive reverse water-gas shift (RWGS) reaction ($CO_2 + H_2 \rightleftarrows CO + H_2O$) [5]. Therefore, alternative catalytic systems are sought after to enable the development of a CO_2-to-methanol technology [6]. Among the materials investigated, a few Cu-based solids exhibited high methanol selectivity but their long-term stability was not demonstrated [7,8]. In contrast, indium oxide, In_2O_3, emerged as a catalyst combining multiple desirable features [9]. In addition to being highly selective to methanol, it can be easily supported on zirconia, leading to higher methanol formation rates and outstanding durability, and prepared in an equivalently performing technical form [10]. Its potential for a prospective industrial implementation has motivated further practically-oriented studies. Indeed, it has been reported that In_2O_3 can be used in bifunctional catalytic systems

[11,12] to produce olefins from CO_2 and that its activity in methanol synthesis can be enhanced through the addition of a noble metal such as Pd, which is claimed to facilitate hydrogen splitting [13,14]. Furthermore, it sparked the idea of combining another reducible oxide, ZnO, with zirconia, attaining a remarkable catalyst [15]. In contrast, fundamental aspects of CO_2 hydrogenation over In_2O_3, such as the reaction mechanism and kinetics, remain insufficiently understood, thus hindering the optimization of this catalytic process. Under the conditions commonly applied (573 K, 5 MPa, molar $H_2:CO_2 = 4$), the thermodynamic equilibrium highly favors the endothermic RWGS reaction over the exothermic hydrogenation to methanol [16]. Hence, the reaction must be carried out under kinetic control to attain a high selectivity to methanol. Nevertheless, basic kinetic information such as the temperature dependence of the transformation and the effect of the partial pressure of reactants and products has not been reported. Characterization through thermal and spectroscopic techniques and CO co-feeding experiments over bulk and ZrO_2-supported In_2O_3 strongly suggested surface oxygen vacancies as the sites where CO_2 and H_2 are activated [10]. This is in line with Density Functional Theory (DFT) studies by Ge et al. [17,18] and Yu et al. [19], which predicted a superior performance for an oxygen defective $In_2O_3(1\,1\,0)$ surface compared to the stoichiometric termination and supported the high methanol selectivity on the basis of greater barriers for the RWGS reaction over the same vacancy-containing surface. Still, the orientation of the surface employed in these studies is not that being associated with the lowest energy (i.e., the most exposed). Indeed, the (1 1 1) facet is the thermodynamically most stable termination of In_2O_3 [20]. In addition, since the electronic structure of this material is rather subtle, the structures of the adsorbates need to be evaluated with some further restrictions to ensure that forbidden energy levels are not artificially populated.

Herein, we investigate the kinetic fingerprints of the CO_2 hydrogenation over bulk In_2O_3 by means of a detailed study covering a wide range of temperature (473–673 K), pressure (1–5 MPa), and reactant (CO_2, H_2) and product (CO, methanol, H_2O) concentrations. These data are correlated with extensive DFT simulations describing the energetics of the reaction over the $In_2O_3(1\,1\,1)$ surface and a microkinetic model. Based on the information obtained at the experimental and theoretical levels, key conclusions are put forward on the operation of this oxide in CO_2 hydrogenation, which set the ground for its more efficient utilization in this relevant reaction.

2. Experimental

2.1. Catalyst preparation

$In(OH)_3$ was obtained by precipitation adding 150 cm^3 of a solution of aqueous NH_4OH (50 cm^3, 25 wt%, Sigma-Aldrich) in ethanol (150 cm^3) to a solution of $In(NO_3)_3 \cdot xH_2O$ (30.1 g, Sigma-Aldrich, 99.99%) in deionized water (120 cm^3) and ethanol (350 cm^3, Merck, 99.8%,) to reach a pH value of 9.2. The resulting slurry was aged for 20 min at 353 K and then separated by high-pressure filtration and washed twice with deionized water (1000 cm^3 each time) followed by drying in a vacuum oven (2 kPa, 323 K, 12 h). The so-obtained hydroxide was calcined for 3 h at 573 K (2 K min^{-1}) in static air to yield nanocrystalline In_2O_3.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) was performed using a PANalytical X'Pert PRO-MPD diffractometer with Ni-filtered Cu Kα radiation ($\lambda = 0.1541$ nm), acquiring data in the 5–70°

2θ range with a step size of 0.05° and a counting time of 12 s per step. The average particle size of In_2O_3 was estimated applying the Scherrer equation. Nitrogen sorption at 77 K was carried out using a Quantacrome Quadrasorb analyzer. Prior to the measurement, the sample was degassed at 573 K under vacuum for 3 h. He pycnometry was conducted at ambient temperature using a Micromeritics AccuPyc II 1340 instrument after pretreatement of the sample in vacuum at 323 K for 12 h. The skeletal density was determined by averaging 200 measurement cycles after equilibration of the system during 30 cycles. High resolution transmission electron microscopy (HRTEM) was performed using a FEI Talos (200 kV) instrument. Samples were prepared by directly depositing the powders on a lacey carbon film supported onto a copper grid. Temperature-programmed desorption of carbon dioxide, water, and methanol (CO_2-, H_2O-, MeOH-TPD) and reduction with hydrogen (H_2-TPR) were conducted using a Micromeritics Auto-Chem II 2920 analyzer. The specific conditions applied during each measurement are detailed in Table S1 in the Supplementary Material. UV–vis spectroscopy was carried out using an Ocean Optics Maya2000-Pro spectrometer equipped with a deuterium light source. Spectra were collected in the 200–600 nm range, with an integration time of 100 ms and averaging 50 scans. Raman spectroscopy was performed using a WITec CRM200 confocal Raman spectroscopy system comprising a source with an excitation wavelength of 532 nm, a 100× objective lens with a numerical aperture of 0.9, and a grating spectrometer (2400 lines mm^{-1}). Spectra were obtained by averaging 200 scans with an individual acquisition time of 1.5 s.

2.3. Kinetic evaluation

Kinetic investigations were performed in a high-pressure continuous-flow fixed-bed reactor with an inner diameter of 2.2 mm housed in an electrically-heated aluminum brass furnace. The experimental setup is described in detail in Fig. S1. The reactor was loaded with 25 or 50 mg of catalyst with a particle size of 100–125 μm, which was held in place by a bed of quartz wool and heated from ambient temperature to 573 K (5 K min^{-1}) at 0.5 MPa under a He (PanGas, ≥99.999%) flow of 20 cm^3_{STP} min^{-1}. After 3 h at 573 K, the pressure was raised to 3.5–5.5 MPa in the same stream, which typically took 20 min. Then, the gas flow was switched to the reaction mixture (20 or 40 cm^3_{STP} min^{-1}) featuring distinct concentrations of CO_2 (40 mol% CO_2 in H_2, Messer, ≥99.997% and ≥99.999%, respectively), H_2 (PanGas, ≥99.999%), methanol (Sigma-Aldrich, 99.9%, anhydrous), H_2O (ABCR-Chemicals, HPLC grade), and CO (Messer, ≥99.999%), corresponding to a gas-hourly space-velocity (GSHV) of 38,000 h^{-1}. The temperature was either kept at 573 K or varied in the range of 473–673 K. The specific experimental conditions applied in the tests are collected in Table 1. The effluent stream was analyzed by gas chromatography after 1 h on stream and then every 20 min. The catalytic data reported for each reaction condition correspond to the average of at least 7 measurements. The absence of intra- and extraparticle diffusion limitations was corroborated by the fulfillment of the Weisz-Prater and Carberry criteria and secured by a test in which a catalyst sample featuring a sieve fraction of <50 μm instead of the typical 100–125 μm was applied that led to identical performance.

2.4. Computational methods

DFT calculations were conducted using the Vienna *Ab initio* Simulation Package (VASP) [21,22], employing the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [23]. The core electrons were described by projector augmented-wave pseudopotentials (PAW) [24] with a plane-wave cutoff energy of