Applied Catalysis B: Environmental 225 (2018) 128–138

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Highly efficient Cu-decorated iron oxide nanocatalyst for low pressure CO_2 conversion

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ARTICLE INFO

Keywords:
Iron oxide
Copper
Nanoparticles
Hydrogen
Carbon dioxide
Heterogeneous catalysis
CO_2 conversion
Carbon monoxide
Methane
Methanol
Benzene

ABSTRACT

We report a nanoparticulate iron oxide based catalyst for CO_2 conversion with high efficiency at low pressures and on the effect of the presence of copper on the catalyst's restructuring and its catalytic performance. *In situ* X-ray scattering reveals the restructuring of the catalyst at the nanometer scale. *In situ* X-ray absorption near edge structure (XANES) shows the evolution of the composition and oxidation state of the iron and copper components under reaction conditions along with the promotional effect of copper on the chemical transformation of the iron component. X-ray diffraction (XRD), XANES and Raman spectroscopy proved that the starting nanocatalyst is composed of iron oxides differing in chemical nature (α-Fe_2O_3, Fe_3O_4, FeO(OH)) and dimensionality, while the catalyst after CO_2 conversion was identified as a mixture of α-Fe, Fe_3C, and traces of Fe_5C_2. The significant increase of the rate CO_2 is turned over in the presence of copper nanoparticles indicates that Cu nanoparticles activate hydrogen, which after spilling over to the neighbouring iron sites, facilitate a more efficient conversion of carbon dioxide.

1. Introduction

Growing energy demands and environmental concerns have resulted in significant research interest for the conversion of CO_2. CO_2 hydrogenation using H_2 from sustainable sources is considered a promising method to help reduce CO_2 emissions by catalytically converting CO_2 into beneficial chemicals like alcohols (e.g. methanol), hydrocarbons (e.g. methane, benzene, etc.) or CO, with the subsequent opportunity for further processing. Although many endeavours have been invested to develop efficient processes for CO_2 conversion, significant improvements can be made by designing innovative catalysts. Moreover, gaining additional insights into CO_2 hydrogenation can aid in developing highly efficient catalyst and integrated process technology to meet the goals of mitigating greenhouse gas production and sustainable development of carbon market demands [1–6]. In essence, methanol is produced in industry from syngas using mostly CuO/ZnO/Al_2O_3 catalyst [7]. However, many studies suggest that methanol can be directly formed from carbon dioxide [8–14]. Methanation of CO_2 or its transformation to CO especially on cheap catalysts, moreover on catalysts working under environmentally benign conditions, are other important routes of CO_2 conversion [6,15].

CO_2 conversion can progress *via* various routes, such as CO_2 hydrogenation to methane and other hydrocarbons, or to methanol. At higher reaction temperatures CO_2 conversion to carbon monoxide may become dominant as a result of the reverse water gas shift reaction (RWGS) [8,16–18]. The catalytic conversion of CO_2 was studied for example on iron-based catalysts as potential cost attractive candidates for CO_2 conversion into hydrocarbons or carbon monoxide [6,15,19,20]. It was also shown that iron-based catalysts with and without potassium promoter possess tunable selectivity and activity in

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https://doi.org/10.1016/j.apcatb.2017.11.047
Received 18 August 2017; Received in revised form 22 October 2017; Accepted 17 November 2017

CO_2 hydrogenation towards hydrocarbons at high pressures and CO formation at atmospheric pressure [21], and carbon nanotube-supported iron nanoparticles were found highly active in converting CO_2 to C_{1-5} products and CO [22]. In an attempt to control selectivity, iron-based catalysts enriched with gold particles or supported on oxides such as alumina, titania, zirconia, and zeolites were prepared and investigated as well [23–26].

There are many reports in the literature on various heterogeneous catalytic systems for the effective synthesis of methanol from CO_2. Copper-based catalysts prevail in these studies due to their high selectivity and less undesired by-products [6,20,27]. A vast number of support materials such as ZnO, ZrO_2, Al_2O_3, TiO_2, Fe_2O_3, $ZnFe_2O_4$, and SiO_2 have been tested for this purpose. In addition, multi-metallic materials with Cu as the main component were also studied [1,6,9,28–30]. Co-precipitation of metal salts with subsequent calcination has been the most widely used procedure to prepare the copper-based catalysts [31–36].

The present study focuses on the characterization and performance of a cost-efficient catalyst for the conversion of CO_2, based on iron oxide and copper, while considering the following. Iron oxide is commonly used for CO_2 or CO methanation/Fischer-Tropsch synthesis and can convert CO_2 into CO as well. Cu on the other hand is a highly efficient catalyst for CO_2 conversion to both CH_4 and CH_3OH [6,20,37,38]. Utilization of sonochemical method in synthesis of the nanocatalytic system can significantly improve its dispersity and therefore also catalytic activity [39,40].

The catalyst for this study was prepared as a nanostructured iron oxide decorated with copper nanoparticles. The synthesis of the catalysts was carried out using a novel sonication reduction method. The evolution of the as-prepared catalysts was monitored under reaction conditions using a combination of *in situ* X-ray scattering and X-ray absorption techniques, the catalytic performance using temperature-programmed reaction. Additional characterization of the catalyst before and after reaction was performed by Raman spectroscopy, XRD, scanning transmission electron microscopy (STEM), and high resolution transmission electron microscopy (HRTEM) including scanning transmission electron microscopy (STEM) and energy dispersive spectrometry (EDS).

2. Experimental

2.1. Synthesis of FeNC and Cu-FeNC nanocomposite catalysts

Synthesis of the iron oxide catalyst supporting material was performed using the following two-step procedure. Briefly, the synthesis protocol starts with direct precipitation of iron(II) oxalate precursor from an equimolar mixture of oxalic acid (≥99%, Aldrich) and Fe(II) chloride (98%, Aldrich) in N,N-dimethylacetamide (anhydrous, 99.8%, Sigma-Aldrich) at room temperature followed by the solid-state isothermal treatment at 175 ° C for 12 h in air [41,42]. Copper was added using a sonication technique as follows. Typically, 200 mg of already-prepared iron oxide nanoparticles were dispersed in 188 mL of distilled water. Next, 2 mL of 15.7 mmol/L aqueous copper sulfate pentahydrate solution (≥99%, Sigma), recalculated to final concentration of 1 wt% of Cu, was added to the mixture and the pH of the dispersion was adjusted to 10 using 1 M sodium hydroxide (≥97%, Fluka). Hydrazine hydrate (reagent grade, Sigma-Aldrich) was utilized as a moderately strong reducing agent. Sonication of the dispersion was performed using a Qsonica (Q700 with Ti horn part 4418) for 10 min under intensity equal to 25.37 kJ. After several seconds of sonication that brought full dispersion of the iron oxide in the entire volume, 10 mL of 4.95 mmol/L solution of hydrazine hydrate was added into the reaction system. After 10-min sonication, the nanocomposite of iron oxide with 1 wt% of Cu (denoted as Cu-FeNC) was separated by centrifugation and washed two times with distilled water. The washed and separated nanocomposite was dried in a flowbox with nitrogen as an inert purging gas. A reference sample (denoted as FeNC or FeNC blank), was prepared using the same procedure excluding the addition of copper sulfate solution which was replaced by distilled water. The sonochemical method of nanocatalyst preparation has a significant benefit over conventional co-precipitation method as it offers the possibility to prepare copper nanoparticles exclusively on the surface of the support [39,40].

For the characterization and reactivity experiments, the Cu-FeNC and the corresponding FeNC blank were drop-casted on oxidized silicon wafers (SiO_2/Si(100)).

2.2. In-situ grazing incidence small-angle X-ray scattering (GISAXS) and X-ray absorption near edge spectroscopy (GIXANES)

A special system designed for simultaneous *in-situ* GISAXS and GIXANES was utilized to characterize the FeNC blank and Cu-FeNC samples under reaction conditions [43–45].

The *in-situ* experiments were performed by placing the samples on a ceramic heater in a custom built reaction cell [46]. The temperature of the sample was measured with a K-type thermocouple inserted into the middle of the heater. The thermocouple was attached to a temperature controller (Lakeshore model 340) which controlled the output of a KEPCO power supply (model ATE 55 − 5DM). The experiment was performed by applying two consecutive identical temperature ramps between 25 °C and 375 °C as shown in Fig. S1. The total measurement took 24 h. Prior to the start of the temperature ramp, the reaction cell and gas lines were evacuated to about 0.02 atm and flushed with pure He three times before the introduction of the reaction gas mixture. A gas-mixing unit consisting of calibrated mass flow controllers (Brooks model SLA5850) was used to control the gas composition and its flow rate into the reaction cell: 1% carbon dioxide and 3% hydrogen in He at a flow rate of 20 sccm and 1.25 atm pressure (*i.e.* 0.0125 atm and 0.0375 atm partial pressure of CO_2 and H_2). Within the individual ramps, the temperature was increased in 50 °C increments at a heating rate of 10 °C per minute between the temperature steps and dwelling 30 min at each temperature. At each temperature, GISAXS and GIXANES data were collected.

The *in-situ* reaction cell was fitted with Kapton windows to facilitate X-ray transmission. The cell was fixed on a computer controlled goniometer to adjust angle and position of the sample for grazing incidence geometry. The X-ray beam was scattered off the sample surface near the critical angle ($\alpha_c = 0.18$ at Cu K-edge and $\alpha_c = 0.2$ at Fe K-edge) of the Si substrate. The GISAXS experiments were performed with X-rays of 8.993 keV and 7.112 keV for Cu-FeNC and FeNC respectively. A 1024 × 1024 pixel two-dimensional CCD detector (Platinum) was used for recording the two dimensional GISAXS images from the samples. The collected data were analyzed by Moore autocorrelation [47]. GIXANES spectra on Cu K-edge and Fe K-edge were collected using a 4-element germanium fluorescence detector (Vortex) arranged perpendicularly to the X-ray beam and parallel to the sample surface. The GIXANES data were analyzed using the ATHENA and MATLAB software packages [46,48,49].

2.3. Temperature-programmed reactivity

The catalytic activity of the samples was measured separately in the laboratory using an identical set-up as used at the synchrotron and under identical reaction conditions (25 °C to 375 °C, with 20 sccm flow of 1% CO_2 and 3% H_2 gas mixture carried in helium at pressure of 1.25 atm, the cell volume was $\sim$ 20 cm^3 resulting in a gas hourly space velocity (GHSV) of 60 h^{-1}) and using the same temperature ramp as at the synchrotron. The reaction products were monitored on a quadrupole mass spectrometer (Pfeiffer Prisma QMS 220) sampling with an electronic gas regulating valve (EVR 116, Pfeiffer) on the inlet of the mass spectrometer set to 5×10^{-6} mbar pressure in the mass spectrometer. Before the start of the temperature ramp, the reaction gas mixture was flown continuously for about 10 h to minimize and