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The anti-sintering catalysts: Fe–Co–Zr polymetallic fibers for CO_2 hydrogenation to $C_2=$–$C_4=$–rich hydrocarbons

Wenhui Li[a], Anfeng Zhang[a], Xiao Jiang[b], Michael J. Janik[b], Jieshan Qiu[a], Zhongmin Liu[c], Xinwen Guo[a,*], Chunshan Song[a,b,**]

[a] *State Key Laboratory of Fine Chemicals, PSU-DUT Joint Center for Energy Research, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, PR China*

[b] *Clean Fuels & Catalysis Program, PSU-DUT Joint Center for Energy Research, EMS Energy Institute, Departments of Energy and Mineral Engineering and of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, USA*

[c] *National Engineering Laboratory for Methanol to Olefins, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China*

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ABSTRACT

Polymetallic fibers of 13Fe2Co/ZrO_2 and 13Fe2Co100Zr were prepared by impregnation and an in situ electrospinning technique. The iron, cobalt and zirconium components in the 13Fe2Co100Zr catalyst are more dispersed than the impregnation one, as indicated by SEM/EDS, TEM, XRD, H_2-TPR and N_2 adsorption techniques. CO_2 conversion increased by a factor of 2 and the selectivity to $C_2{}^{+}$ hydrocarbons increased 15 times on the 13Fe2Co100Zr polymetallic fibers compared with the 13Fe2Co/ZrO_2 supported catalyst. The 0.18 s^{-1} TOF (turnover frequency) of the polymetallic fibers exceeded that of the supported catalyst (0.12 s^{-1}). Potassium addition to the 13Fe2Co100Zr catalyst further improved the selectivity to $C_2{}^{=}$–$C_4{}^{=}$, which increased to 27.5% on a 10K13Fe2Co100Zr catalyst. The polymetallic fibers showed stable activity over the reaction period. The activity of the 13Fe2Co/ZrO_2 catalyst, however, decreased rapidly due to metal sintering as observed with TEM and XRD. The in situ electrospinning technique can effectively prevent metal sintering and provide high CO_2 conversion efficiency.

1. Introduction

CO_2 hydrogenation [1,2] is a promising approach to produce hydrocarbon compounds and reduce CO_2 emissions. CO_2 hydrogenation has been studied mainly on traditional metal-supported catalysts, e.g., Fe, Co, Ni and Ru catalysts, that are also used for Fischer–Tropsch synthesis (FTS) [3]. When pure Co, Ni or Ru catalyze CO_2 hydrogenation, a large amount of CH_4 is produced. Co addition to an Fe-based supported catalyst, however, promotes $C_2{}^{+}$ hydrocarbon formation significantly and increases the CO_2 conversion when a low Co/(Co + Fe) ratio is used [4].

Common catalyst supports are oxides, such as Al_2O_3 [5], SiO_2 [6], TiO_2 [7], ZrO_2 [8] and CeO_2 [9]. Among them, Oukaci et al. [10] concluded that Zr played an critical role in moderating Co-support interactions and improving the catalyst stability. Chen et al. [7] tested PtCo bimetallic catalysts supported on TiO_2 and ZrO_2 for CO_2 hydrogenation and found that the PtCo/TiO_2 catalyst converts CO_2 and H_2 into CO, whereas PtCo/ZrO_2 catalyzes the selective formation of CH_4. ZrO_2 provides interesting chemical properties as a support, as it contains both weak acidic sites and basic sites and has multiple stable phases [11]. Furthermore, a higher concentration of active oxygen defects on reduced m-ZrO_2 improves the adsorption and activation of oxygenated species including CO_2 [12,13]. Although Fe-Co metals supported on oxide supports showed good performance for CO_2 conversion, limitations and challenges remain. The poor dispersion of the active metal obtained through traditional impregnation limits activity and stability. Active metal sintering on the support leads to rapid deactivation [14].

A coprecipitation method homogeneously mixes the metal and support precursors and has strengthened the metal-support interaction resulting in a somewhat improved metal dispersion [15]. During the synthesis process, however, uncontrolled sintering of single-metal particles may occur. Electrospinning is a simple and versatile method to transform polymer solutions into nanofibers [16–19]; the long fibers

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* Corresponding author.

** Corresponding author at: State Key Laboratory of Fine Chemicals, PSU-DUT Joint Center for Energy Research, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, PR China.

E-mail addresses: guoxw@dlut.edu.cn (X. Guo), csong@psu.edu (C. Song).

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can possess larger specific surface areas and higher porosity for reactant adsorption compared with spherical particles. Nanofibers have been widely employed in biomedical research [20], reinforced composites materials [21], electrode materials [18] and catalysis [22]. Compared with traditional supported oxide catalysts, the fiber catalysts can be easily prepared with various polymetallic ratios, and allow for shorter preparation times by avoiding slow crystallization processed and subsequent tabletting processes. More importantly, good dispersion of the different metals in electrospun fibers strengthens the intermetallic synergistic interaction and prevents sintering of single metal particles. Although various nanofibers prepared by electrospinning techniques have been applied for catalysis, the preparation and application of ZrO_2 or Fe-Co-Zr polymetallic fibers as catalysts for CO_2 hydrogenation is a novel approach reported in this study.

Herein, Fe-Co-Zr polymetallic fibers with different Fe/Co molar ratios were prepared through in situ electrospinning, and subsequently tested for CO_2 hydrogenation. A supported FeCo/ZrO_2 catalyst was prepared by impregnation onto ZrO_2 fibers to serve as a reference material. The Fe-Co-Zr polymetallic fibers catalysts exhibited superior catalytic performance and stability than the supported FeCo/ZrO_2 catalyst.

2. Experimental section

2.1. Fe-Co-Zr polymetallic oxide fiber preparation

Fe-Co-Zr polymetallic fibers were fabricated by an in situ electrospinning method according to a previously reported procedure [20]. Briefly, a solution containing 12 g iron acetylacetone, cobalt acetylacetonate and zirconium acetylacetonate with mass ratios Fe:Co:Zr = 10:5:100, 13:2:100 or 14:1:100; 1.2 g PVP (polyvinyl pyrrolidone); 15.8 g ethanol and 8.4 g acetic acid were mixed by stirring at 60 °C for 30 min. Subsequently, the “sol” was passed through a syringe at a flow rate of 1.0 ml/h with a 22 gauge-blunt needle as the electrospinning tip. The voltage applied for the electrospinning was 22 kV and the distance between needle and collector was 15 cm. The generated fibers were collected onto the aluminum foil and calcined in air at 500 °C for 4 h.

10K13Fe2Co100Zr and 20K13Fe2Co100Zr catalysts were prepared by impregnating the calcined Fe-Co-Zr fibers with an aqueous solution of potassium nitrate to obtain 10 wt% and 20 wt% K loading. The catalysts were obtained after drying at 100 °C for 12 h, followed by calcination in air at 500 °C for 4 h. The catalysts prepared in this work are denoted as (x)K(y)Fe(z)Co(w)Zr, where x, y, z and w represent the mass fraction of the corresponding metals, respectively. The metal contents detected by ICP are listed on Table S1.

2.2. FeCo/ZrO_2 catalyst preparation

ZrO_2 nanofiber was first synthesized by electrospinning following the procedure used for Fe-Co-Zr polymetallic fibers. The 13Fe2Co/ZrO_2 supported catalyst, was prepared by the impregnation method using solutions of iron acetylacetone, cobalt acetylacetonate and the ZrO_2 nanofibers. The fresh catalyst was obtained after drying at 100 °C for 12 h, followed by calcination using a similar procedure as described above.

2.3. Catalytic testing

The catalytic hydrogenation of carbon dioxide was carried out in a pressurized fixed-bed flow reactor (inner diameter 8 mm), with 0.5 g catalyst loaded for each test. Prior to the reaction, the catalyst was pretreated by reduction with pure H_2 at 400 °C overnight. After the reduction, the feed gas was changed to the mixture of carbon dioxide and hydrogen under the reaction conditions of $n(H_2)/n(CO_2) = 3$ (molar ratio), P = 3 MPa, and T = 400 °C. The gaseous hourly space velocity was 7200 ml g^{-1} h^{-1}.

The products were analyzed on-line using a gas chromatograph (FULI GC 97). Carbon monoxide, carbon dioxide and methane were analyzed using a carbon molecular sieve column equipped with a thermal conductivity detector (TCD), while methane and C_2–C_8 hydrocarbons ($C_2{}^+$) were analyzed with a flame ionization detector (FID) with a HayeSep Q column. Chromatograms of FID and TCD were correlated through methane, and product selectivity was obtained based on molar amounts of the carbon-containing products.

The conversion of CO_2 and the selectivities of products were calculated as Eqs. (1) and (2):

$$CO_2\ \text{Conversion}(\%) = \frac{n_{CO_2,in} - n_{CO_2,out}}{n_{CO_2,in}} \times 100\% \tag{1}$$

$$S_i(\%) = \frac{m_i n_{i,out}}{n_{CO_2,in} - n_{CO_2,out}} \times 100\% \tag{2}$$

where $n_{co_2,in}$ and $n_{co_2,out}$represent the molar concentration of CO_2 in the feed and effluent, respectively; $n_{i,out}$ represents the molar concentration of product i in the effluent and m_i represents the number of carbon atoms in product i.

2.4. Characterization

XRD patterns of fresh and spent catalysts were collected on a RigakuSmartLab (9) diffractometer with Cu Kα radiation (λ = 1.5406 Å) with a 0.02 step size over the range of 5° and 80°.

Scanning electron microscopy (SEM) images and energy dispersive spectrometer (EDS) maps were obtained on a field emission scanning electron microscopy (NOVA NanoSEM 450) at an accelerating voltage of 10.0 kV. The samples were also studied by high resolution transmission electron microscopy (TEM) and scanning transmission electron microscopy/energy-dispersive X-ray spectroscopy (STEM/EDS) using a JEM-2100F instrument (JEOL Company) with an acceleration voltage of 200 kV. The samples for TEM analysis were prepared by dipping the carbon-coated copper grids into ethanol solutions of the samples and drying at ambient conditions.

The textural properties of the samples were determined by N_2 adsorption on a Quantachrome AUTO-SORB-1-MP sorption analyzer at liquid nitrogen temperature. Prior to the measurements, the samples were degassed at 350 °C for 2 h. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method. The total pore volume was obtained from the amount of vapor adsorbed at a relative pressure (P/P_0) close to unity, where P and P_0 are the measured and equilibrium pressure, respectively. The pore size distribution was obtained using the adsorption data through the Barrett-Joyner-Halenda (BJH) method.

H_2-temperature programmed reduction (H_2-TPR) measurements were carried out using a ChemBETPulsar TPR/TPD device (Quantachrome, USA) to analyze the reducibility of the calcined catalysts. Prior to reduction, 0.10 g of the calcined sample was charged into the quartz tube and flushed with high purity Ar at 300 °C for 1 h, followed by cooling to room temperature. The TPR program was then initiated by switching to 5 vol% H_2/Ar with a total flow rate of 30 ml min^{-1} and heating to 850 °C at 10 °C min^{-1}.

Dispersion of the oxide particles was characterized by CO titration using the same equipment. Samples were reduced in H_2 at 400 °C for 2 h. After reduction, the gas was changed to high purity Ar for 1 h and then allowed to cool to 30 °C, followed by CO titration. The dispersion was estimated with the assumption of a CO/Fe = 1:2 ratio [23,24].

The iron, cobalt, zirconium and potassium content of the as-prepared samples was measured by ICP-OES (PerkinElmer OPTIMA 2000DV ICP optical emission spectrometer).

Thermogravimetric analysis (TGA) was conducted on a TGA/SDTA851e thermobalance (Mettler Toledo). The TGA data was collected in the range of 30–850 °C in an air flow. The heating rate was

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