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Pyrolyzing ZIF-8 to N-doped porous carbon facilitated by iron and potassium for CO_2 hydrogenation to value-added hydrocarbons

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ABSTRACT

The iron-based catalysts derived from modified ZIF-8 were prepared, characterized, and applied to CO_2 hydrogenation reaction. The addition of iron and iron/potassium evidently tuned the pyrolysis behavior by forming carbon encapsulated iron nanoparticles and metal nanoparticles inserted hollow sphere, respectively. FeZn-NC and FeZnK-NC exhibited high activity with 29.3% and 34.6% CO_2 conversion, respectively. More importantly, the selectivity to value-added hydrocarbons (i.e., C_2–$C_4{}^=$ and C_{5+}), which are of great importance to chemical industry and energy, was prominent over these two catalysts, and higher than 54 C-mol%. The FeZn-NC with carbon-encapsulated iron nanoparticles showed a remarkable stability for 126 h on stream, suggesting a promising prospect for industrial application.

1. Introduction

CO_2 has recently attracted global attention because of its huge amounts of emissions and negative impact on global warming and climate change. A myriad of efforts has been devoted to studying the conversion of CO_2 into valuable chemicals [1–3]. Light olefins, traditionally derived from nonpetroleum carbon resources, are key building blocks and widely used in the chemical industry [4]. The long-chain hydrocarbons are more suitable for transportation fuels [5]. However, it is more difficult to produce C_{2+} hydrocarbons than methane or oxygenates (like CH_3OH and dimethyl ether) due to the chemical stability of the CO_2 molecule and high kinetic barriers for C—C coupling [6,7].

Synthesis of hydrocarbons from CO_2 hydrogenation can be divided into two categories, direct route (CO_2-Fischer-Tropsch Synthesis) and indirect route (CO_2-methanol-mediate). The bifunctional catalysts are used to finish both CO_2 hydrogenation to methanol and methanol-to-olefins (MTO) or methanol-to-gasoline (MTG) process for indirect route [7–9]. The iron-based catalysts are usually selected for the direct route, which combines the reverse water-gas shift (RWGS) reaction and the Fischer-Tropsch synthesis (FTS) [10–12]. FeK/Al_2O_3 had been widely applied to the CO_2 hydrogenation, wherein metal oxides are considered as the good support for this reaction [13,14]. Meanwhile, other materials, like CNTs and MOFs, also exhibited good catalytic performance [10,15]. Moreover, K, Mn, Cu, Zn, and Ce, which acted as structural and/or electronic promoters, were often added to catalysts to improve the catalytic activity and optimize product distribution [16–20].

Metal-organic frameworks (MOFs) are hybrid crystalline materials constructed from metal ions or clusters with organic ligands, which have a myriad of applications [21–25]. In particular, owing to their unique structure and textural properties, MOFs have emerged as promising candidates to prepare carbon-based nano-materials for energy storage and catalytic conversion [26–30]. Zeolitic imidazolate frameworks (ZIFs), which are rich in carbon, nitrogen, and transition metals, are easily prepared and can be utilized as precursors for the synthesis of nitrogen-doped carbon materials (NC) [31–34]. The N atoms in materials could influence the nucleation and growth of metal nanoparticles, increase the metal-support interaction, and lead to the unique metal-support-reactant interactions because of the interfacial charge transfer [35–38]. However, the application of MOF- or ZIF-derived materials in the thermal catalysis is still limited. Our research group has recently reported on the MOF-derived carbon materials for CO_2 hydrogenation, and it exhibited superior activity performance and stability [39,40].

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Inspired by such excellent achievement, we would like to further turn the catalytic property of ZIF-derived materials by adding metals. Based on these motivations, we chose ZIF-8 as the precursor to synthesize Zn- and N-containing catalysts for CO_2 conversion.

Herein, we report two novel Fe-based N-doped porous carbon materials which were prepared by the pyrolysis of Fe and Fe/K modified ZIF-8. The structure of Fe@C on carbon matrix was obtained by using the Fe modified ZIF-8 as precursor, while the addition of Fe and K promoted the sample to transform to the metal particles-inserted hollow sphere. With the opportune merits in terms of composition and structure, the two samples were evaluated as catalysts for hydrogenation of CO_2. Just as we expected, the as-prepared catalysts showed excellent catalytic activity and valuable hydrocarbons selectivity.

2. Experimental section

2.1. Catalysts preparation

2.1.1. Synthesis of ZIF-8

The preparation method is described elsewhere [41], and the procedure is described here with some modification. 6.5 g 2-methylimidazole was dissolved in 100 mL methanol with stirring to get a clear solution. Then 2.94 g $Zn(NO_3)_2{\cdot}6H_2O$ was added, and the solution was stirred for 24 h. The obtained white powders were collected by centrifugation, washed with methanol for several times, and dried overnight at 100 °C.

2.1.2. Preparation of Fe/ZIF-8, K/ZIF-8, and FeK/ZIF-8

Incipient wetness impregnation (IWI) method was applied to prepare Fe/ZIF-8, K/ZIF-8, and FeK/ZIF-8. For Fe/ZIF-8, $Fe(acac)_3$ methanolic solution (0.1 g $Fe(acac)_3$ dissolved in 1.375 g methanol) was dropped onto 1.5 g ZIF-8 sample, and the impregnation process was repeated for 9 times. The obtained sample was dried at 100 °C overnight. For FeK/ZIF-8, KNO_3 aqueous solution (0.125 g KNO_3 dissolved in 1.163 g DI water) was dropped onto 1.0 g as-synthesized Fe/ZIF-8 sample. The obtained sample was dried at 100 °C overnight.

2.1.3. Preparation of Zn-NC, FeZn-NC, and FeZnK-NC

Zn-NC, FeZn-NC, and FeZnK-NC were prepared by the pyrolysis of as-prepared ZIF-8, Fe/ZIF-8, and FeK/ZIF-8, respectively. Typically, 1 g as-prepared sample was heated up to 500 °C in N_2 (ca. 50 mL min^{-1}) with a heating rate of 2 °C min^{-1} and held for 2 h, followed by cooling down to room temperature. The metal loadings are 21.07 wt% Zn in Zn-NC, 18.67 wt% Zn and 5.32 wt% Fe in FeZn-NC, and 17.51 wt% Zn, 5.53 wt% Fe, and 3.56 wt% K in FeZnK-NC (Table S1).

2.1.4. Preparation of 5Fe10Zn-CS and 5Fe10Zn-AC

The carbon spheres (CS), synthesized according to the literature [42], and the commercial activated carbon (AC) were used as the support materials. The catalysts were prepared by the IWI method using aqueous solution of iron nitrate and zinc nitrate. Then the samples were dried at 60 °C overnight, followed by carbonization in N_2 at 500 °C for 2 h. The Fe and Zn loading on the two catalysts are 5 wt% and 10 wt%, respectively.

2.2. Catalysts characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku SmartLab(9) diffractometer using a Cu Kα radiation ($\lambda = 1.5406$ Å) source at a step size of 0.02°. Scanning electron microscopy (SEM) images were obtained on a Hitachi SU8220 instrument with an acceleration voltage of 5 kV. Transmission electron microscopy (TEM) images were taken by using a Tecnai G2 20 S-twin instrument (FEI Company) with an acceleration voltage of 200 kV. The samples were ultrasonicated in ethanol, and a few droplets of ethanol suspension were dropped onto a copper grid, followed by drying at ambient temperature. Raman spectra were collected by using a Nicolet Almega XR Raman system with a 532 nm excitation laser from Thermo Fisher Scientific Inc. N_2 adsorption-desorption isotherms were obtained at 77 K using a Quantachrome Autosorb-iQ_2 gas adsorption analyzer. Prior to the measurement, the samples were degassed in vacuum at 300 °C for 10 h. The CO_2 sorption properties of the samples were obtained by CO_2 adsorption on the same instrument at 298 K. Thermo gravimetric analysis (TGA) was performed on an SDT Q600 (TA Instruments, USA) in the temperature range of 50–800 °C under air or N_2 with a heating rate of 10 °C min^{-1}. ^{57}Fe Mössbauer spectra were recorded at room temperature using a Topologic 500 A spectrometer with a proportional counter. X-ray photoelectron spectroscopy (XPS) measurement was measured on a Thermo Scientific ESCA Lab250 spectrometer consisting of a monochromatic Al Kα as the X-ray source. All binding energies were calibrated by the C 1s peak at 284.6 eV. Elemental analysis was conducted by Inductively Coupled Plasma (ICP) over a Perkin Elmer OPTIMA 2000DV apparatus.

2.3. Catalytic tests

The CO_2 hydrogenation was conducted using a fixed-bed reactor with 8 mm inner diameter. 0.5 g of the catalyst was loaded for each test. The catalysts were reduced in H_2 with a flow rate of 45 mL min^{-1} at 400 °C for 4 h prior to reaction. Then the reactor was cooled down to 320 °C, and the feed gas was switched to the mixture of CO_2 and H_2 under the reaction conditions of $n(H_2)/n(CO_2) = 3$ (molar ratio), P = 3 MPa, and space velocity = 7200 mL g^{-1} h^{-1}.

The products were analyzed on-line by using a gas chromatograph (FULI GC 97). Carbon monoxide, carbon dioxide, and methane were analyzed on a carbon molecular sieve column with TCD, while methane and C_2–C_8 hydrocarbons (C_{2+}) were analyzed by FID with a HayeSep Q column. Chromatograms of FID and TCD were correlated through methane, and product selectivity was obtained based on carbon balance. The catalytic performance at 5 h on stream was typically used for discussion.

3. Results and discussion

3.1. Physicochemical properties

The fabrication process of the Fe-based catalysts is schematically illustrated in Fig. 1. The ZIF-8 was first synthesized with the mean particle size of 150 nm (Fig. S1). Incipient wetness impregnation method was applied to prepare Fe/ZIF-8 and FeK/ZIF-8, which were then used as the precursors to synthesize Fe-based catalysts by thermal treatment under a flow of N_2 at 500 °C. The modification methods have intrinsic effects on the morphology of samples.

The morphology and structure of as-prepared Zn-NC, FeZn-NC, and FeZnK-NC were characterized by SEM and TEM, and resulting images are presented in Fig. 2. After direct pyrolysis of ZIF-8 under N_2 atmosphere, Zn-NC was obtained by the distortion and adhesion of the ZIF-8 spheres (Fig. 2a and d). For the FeZn-NC, nanoparticles were generated on the carbon matrix. The carbon matrix has been a whole piece, and it was unable to find the trace of ZIF-8 spheres (Fig. 2b and e). Interestingly, FeZnK-NC maintained the morphology of ZIF-8 spheres. Moreover, the as-synthesized material displayed a well-defined 3D structure with hollow interiors (Fig. 2c and f). Compared with Zn-NC, the unique structures of FeZn-NC and FeZnK-NC suggest that both iron and potassium play important roles during the pyrolysis process.

TEM was conducted to further investigate the structures of FeZn-NC and FeZnK-NC, as depicted in Fig. 3. Metal nanoparticles on FeZn-NC were encapsulated by a layer of carbon (Fig. 3a and b), which may protect the particles from agglomerating during reaction [43]. Fig. 3b and c showed the high-resolution TEM (HRTEM) images of FeZn-NC. The measured spacing of crystalline lattices, namely 0.21 nm and 0.205 nm, corresponded to the (400) plane of Fe_3O_4 and (510) plane of