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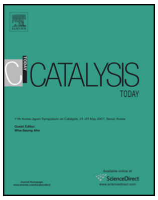

Synthesis of lower olefins by hydrogenation of carbon dioxide over supported iron catalysts

Jingjuan Wang, Zhenya You, Qinghong Zhang, Weiping Deng, Ye Wang*

State Key Laboratory of Physical Chemistry of Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

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ABSTRACT

The hydrogenation of carbon dioxide to lower (C_2–C_4) olefins is an important reaction for the utilization of CO_2 as a carbon feedstock for the production of building-block chemicals. We found that an Fe/ZrO_2 catalyst could catalyze the hydrogenation of CO_2, but the main products were CH_4 and lower (C_2–C_4) paraffins. The modification of the Fe/ZrO_2 catalyst by alkali metal ions except for Li^+ significantly decreased the selectivities to CH_4 and lower paraffins and increased those to lower olefins and C_{5+} hydrocarbons, particularly C_{5+} olefins. The modification by Na^+, K^+, or Cs^+ also increased the conversion of CO_2. The best performance for lower olefin synthesis was obtained over the K^+-modified Fe/ZrO_2 catalyst with a proper K^+ content (0.5–1.0 wt%). Among several typical supports including SiO_2, Al_2O_3, TiO_2, ZrO_2, mesoporous carbon, and carbon nanotube, ZrO_2 provided the highest selectivity and yield to lower olefins. Our characterizations suggest that the modification by K^+ accelerates the generation of χ-Fe_5C_2 phase under the reaction conditions. This together with the decreased hydrogenation ability in the presence of K^+ has been proposed to be responsible for the enhanced selectivity to lower olefins.

1. Introduction

The concerns on the emissions of CO_2, which is a major anthropogenic greenhouse gas, have grown rapidly in recent years because of the worsening global environment. This has driven research activities in the capture and transformation of CO_2 [1–5]. The diminishing of fossil resources has also increased the research interests in the utilization of CO_2 as an alternative carbon feedstock for the production of chemicals and fuels [6–10]. CO_2 possesses advantages of being nontoxic, abundant, and renewable as a chemical feedstock. However, the conversion of CO_2 typically requires external energy input such as photo or electric energy [11–13] and/or high energy co-reactants such as H_2 and reactive organic compounds (e.g., epoxide) [7] because CO_2 is a highly stable molecule. Although there are only limited industrial processes utilizing CO_2 at this moment, many promising reactions for the transformation of CO_2 have been reported [6–10].

Among various transformations of CO_2, the hydrogenation of CO_2 is a versatile route capable of producing various chemicals such as methanol, higher alcohols, formic acid, CH_4, and C_{2+} hydrocarbons [10,14]. Lower (C_2–C_4) olefins are important building-block chemicals and are currently being produced mainly from petroleum by steam-cracking of naphtha. Numerous studies have been contributed to producing lower olefins through non-petroleum routes such as the dehydrogenation of lower paraffins [15], the two-step process from methane [16,17], and the conversion of synthesis gas, which may be obtained from natural gas, coal or biomass, either directly [18] or via methanol [19]. The production of lower olefins by the hydrogenation of CO_2, which is an exothermic reaction (Eq. (1)), would be highly desirable from the viewpoint of utilizing CO_2 as a carbon feedstock for the production of building-block chemicals.

$$nCO_2 + 3nH_2 \rightarrow C_nH_{2n} + 2nH_2O \quad \Delta_r H_{573\ K} = -128 \ \ \text{kJ mol}^{-1} \tag{1}$$

Iron-based catalysts have been studied for the hydrogenation of CO_2 to C_{2+} hydrocarbons [20–31], but only a few of these studies have focused on the formation of lower olefins [24,25,31]. It is generally accepted that, instead of direct hydrogenation of CO_2, the reverse water-gas shift reaction (Eq. (2)) proceeds over these catalysts, followed by the hydrogenation of CO to hydrocarbons (Eq. (3)) via the Fischer–Tropsch (FT) mechanism. Fe-based catalysts can catalyze both the reverse water–gas shift reaction [32,33] and the hydrogenation of CO to light olefins [18], and thus, are expected to show good performances for the hydrogenation of CO_2 to C_2–C_4 olefins.

$$CO + H_2 \rightarrow CO + H_2O \quad \Delta_r H_{573\ K} = 38 \ \ \text{kJ mol}^{-1} \tag{2}$$

$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O \quad \Delta_r H_{573\ K} = -166 \ \ \text{kJ mol}^{-1} \tag{3}$$

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[*] Corresponding author. Tel.: +86 592 2186156; fax: +86 592 2183047.
E-mail address: wangye@xmu.edu.cn (Y. Wang).

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However, the selectivity to C_2–C_4 olefins is still low in the hydrogenation of CO_2 over most of the reported catalysts. It can be expected that both the support and the promoter may affect the activity and the selectivity of Fe-based catalysts. However, little information is available on how to increase the selectivity to lower olefins. Undoubtedly, more fundamental studies are needed to develop an efficient Fe-based catalyst for the selective production of C_2–C_4 olefins from CO_2. This paper reports our recent studies on the effects of alkali metal ions on the hydrogenation of CO_2 to C_2–C_4 olefins over supported Fe catalysts.

2. Experimental

2.1. Catalyst preparation

Metal oxide supports including SiO_2, TiO_2, Al_2O_3, and ZrO_2 were purchased from Alfa Aesar (for ZrO_2) or Sinopharm Chemical Reagent Co. (for the other metal oxides). Carbon nanotubes (CNTs) were synthesized by a method reported previously [34], and were pretreated with a 68 wt% nitric acid at 393 K to remove the Ni catalyst used for CNT synthesis, followed by washing and drying. The supported Fe catalysts were prepared by the conventional impregnation method. For example, for the preparation of the 10 wt% Fe/ZrO_2 catalyst, ZrO_2 (4.5 g) was first added into an aqueous solution of $Fe(NO_3)_3$ (0.2 mol dm^{-3}, 45 mL). The suspension was then stirred for 8 h, followed by evaporation at 353 K to dryness. The obtained powdery catalyst was further dried at 393 K for 12 h and calcined in air at 773 K for 5 h. The alkali metal ion-modified supported Fe catalysts were prepared by a co-impregnation method using a mixed aqueous solution containing certain amount of an alkali metal salt ($LiNO_3$, $NaNO_3$, KNO_3, RbCl or CsCl) and $Fe(NO_3)_3$ with a similar procedure.

2.2. Catalyst characterization

X-ray diffraction (XRD) measurements were carried out on a Panalytical X'pert Pro Super X-ray diffractometer with Cu-K_α radiation (40 kV and 30 mA). For in situ XRD measurements, the powdery sample was loaded into an XRK-900 cell, which was directly attached with the X-ray diffractometer. The XRD pattern for the fresh sample was first recorded. Then, a H_2 gas flow with a flow rate of 50 mL min^{-1} was introduced into the XRK-900 cell and the temperature was raised at a rate of 10 K min^{-1}. When the desired temperature was reached, the catalyst was kept at that temperature for 5 min, and the XRD pattern was recorded. 25 min were typically required for the collection of one pattern with 2θ ranging from 20° to 50°. Before the appearance of the characteristic peaks ascribed to Fe species (32°–45°), the catalyst had been kept at the desired temperature for >15 min. The in situ XRD patterns under the reactant gas mixture of ($H_2 + CO_2$) were also recorded at 618 K. For these measurements, the sample was first reduced in the in situ XRK-900 cell with H_2 gas flow with a rate of 50 mL min^{-1} at 673 K. After being cooled down to 618 K, the reactant gas mixture was introduced to the in situ XRK-900 cell, and then the XRD pattern was recorded after a certain time.

CO_2 temperature-programmed desorption (CO_2-TPD) was performed on a Micromeritics AutoChem 2920II instrument. Typically, the sample loaded in a quartz reactor was first pretreated with high-purity He at 623 K for 1 h. After the sample was cooled down to 373 K, CO_2 adsorption was performed by switching the He flow to a CO_2–He (10 vol% CO_2) gas flow and then keeping at 373 K for 1 h. Then, the gas phase or the weakly adsorbed CO_2 was purged by high-purity He at the same temperature. CO_2-TPD was performed in the He flow by raising the temperature to 1073 K at a rate of 10 K min^{-1}, and the desorbed CO_2 molecules were detected by ThermoStar GSD 301 T2 mass spectrometer with the signal of $m/e = 44$.

2.3. Catalytic reaction

Catalytic reactions were performed on a high-pressure fixed-bed flow reactor. The catalyst (typically 1.0 g) loaded in the reactor was first reduced by H_2 with a flow rate of 50 mL min^{-1} at 673 K for 5 h. After the catalyst was cooled down to 353 K, a reactant gas mixture of ($H_2 + CO_2$) with a H_2/CO_2 molar ratio of 3.0 and a flow rate of 20 mL min^{-1}, which contained 5% argon as an internal standard for the calculation of CO_2 conversions, was introduced to the reactor. Then, the pressure and temperature were increased typically to 2.0 MPa and 613 K, respectively. The products were analyzed by online gas chromatography. The data at steady states, which were obtained typically after 10 h of reaction, were used for discussion.

3. Results and discussion

3.1. Catalytic behaviors of Fe-based catalysts for hydrogenation of CO_2

3.1.1. Effect of modification by alkali metal ions on catalytic behaviors of Fe/ZrO_2 catalysts

It has been demonstrated that ZrO_2 is a unique support for the hydrogenation of CO_2 to CH_3OH or CH_4 when Cu, Ag or Ni is used as the active metal [35]. However, few studies have used ZrO_2 for the hydrogenation of CO_2 to hydrocarbons. Here, we first investigated the catalytic behavior of the Fe/ZrO_2 catalyst for the hydrogenation of CO_2. The conversion of CO_2 was 32% over the 10 wt% Fe/ZrO_2 under our reaction conditions (Table 1). The selectivity to CO was 25% and that to hydrocarbons (C_nH_m) was 75% over this catalyst. CH_4 and C_2–C_4 paraffins were the dominant products in hydrocarbons. Thus, the Fe/ZrO_2 catalyst without modification is not suitable for the hydrogenation of CO_2 to lower olefins.

We investigated the effect of the modification by alkali metal ions on catalytic behaviors of the Fe/ZrO_2 catalyst. Table 1 shows that the addition of Li^+ decreases the conversion of CO_2. The selectivity to hydrocarbons also became lower while that to CO became higher by the addition of Li^+ to the Fe/ZrO_2 catalyst. These indicate that Li^+ suppresses both the reverse water-gas shift reaction and the hydrogenation of CO to hydrocarbons. The inhibiting roles of Li^+ in the water-gas shift and FT reactions were reported in previous studies [36,37]. The distribution of hydrocarbons did not change significantly after the modification by Li^+; CH_4 and C_2–C_4 paraffins were still the dominant products. This indicates that the presence of Li^+ in the Fe/ZrO_2 does not affect the ability of catalyst for the hydrogenation of CH_x intermediates or olefins, which are believed to be the primary products, but decreases the ability of catalyst for the activation of CO and CO_2. On the other hand, the addition of other alkali metal ions to the Fe/ZrO_2 catalyst did not decrease the conversion of CO_2. The modification by Na^+, K^+ and Cs^+ rather increased the conversion of CO_2. Particularly, K^+ showed a significant enhancing effect on the catalytic activity, while the promoting effects of Rb^+ and Cs^+ were less significant on CO_2 conversions. This might be caused by the residual chlorine [38], since RbCl and CsCl were used as the precursors. The selectivity to CO decreased from 25% to 15–21% after the modification by Na^+, K^+, Rb^+, or Cs^+. Organic oxygenates were also formed with considerable selectivities (17–20%) in addition to hydrocarbons over these catalysts. More significantly, the modification of the Fe/ZrO_2 catalyst by Na^+, K^+, Rb^+ or Cs^+ remarkably changed the hydrocarbon distributions. The fractions of CH_4 and C_2–C_4 paraffins decreased significantly from 70% to 18–26% and from 29% to <10%, respectively. Simultaneously, the fractions of C_2–C_4 olefins and C_{5+} hydrocarbons increased