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Synthesis of higher alcohols from CO_2 hydrogenation over Mo–Co–K sulfide-based catalysts

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ABSTRACT

A series of Mo–Co–K sulfide catalysts were prepared by co-precipitation, and their catalytic performance in CO_2 hydrogenation to C_{2+} alcohols and other products was studied. The catalysts with K/Mo molar ratio of 0.3–1.2 and Co/Mo molar ratio of 1.0 showed relatively high CO_2 conversions and high selectivities to total alcohols and C_{2+} alcohols. Under optimal reaction conditions (320 °C, 12.0 MPa, and 3000 ml/(g h)), the CO_2 total conversion and CO_2 conversion free of CO reached 28.8% and 12.6%, respectively, over $Mo_1Co_1K_{0.8}$ sulfide, and the corresponding selectivities to alcohols and C_{2+} alcohols (free of CO) are 81.8% and 10.9%, respectively. The catalytic performance can be modified by the addition of SiO_2, Al_2O_3, TiO_2, or activated carbon to $Mo_1Co_1K_{0.6}$ sulfide during the synthesis. The physicochemical properties of the modified catalysts were characterized by XRD, N_2 adsorption–desorption, SEM, XPS, CO_2-TPD, and H_2-TPD. In particular, the activated carbon-modified catalyst has a stronger interaction between Mo and Co, more Mo^{4+} content on catalyst surface, and appropriate ability for adsorbing CO_2 and H_2, which may be beneficial for achieving high selectivity to C_{2+} alcohols.

1. Introduction

In recent decades, the control or reduction of CO_2 emission has become more and more impendent due to the notable greenhouse effect caused by the continuous rise of CO_2 concentration in the atmosphere and the accelerated consumption of carbon-based energy [1]. Strategies for reducing CO_2 emissions include the use of non-fossil fuels such as hydrogen, renewable, and nuclear energies, the capture and storage of CO_2 emissions, and the utilization of CO_2 [2]. In particular, the conversion of CO_2 to chemicals and fuels via catalytic hydrogenation, photocatalysis, or electrochemical reduction has attracted much attention for its sustainability and economy in waste reclamation [3–8].

Considering the thermodynamic stability of CO_2 and extensive usage of hydrogen in petrochemical industry, catalytic hydrogenation of CO_2 to produce chemicals and fuels may be a relatively promising route [9]. These products (such as alcohols [10–18] and hydrocarbons [19–25]) can be used as fuels in internal combustion engines or raw materials in chemical industry. However, most reports on the synthesis of alcohols from CO_2 hydrogenation focus on methanol production [9–17]. The synthesis of higher alcohols (C_{2+} alcohols) via catalytic CO_2 hydrogenation has been seldom reported [18, 26–32].

Higher alcohols have been regarded as better and cleaner fuels than methanol, because higher alcohols have high octane numbers and the combustion of these fuels leads to low emissions of NO_x, ozone, CO, and volatile aromatic vapors [33]. Moreover, useful chemicals such as ethanol and propanol can be separated with downstream separation units. Kusama et al. [27,28] studied CO_2 hydrogenation over Fe-promoted Rh/SiO_2 catalysts and obtained an ethanol selectivity of 16.0% at a CO_2 conversion of 26.7%. Inui et al. [29] and Guo et al. [30] coupled Fischer–Tropsch (F–T) catalysts with Cu-based reverse water–gas shift (RWGS) catalysts to produce higher alcohols. CO_2 hydrogenation could also be carried out at lower temperatures in a mixed solvent over homogeneous catalysts [26,31], Pt/Co_3O_4 [18], or Mo_2C supported metal catalysts [32].

Although the hydrogenation of CO_2 to produce C_{2+} alcohols has been studied to some extent, it is common that the economy of the previous catalytic system is not very satisfactory. Rh-based catalysts suffer from the expensive price of Rh metal, RWGS and FT-type mixed catalysts show high hydrocarbon selectivity, and the homogeneous catalysts used at low temperatures are limited by the difficulties in recovery and separation as well as the consumption of solvents. Therefore, the development of catalysts and technologies for the efficient synthesis of alcohols (especially

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higher C_{2+} alcohols) from CO_2 hydrogenation is attractive for potential commercial applications.

In CO_2 hydrogenation for methanol or hydrocarbons synthesis, a highly attractive route of CO_2 conversion is described as a two-step direct hydrogenation process consisting of the reduction of CO_2 to CO via the RWGS reaction (Eq. (1)) followed by the tandem conversion of the more reactive CO molecules into organic products (Eqs. (2), (3)) [34]. Accordingly, bi-functional catalysts (with both RWGS and CO hydrogenation performance) are proposed, and the catalysts for methanol and hydrocarbon synthesis were designed by this idea in previous research [9].

Reverse water gas shift reaction

$$CO_2 + H_2 \rightarrow CO + H_2O \tag{1}$$

Alcohol formation reaction

$$nCO + 2n\ H_2 \rightarrow C_nH_{2n+1}OH + (n-1)\ H_2O \tag{2}$$

Fischer–Tropsch reaction

$$nCO + (2n+1)\ H_2 \rightarrow C_nH_{2n+2} + nH_2O \tag{3}$$

Alkali doped Co–MoS_2, as a modified F–T catalyst, has attracted much attention for its unique catalytic performance in CO hydrogenation to mixed low-carbon alcohols, especially the C_{2+} alcohols [35,36,37]. Meanwhile, this kind of catalyst was also reported to be effective in the water–gas shift (WGS) reaction [38,39]. Hence, the bi-functional catalytic property of the alkali doped Co–MoS_2 indicates its possibility for C_{2+} alcohol production in CO_2 hydrogenation. However, so far only a short communication reported CO_2 hydrogenation for the synthesis of methanol and higher alcohols over an alkali salt doped CoMoS based catalyst [40], and there is virtually no more publication dealing with the catalyst properties, the reaction mechanism, or the optimization of similar catalysts.

In the present work, a series of Mo–Co–K sulfide-based catalysts were prepared and their performance in catalytic CO_2 hydrogenation was studied systematically. The effects of potassium and cobalt content in catalyst, reaction temperature, pressure, and space velocity were investigated. In addition, in order to improve the distribution of active components [41,42,43] and thus to improve the catalytic properties of the Mo–Co–K sulfide-based catalysts, various additives such as SiO_2, Al_2O_3, TiO_2, and activated carbon were added in the preparation step. The physicochemical properties of the additive-modified samples were characterized by XRD, N_2 adsorption–desorption, SEM, XPS, CO_2-TPD, and H_2-TPD techniques to reveal the correlation between the physicochemical properties and the performance of catalysts.

2. Experimental

2.1. Catalyst preparation

Mo–Co–K sulfide catalysts were prepared by co-precipitation. Typically, a solution (0.32 mol/l, 60 ml) of ammonium tetrathiomolybdate (ATTM, $(NH_4)_2MoS_4$, synthesized according to the literature [44]) and a solution (0.16 mol/l, 60 ml) of cobalt acetate (prepared by dissolving $Co(CH_3COO)_2 \bullet 4H_2O$, AR, in deionized water) were simultaneously dropped to a three-necked flask containing 40 ml deionized water under vigorous stirring. During the whole co-precipitation process, the pH value of the solution phase was carefully controlled at 5.6 with acetic acid (36–38%). The products were aged at room temperature for 2 h and then filtered and washed with deionized water. The filter cakes were dried at 80 °C overnight, mechanically mixed with a calculated amount of potassium carbonate (K_2CO_3, AR) and grinded. The precursors were then heated in N_2 toward 500 °C at a heating-up rate of 5 °C/min, and then heated in N_2 at 500 °C for 4 h. The obtained sulfide catalysts are denoted as $Mo_1Co_xK_y$ (x and y are the molar ratios of Co/Mo and K/Mo respectively).

Mo–Co–K sulfide-based catalysts containing SiO_2, Al_2O_3, TiO_2, or activated carbon (AC) were prepared by a similar method as described above except for the existence of the additive powders in the solution phase during the co-precipitation step. The weight ratio of the additive to Mo element is 54/100. The obtained sulfide catalysts are denoted as Mo–Co–K–M (M represents different additives).

2.2. Catalytic evaluation

The catalytic test was carried out in a fixed-bed continuous flow reactor equipped with on-line gas chromatograph (Fig. S1 in the Supporting Information). For each experiment, 2 g sample (20–40 mesh particles) was charged into a stainless reactor with quartz lining (inner diameter 8 mm). CO_2 hydrogenation was carried out under the reaction conditions of 280–340 °C, 3.0–12.0 MPa, $V(H_2)/V(CO)/V(N_2) = 67.5/22.5/10$, and GHSV = 750–6000 ml/(g h). Detailed reaction conditions are specified in figure captions. The reactants and products were analyzed by two tandem gas chromatographs (Agilent-6820). A packed column (TDX-01) was connected to a TCD detector using He as the carrier gas to separate H_2, N_2, CO, CH_4, and CO_2. A capillary column (Propake-Q) was connected to an FID using N_2 as the carrier gas to separate C_1–C_4 alcohols and C_1–C_6 hydrocarbons. CO_2 conversion and CO selectivity were determined using an internal standard, and the carbon-based selectivity of the carbon-containing organic products (including alcohols, hydrocarbons, and other oxygenates) was calculated by an internal normalization method.

The catalysis data reported in the main text refer to the data collected after 20 h on stream (when a steady state was reached, Fig. S2). The reproducibility of the data is guaranteed, especially when the reaction reaches a steady state (Figs. S3 and S4).

2.3. Characterization

Powder XRD patterns were recorded on a Bruker-AXS D8 Advance X-ray diffractometer using Cu Kα radiation at 40 kV and 200 mA. The 2θ angles were scanned from 5° to 70° at a rate of 5°/min. N_2 adsorption–desorption isotherms were measured at 350 °C with a Micromeritics ASAP-2020 instrument. Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface areas, and the micropore volumes were calculated by using the *t*-plot approach. Scanning electron microscope (SEM) images were taken with a XL30E electron probe X-ray microanalyzer. The samples were deposited on a sample holder and coated with Au. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Perkin Elmer PHI 5000C system equipped with a hemi-spherical electron energy analyzer. The energy scale was calibrated by setting the C1s peak at 284.6 eV.

CO_2 temperature programmed desorption (CO_2-TPD) was performed in a quartz U-tube reactor, using a 100 mg powder catalyst. Prior to measurement, the sample was pretreated in a N_2 flow (40 ml/min) at 500 °C for 1 h. After the reactor was cooled to 30 °C, a flow of CO_2/N_2 mixed gas ($V(CO_2)/V(N_2) = 50/50$, 40 ml/min) was passed through the sample for 0.5 h to achieve the adsorption equilibrium. After 1 h of He flush (30 ml/min) at 100 °C, the sample was heated (10 °C /min) up to 550 °C under flowing He (30 ml/min). The CO_2 content was detected by an Agilent 4890D gas chromatograph with TCD.

H_2 temperature programmed desorption (H_2-TPD) was performed in a quartz U-tube reactor, using a 100 mg powder catalyst. Prior to measurement, the sample was pretreated in a N_2

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