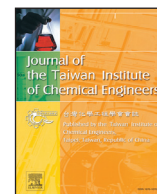




Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Synthesis of higher alcohols from CO₂ hydrogenation over Mo–Co–K sulfide-based catalysts

Su Liu^{a,b}, Haibo Zhou^b, Qingying Song^b, Zhen Ma^{a,*}

^aShanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP³), Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, PR China

^bSinopec Shanghai Research Institute of Petrochemical Technology, Shanghai 201208, PR China

ARTICLE INFO

Article history:

Received 6 February 2017

Revised 6 April 2017

Accepted 7 April 2017

Available online xxx

Keywords:

Mo–Co–K sulfide

CO₂ hydrogenation

C₂₊ alcohols

Promoter

ABSTRACT

A series of Mo–Co–K sulfide catalysts were prepared by co-precipitation, and their catalytic performance in CO₂ hydrogenation to C₂₊ 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 CO₂ conversions and high selectivities to total alcohols and C₂₊ alcohols. Under optimal reaction conditions (320 °C, 12.0 MPa, and 3000 ml/(g h)), the CO₂ total conversion and CO₂ conversion free of CO reached 28.8% and 12.6%, respectively, over Mo₁Co₁K_{0.8} sulfide, and the corresponding selectivities to alcohols and C₂₊ alcohols (free of CO) are 81.8% and 10.9%, respectively. The catalytic performance can be modified by the addition of SiO₂, Al₂O₃, TiO₂, or activated carbon to Mo₁Co₁K_{0.6} sulfide during the synthesis. The physicochemical properties of the modified catalysts were characterized by XRD, N₂ adsorption–desorption, SEM, XPS, CO₂-TPD, and H₂-TPD. In particular, the activated carbon-modified catalyst has a stronger interaction between Mo and Co, more Mo⁴⁺ content on catalyst surface, and appropriate ability for adsorbing CO₂ and H₂, which may be beneficial for achieving high selectivity to C₂₊ alcohols.

© 2017 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

1. Introduction

In recent decades, the control or reduction of CO₂ emission has become more and more impendent due to the notable greenhouse effect caused by the continuous rise of CO₂ concentration in the atmosphere and the accelerated consumption of carbon-based energy [1]. Strategies for reducing CO₂ emissions include the use of non-fossil fuels such as hydrogen, renewable, and nuclear energies, the capture and storage of CO₂ emissions, and the utilization of CO₂ [2]. In particular, the conversion of CO₂ 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 CO₂ and extensive usage of hydrogen in petrochemical industry, catalytic hydrogenation of CO₂ 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 CO₂ hydrogenation focus on methanol production [9–17]. The synthesis of higher alcohols

(C₂₊ alcohols) via catalytic CO₂ 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 CO₂ hydrogenation over Fe-promoted Rh/SiO₂ catalysts and obtained an ethanol selectivity of 16.0% at a CO₂ 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. CO₂ hydrogenation could also be carried out at lower temperatures in a mixed solvent over homogeneous catalysts [26,31], Pt/Co₃O₄ [18], or Mo₂C supported metal catalysts [32].

Although the hydrogenation of CO₂ to produce C₂₊ 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

* Corresponding author.

E-mail addresses: zhenma@fudan.edu.cn, zma001@student.ucr.edu (Z. Ma).

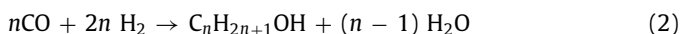
higher C₂₊ alcohols) from CO₂ hydrogenation is attractive for potential commercial applications.

In CO₂ hydrogenation for methanol or hydrocarbons synthesis, a highly attractive route of CO₂ conversion is described as a two-step direct hydrogenation process consisting of the reduction of CO₂ 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].

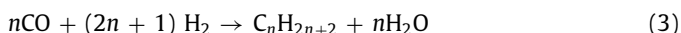
Reverse water gas shift reaction



Alcohol formation reaction



Fischer–Tropsch reaction



Alkali doped Co–MoS₂, 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 C₂₊ 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–MoS₂ indicates its possibility for C₂₊ alcohol production in CO₂ hydrogenation. However, so far only a short communication reported CO₂ 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 CO₂ 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 SiO₂, Al₂O₃, TiO₂, and activated carbon were added in the preparation step. The physicochemical properties of the additive-modified samples were characterized by XRD, N₂ adsorption–desorption, SEM, XPS, CO₂-TPD, and H₂-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), (NH₄)₂MoS₄, synthesized according to the literature [44] and a solution (0.16 mol/l, 60 ml) of cobalt acetate (prepared by dissolving Co(CH₃COO)₂•4H₂O, 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 (K₂CO₃, AR) and grinded. The

precursors were then heated in N₂ toward 500 °C at a heating-up rate of 5 °C/min, and then heated in N₂ at 500 °C for 4 h. The obtained sulfide catalysts are denoted as Mo₁Co_xK_y (x and y are the molar ratios of Co/Mo and K/Mo respectively).

Mo–Co–K sulfide-based catalysts containing SiO₂, Al₂O₃, TiO₂, 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). CO₂ hydrogenation was carried out under the reaction conditions of 280–340 °C, 3.0–12.0 MPa, V(H₂)/V(CO)/V(N₂) = 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 H₂, N₂, CO, CH₄, and CO₂. A capillary column (Propake-Q) was connected to an FID using N₂ as the carrier gas to separate C₁–C₄ alcohols and C₁–C₆ hydrocarbons. CO₂ 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. N₂ 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 hemispherical electron energy analyzer. The energy scale was calibrated by setting the C1s peak at 284.6 eV.

CO₂ temperature programmed desorption (CO₂-TPD) was performed in a quartz U-tube reactor, using a 100 mg powder catalyst. Prior to measurement, the sample was pretreated in a N₂ flow (40 ml/min) at 500 °C for 1 h. After the reactor was cooled to 30 °C, a flow of CO₂/N₂ mixed gas (V(CO₂)/V(N₂) = 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 CO₂ content was detected by an Agilent 4890D gas chromatograph with TCD.

H₂ temperature programmed desorption (H₂-TPD) was performed in a quartz U-tube reactor, using a 100 mg powder catalyst. Prior to measurement, the sample was pretreated in a N₂

Download English Version:

<https://daneshyari.com/en/article/4998595>

Download Persian Version:

<https://daneshyari.com/article/4998595>

[Daneshyari.com](https://daneshyari.com)