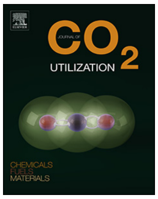
Journal of CO_2 Utilization 26 (2018) 221–229

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

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



CO_2 hydrogenation to methane over mesoporous Co/SiO_2 catalysts: Effect of structure

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ARTICLE INFO

Keywords:
Mesoporous Co/SiO_2 catalysts
Structure
Carbon dioxide
Catalytic hydrogenation
Methanation

ABSTRACT

The mesoporous Co/SiO_2 catalysts with 10 wt.% Co loading were prepared by grind-impregnation method for CO_2 hydrogenation, and the mesoporous SiO_2 materials with different structures were used as the supports. The physicochemical properties of the Co/SiO_2 catalysts were characterized by TEM, BET, H_2-TPR, XRD, and CO_2-TPD. The results indicate that the pore size, specific surface area, and the Co° species crystallinity of the Co/SiO_2 catalyst increase with increasing crystallization temperature of preparing SiO_2 support. The Co/SiO_2 catalyst has the best CO_2 adsorption property when SiO_2 support is prepared at the crystallization temperature of 100 °C. The CO_2 reaction rate (CO_2 conversion) of the Co/SiO_2 catalysts is as follows: CK100 > CK080 > CK120 > CK060 > CK140 > CK040, and the CH_4 selectivity follows the order: CK100 > CK080 > CK120 > CK140 > CK060 > CK040, accompanied by a certain amount of by-product CO molecules. At 360 °C, the CO_2 reaction rate (CO_2 conversion) of the CK100 catalyst is up to 3.29×10^{-5} mol/g_{cat}/s (44.3%), the CH_4 and CO selectivity are 86.5% and 13.5%, respectively.

1. Introduction

The intensive use of fossil fuels causes the sharp increase of CO_2 concentration in atmosphere, the serious global energy shortage, and environmental problems. Thus, the chemical transformation and utilization of CO_2 as C_1 resource have received more attentions [1]. In the early 20th century, Paul Sabatier had pointed out that the CO_2 methanation technology (Sabatier reaction) was an effective way to realize the recycling and regeneration of the carbon resources [2,3]. CO_2 is a kind of cheap, safe and renewable carbon resource, while CH_4 is an important chemical raw material and fuel, thus the conversion of CO_2 to CH_4 can not only achieve the recycling of the carbon resources, but also realize the chemical storage of hydrogen obtained from water electrolysis [4]. Therefore, CO_2 methanation technology is gradually becoming a hot spot in the utilization of CO_2.

The CO_2 methanation is a strongly exothermic reaction ($\Delta H_{298K} = -165$ kJ/mol), and can be carried out at atmospheric pressure [4]. However, as a linear symmetric nonpolar molecule, the CO_2 molecule with stable thermodynamic properties and excellent chemical inertness is not easy to be activated and converted. The electronic ground state composition of the CO_2 molecule is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(1\pi_g)^4(2\pi_u)^\circ$, indicating that the CO_2 molecule has a low energy level of the empty orbit ($2\pi_u$), meanwhile, the electron affinity of CO_2 molecule is up to 38 eV [5]. The results indicate that the CO_2 molecule is a strong electron acceptor and a weak electron donor. Consequently, the catalysts, which can effectively input the electrons to the CO_2 molecule to realize the activation and methanation of the CO_2 molecule, are required [6]. At present, Ru [2,7], Rh [8], Pd [9], Ni [10], and Co [11–13] catalysts have been applied to the CO_2 catalytic hydrogenation reaction. The noble metal based catalysts such as Ru, Rh, and Pd catalysts have an excellent CO_2 catalytic hydrogenation performance, but the high cost and scarcity restrict their large-scale applications. Therefore, the application of non precious metal catalysts to CO_2 catalytic hydrogenation reaction has become the focus of the researchers. The problem of deactivation for Ni catalysts because of Ni sintering and carbon poisoning in the low reaction temperature restricts their application [14,15], while the low reaction temperature is beneficial to the CO_2 catalytic hydrogenation reaction with high CH_4 selectivity[14,16]. Weatherbee et al. [17] found that the Co/SiO_2 catalyst showed better CO_2 catalytic hydrogenation performance than Ni/SiO_2 catalyst at the reaction temperature of 250 °C and atmospheric pressure. Then Co catalysts have attracted the attention of researchers because of their superior activity, good stability, low cost, and strong resistance to carbon deposition. Furthermore, the Co/SiO_2 catalyst with the ordered mesoporous structure shows the optimal CO_2 catalytic hydrogenation performance [12]. This result is closely related to the structure of the

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https://doi.org/10.1016/j.jcou.2018.04.023
Received 24 March 2018; Received in revised form 17 April 2018; Accepted 24 April 2018

SiO_2 support, the large specific surface area, ordered mesoporous structure, and good structural stability of the mesoporous SiO_2 support can provide favorable conditions for the CO_2 catalytic hydrogenation reaction on the Co/SiO_2 catalyst [12]. The pore structure of the mesoporous SiO_2 support can not only affect the dispersion and reducibility of CoO_x species[18,19], but also affect the interaction between the active Co° species and mesoporous SiO_2 support [20]. In addition, the mass transfer phenomenon of the reactant and product molecules can also be adjusted by its pore structure [21,22]. Thus, it is important to study the effect of the crystallization temperature used for preparing mesoporous SiO_2 support on the CO_2 catalytic hydrogenation performance of the Co/SiO_2 catalysts.

In this paper, a series of 10 wt.% mesoporous Co/SiO_2 catalysts, using the mesoporous SiO_2 materials which were prepared at different crystallization temperatures (40 ~ 140 °C) as supports, were obtained by grind-impregnation method. The obtained Co/SiO_2 catalysts were further characterized by Transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET), hydrogen temperature-programmed reduction (H_2-TPR), X-ray diffraction (XRD), and CO_2-temperature programmed desorption (CO_2-TPD). The catalytic performance of the prepared Co/SiO_2 catalysts was evaluated via CO_2 catalytic hydrogenation reaction.

2. Experimental

2.1. Catalyst preparation

The synthesis of the mesoporous SiO_2 material was based on the reference [23]. 6.0 g P123 surfactant, 217.0 g deionized water, and 10 ml concentrated hydrochloric acid were mixed in the closed polytetrafluoroethylene bottle at 35 °C for 4.0 h. Then, 7.5 ml *n*-butanol was added into the bottle. After another 1.0 h mixing, 13.8 ml tetraethyl orthosilicate (ACROS, 98%) were added into the bottle and mixed for another 24.0 h. Next, the crystallization treatments of the mixtures were conducted at the oven of 40, 60, 80, 100, 120, and 140 °C for 24.0 h, respectively. Afterwards, the corresponding solid products were obtained by filtering the mixture. After the following washing and drying, the corresponding solid products were calcined at 550 °C for 6.0 *h* to obtain mesoporous SiO_2 supports, labeled as the K040, K060, K080, K100, K120, and K140 based on the used hydrothermal temperature, respectively.

Co/SiO_2 catalysts with metal Co content of 10 wt.% were prepared by grind-impregnation method using K040, K060, K080, K100, K120, and K140 as the supports. Firstly, the required amounts of $Co(NO_3)_3{\cdot}6H_2O$ (Guangzhou Jinhuada Chemical Reagent Co., Ltd) and mesoporous SiO_2 were pestled in a mortar for 0.5 h, then the finite deionized water were added to the mixture by drop, and pestled for another 0.5 h. Next, the formed slurries were dried at 60 °C overnight. Finally, the powders were calcined at 450 °C for 3.0 h to obtain the COK040, COK060, COK080, COK100, COK120, and COK140 precursors. The CK040, CK060, CK080, CK100, CK120, and CK140 catalysts were prepared via reducing the obtained precursors by H_2 at 400 °C for 2.0 h, respectively.

2.2. Catalyst characterization

2.2.1. TEM characterization

The morphology and microstructure of the Co/SiO_2 catalysts were examined on a transmission electron microscopy (TEM, Hitachi 7700, 100 kV, Japan). For the TEM measurement, the samples were prepared by ultrasonication in ethanol, evaporating a drop of the resultant suspension onto a carbon-coated copper grid.

2.2.2. BET characterization

The N_2 adsorption-desorption isotherms and the pore size distributions were measured by Tri StarII3020 equipment. All the samples were degassed at 300 °C for 4.0 h before the measurement, and the N_2 adsorption-desorption isotherms of the samples were tested under the liquid nitrogen. The specific surface area was computed from the BET equation and the pore size was calculated by the desorption branch of the isotherms by BJH method.

2.2.3. H_2-TPR studies

15 mg Co/SiO_2 catalyst precursors were loaded into the U-type quartz tube reactor, and 5 vol.% H_2/Ar was introduced into the tube at a flow rate of 25 ml/min. Then, the H_2-TPR profiles were obtained by heating the precursor sample from 100 to 700 °C at a heating rate of 10 °C/min.

2.2.4. XRD characterization

XRD patterns of the prepared Co/SiO_2 catalysts were analyzed on the Shimadzu/XRD-6100 diffractometer with Cu $K\alpha$ ($\lambda = 0.15418$ nm) radiation as the radiation source. The operating voltage and current were 40 Kv and 200 mA, respectively. The XRD signals are collected at a 2θ range of 20–80° with a scanning rate of 2°/min.

2.2.5. CO_2-TPD analysis

30 mg Co/SiO_2 catalyst was packed into the U-type quartz tube with an inner diameter of 4 mm. The prepared catalyst was pre-reduced at 400 °C for 1.0 h by 5 vol.% H_2/Ar gas. After the reduction, He flow was fed into the tube at the same temperature for 30 min. When the catalyst cooled down to the room temperature, 5 vol.% CO_2/He mixed gas was supplied to the tube for another 40 min. Finally, the sample was exposed to the He flow to remove the physically adsorbed CO_2 molecules. The CO_2-TPD profiles were obtained by heating the catalyst from 30 to 400 °C at a heating rate of 10 °C/min under the flow of He. The flow rate of all the used gases was 25 ml/min.

2.3. Catalytic activity tests

CO_2 catalytic hydrogenation tests of all the prepared Co/SiO_2 catalysts were carried out in a micro fixed-bed reactor at atmospheric pressure. 50 mg Co/SiO_2 catalyst was packed into the U-type quartz tube, and then reduced at 400 °C for 2.0 h in H_2 flow. When the catalyst cooled down to 240 °C in the H_2 flow, the gas mixture, comprised 10 vol.% CO_2, 40 vol.% H_2, and 50 vol.% Ar, was introduced into the tube with the gas hourly space velocity (GHSV) of 60,000 ml/g/h. The CO_2 catalytic hydrogenation reaction for each prepared Co/SiO_2 catalyst was conducted at the temperature range of 240– 400 °C. The compositions of the feed gas and reaction products were detected by online gas chromatography (GC6890), equipped with TCD.

3. Results and discussion

3.1. TEM characterization

The TEM images of the prepared CK040, CK060, CK080, CK100, CK120, and CK140 catalysts are shown in Fig. 1. All the prepared Co/SiO_2 catalysts remained the developed ordered mesoporous structure from SiO_2 support after the introduction of Co species [12]. The pore size and pore wall thickness of the prepared Co/SiO_2 catalysts obtained from the TEM images are exhibited in Table 1. The results indicate that all the prepared Co/SiO_2 catalysts are typical mesoporous catalysts, and the pore size of the prepared Co/SiO_2 catalysts increases with the increasing crystallization temperature for preparing mesoporous SiO_2 support, while the pore wall thickness decreases. This phenomenon is directly related to the pore size and pore wall thickness of mesoporous SiO_2 support. In the acidic solution, P123 surfactant used as the template to synthesize mesoporous SiO_2 support, follows the ($S^{\circ}H^+$)(Cl^-I^+) mechanism [24]. Namely, the stable micelles (S°) formed by P123 surfactant can interact with the protonated silica (I^+) in the acidic environment. The core of the formed micelle is mainly composed by the