



## Research paper

ZrO<sub>2</sub> support imparts superior activity and stability of Co catalysts for CO<sub>2</sub> methanation

Wenhui Li<sup>a</sup>, Xiaowa Nie<sup>a</sup>, Xiao Jiang<sup>c</sup>, Anfeng Zhang<sup>a</sup>, Fanshu Ding<sup>a</sup>, Min Liu<sup>a</sup>, Zhongmin Liu<sup>b</sup>, Xinwen Guo<sup>a,\*</sup>, Chunshan Song<sup>a,c,\*</sup>

<sup>a</sup> State Key Laboratory of Fine Chemicals, PSU-DUT Joint Center for Energy Research, School of Chemical Engineering, Dalian University of Technology, Dalian, 116024, PR China

<sup>b</sup> National Engineering Laboratory for Methanol to Olefins, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, PR China

<sup>c</sup> Clean Fuels & Catalysis Program, EMS Energy Institute, PSU-DUT Joint Center for Energy Research, Departments of Energy and Mineral Engineering and of Chemical Engineering, The Pennsylvania State University, University Park, PA, 16802, USA

## ARTICLE INFO

## Keywords:

CO<sub>2</sub> methanation  
Cobalt catalyst  
ZrO<sub>2</sub>  
Al<sub>2</sub>O<sub>3</sub>  
Interface

## ABSTRACT

Screening of various supports reveals that Co catalysts supported on ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> show good initial activity for CO<sub>2</sub> methanation. Co/ZrO<sub>2</sub> and Co/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by impregnation with different metal loadings were further examined comparatively. The 10Co/ZrO<sub>2</sub> catalyst showed high activity with CO<sub>2</sub> conversion of 92.5% and CH<sub>4</sub> selectivity of 99.9% without deactivation after 300 h time on stream (TOS). However, the 10Co/Al<sub>2</sub>O<sub>3</sub> catalyst gave a lower CO<sub>2</sub> conversion of 77.8% which decreased to 38.6% after 300 h TOS. The catalysts were characterized by STEM/EDS (scanning transmission electron microscopy/energy-dispersive X-ray spectroscopy), in situ XRD(X-ray diffractometer), H<sub>2</sub>-TPR(temperature programmed reduction), XPS (X-ray photoelectron spectroscopy), chemisorption of H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub> and NH<sub>3</sub>-TPD (temperature programmed desorption). Re-dispersion of Co species on the ZrO<sub>2</sub> support during reduction by H<sub>2</sub> was observed by STEM/EDS. New Co-Zr phase formed on the Co-ZrO<sub>2</sub> interface was directly observed by TEM for the first time; the Co/ZrO<sub>2</sub> catalyst exhibited high stability with high activity for CO<sub>2</sub> conversion. In situ XRD, H<sub>2</sub>-TPR and XPS results indicate the promoting effect of ZrO<sub>2</sub> on the reduction of Co<sub>3</sub>O<sub>4</sub> to Co metal along with the negative effect of Al<sub>2</sub>O<sub>3</sub>. The oxygen vacancies on the ZrO<sub>2</sub> detected by XPS may help to activate CO<sub>2</sub> and H<sub>2</sub>O and resist deactivation. Co/Al<sub>2</sub>O<sub>3</sub> catalyst deactivates rapidly due to coke deposition and spinel formation.

## 1. Introduction

Continuing consumption of fossil fuels worldwide led to increasing CO<sub>2</sub> concentration in the atmosphere, and global climate change caused by greenhouse gases dominated by CO<sub>2</sub> has become a major challenge [1–11]. At present, CO<sub>2</sub> can be reduced in three ways: control of CO<sub>2</sub> emissions, CO<sub>2</sub> capture and storage, and chemical conversion and utilization of CO<sub>2</sub> [5,7]. Carbon storage is important for cutting CO<sub>2</sub> emissions quickly but has issue of potential leakage of CO<sub>2</sub> [3,5]; CO<sub>2</sub> conversion requires energy input but is receiving increasing attention in conjunction with renewable energy utilization.

CO<sub>2</sub> hydrogenation [2,6,8,11] using H<sub>2</sub> produced with renewable energy sources [12,13] is a promising research direction to produce methanol [14–19], hydrocarbons [20–22], synthetic natural gas (methane) [23–29] and chemicals [30]. Currently uses of renewable energy

sources are limited by their inherent intermittency and require scalable means of storage [31]. Electrolysis of water to generate H<sub>2</sub> is a potential storage approach. Effective conversion of CO<sub>2</sub> to fuels and chemicals with renewable energy can be achieved using H<sub>2</sub> produced with renewable energy [32–34]. On the other hand, the above applications for CO<sub>2</sub> methanation also require inexpensive and stable catalysts with high performance.

CO<sub>2</sub> methanation was first reported by the French chemist Paul Sabatier [35]. This reaction with inexpensive and stable catalysts is a promising new way to store renewable energy such as wind and solar power, to transform biogas effectively to biomethane and to convert CO<sub>2</sub> to chemical feedstock and fuel [36,37]. CO<sub>2</sub> methanation is exothermic with high equilibrium conversion between 25 °C to 400 °C as shown in Fig. 1 which is plotted using the data from literature [38,39].

CO<sub>2</sub> methanation can be catalyzed by transition metals such as Co

\* Corresponding authors at: State Key Laboratory of Fine Chemicals, PSU-DUT Joint Center for Energy Research, School of Chemical Engineering, Dalian University of Technology, Dalian, 116024, PR China

E-mail addresses: [guoxw@dlut.edu.cn](mailto:guoxw@dlut.edu.cn) (X. Guo), [csong@psu.edu](mailto:csong@psu.edu), [hoscxs@gmail.com](mailto:hoscxs@gmail.com) (C. Song).

<http://dx.doi.org/10.1016/j.apcatb.2017.08.048>

Received 26 May 2017; Received in revised form 13 August 2017; Accepted 14 August 2017

Available online 19 August 2017

0926-3373/ © 2017 Published by Elsevier B.V.

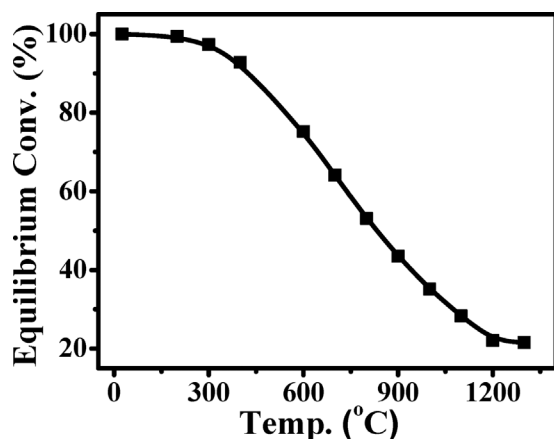


Fig. 1. Equilibrium conversion of CO<sub>2</sub> in methanation at different temperatures.

[40–43], Ni [44,45], Ru [46,47], Rh [48] and Pd [49,50]. Co and Ni-based catalysts are preferred because of their low costs compared with the noble metals (Ru, Rh, Pd). Weatherbee and Bartholomew studied various Group VIII metal catalysts supported on SiO<sub>2</sub> and found Co is more active than Ni in CO<sub>2</sub> methanation [51]. Other researchers have used Al<sub>2</sub>O<sub>3</sub> [27,52], SiO<sub>2</sub> [53,54], ZrO<sub>2</sub> [55], TiO<sub>2</sub> [26,56], CeO<sub>2</sub> [25] and zeolites [44] to support Ni or Co [41,42,57] to catalyze methanation of synthesis gas or CO<sub>2</sub>. Among the results reported so far, only a few Co-based catalysts show high CO<sub>2</sub> conversion [41,42], high selectivity to CH<sub>4</sub> and long lifetime at the same time. There are many factors concerning supports that can influence the performance of metal catalysts [58], such as pore size [59], structure of supports [41], surface chemistry and metal-support interaction [45,60–62]. The activity and selectivity of these catalysts have been shown to be sensitive to the interaction between the active metals and oxide supports [45,60–62]. Previous studies suggested that the reduction of CO<sub>2</sub> requires the co-operation of metal which can dissociate H<sub>2</sub>, and the metal-support interface which can activate CO<sub>2</sub> [47,50]. Therefore, the support and reduction degree of the metal oxide affect the activity of the catalysts. Schulz et al. found that the right amount of zirconium oxide was conducive to the reduction of cobalt [63]. Oukaci et al. reported that Zr played an important role in moderating Co-support interactions and improving the catalyst stability [64]. ZrO<sub>2</sub> may contain both weak acid sites and basic sites and have different phases [65]. The higher concentration of oxygen defects on the m-ZrO<sub>2</sub> could improve the adsorption of oxygenated species including CO<sub>2</sub> [66,67]. In addition, ZrO<sub>2</sub> has excellent hydrothermal stability to adapt to the high temperature and high pressure of CO<sub>2</sub> methanation [68]. ZrO<sub>2</sub> is frequently used as a promoter [55]. The γ-Al<sub>2</sub>O<sub>3</sub> is commonly used as an oxide support and known for its strong metal-support effect [22]. There have been some theoretical studies examining the effect of supports on the performance of metal catalysts [69–76], and these studies illustrate that the metal-support interaction plays a very important role in the activity and selectivity.

Despite these efforts, the substantial differences between ZrO<sub>2</sub>- and Al<sub>2</sub>O<sub>3</sub>-supported catalysts including adsorption and activation of reactants, influence on metal oxide reducibility and catalytic properties have not been fully studied. Understanding the influence of the support on the metal nanoparticles has been an important issue in heterogeneous catalysis for decades [77].

In the present work, various supports including ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, SiC, TiO<sub>2</sub> and activated carbon (AC) loaded with 10 wt% Co were first screened in CO<sub>2</sub> methanation. The Co/ZrO<sub>2</sub> catalyst has the highest CH<sub>4</sub> yield, while Al<sub>2</sub>O<sub>3</sub> is the most studied support. The Co/ZrO<sub>2</sub> catalyst shows both a high CO<sub>2</sub> conversion (close to the equilibrium) and high stability. No deactivation is observed after 300 h on 10Co/ZrO<sub>2</sub>, but on 10Co/Al<sub>2</sub>O<sub>3</sub>, CO<sub>2</sub> conversion decreased rapidly from 77.8% to 36.8%

after 300 h. Another aim of the present work is to address the following questions: Why is the cobalt on ZrO<sub>2</sub> more easily reduced? Why is the ZrO<sub>2</sub> supported Co catalyst more active? Why does the 10Co/Al<sub>2</sub>O<sub>3</sub> catalyst deactivate rapidly?

## 2. Experimental section

### 2.1. Catalysts preparation

Nano monoclinic ZrO<sub>2</sub> and γ-Al<sub>2</sub>O<sub>3</sub> were used as the support materials. γ-Al<sub>2</sub>O<sub>3</sub> was obtained after calcining pseudo-boehmite in a Maffler furnace in air at 400 °C for 4 h. ZrO<sub>2</sub> samples were prepared by dissolving ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (> 45% ZrO<sub>2</sub>, Aladdin Chemicals) in a mixture (ca. 70 ml) of urea (> 99%, Aladdin Chemicals) and deionized water, followed by the thermal treatment in a Teflon-lined stainless-steel autoclave (ca. 100 ml) at 160 °C under autogenous (self-generated) pressure for 20 h. The concentration of Zr<sup>4+</sup> in the solution was 0.4 M, and the urea/Zr<sup>4+</sup> molar ratio was 10. The resulting precipitate was washed thoroughly with water and dried at 110 °C overnight in ambient air and then calcined at 400 °C for 4 h in dry air [78]. Co/ZrO<sub>2</sub> and Co/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by the impregnation method using aqueous solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (> 99%, Aladdin Chemicals) with Co loadings of 2, 10, and 15 wt%. The impregnated samples were dried at 120 °C for 12 h and calcined at 500 °C for 4 h with heating rate at 2 °C min<sup>-1</sup>. The catalysts prepared in this work are denoted as (x) Co/Al<sub>2</sub>O<sub>3</sub> or (x) Co/ZrO<sub>2</sub>, where x represents the mass fraction of the Co metal on the basis of support weight.

### 2.2. Catalytic test

The catalytic hydrogenation of CO<sub>2</sub> was carried out in a pressurized fixed-bed flow reactor (inner diameter 8 mm) where a weighed 1 g catalyst (10–20 mesh) was loaded for each test. Prior to the reaction, the catalyst was pre-reduced in H<sub>2</sub> at 400 °C overnight. After the reduction, the feed gas was switched to the mixture of CO<sub>2</sub> and H<sub>2</sub> with H<sub>2</sub>/CO<sub>2</sub> molar ratio of 4 under pressure of 3 MPa at 400 °C; the space velocity was 3600 ml g<sup>-1</sup> h<sup>-1</sup>.

The products were analyzed on-line by a gas chromatograph (FULI GC 97). CO<sub>2</sub>, CO and CH<sub>4</sub> were analyzed on a carbon molecular sieve column with a thermal conductivity detector (TCD). The conversion of CO<sub>2</sub> and CH<sub>4</sub> selectivity were calculated as Eq. (1) and (2):

$$CO_2 \text{ Conversion (\%)} = \frac{n_{CO_2, in} - n_{CO_2, out}}{n_{CO_2, in}} \times 100\% \quad (1)$$

$$CH_4 \text{ Selectivity (\%)} = \frac{n_{CH_4, out}}{n_{CO_2, in} - n_{CO_2, out}} \times 100\% \quad (2)$$

where  $n_{CO_2, in}$  and  $n_{CO_2, out}$  represent the molar concentration of CO<sub>2</sub> in the feed and effluent, respectively;  $n_{CH_4, out}$  represents the molar concentration of CH<sub>4</sub> in the effluent.

### 2.3. Characterization of catalysts

The textural properties of the samples were determined by N<sub>2</sub> adsorption on a Quantachrome AUTO-SORB-1-MP sorption analyzer at liquid nitrogen temperature. Prior to the measurements, the samples were degassed at 350 °C for 2 h. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method. The total pore volume was obtained from the amount of vapor adsorbed at a relative pressure ( $P/P_0$ ) close to unity, where  $P$  and  $P_0$  are the measured and equilibrium pressure, respectively. The pore size distribution was obtained using the adsorption isotherm through Barrett-Joyner-Halenda (BJH) method.

The morphological properties of Co-based catalysts were studied by high resolution transmission electron microscopy (TEM) and scanning TEM/energy-dispersive X-ray spectroscopy (STEM/EDS) using a FEI

Download English Version:

<https://daneshyari.com/en/article/6453623>

Download Persian Version:

<https://daneshyari.com/article/6453623>

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