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A comparative study of CeO_2-Al_2O_3 support prepared with different methods and its application on MoO_3/CeO_2-Al_2O_3 catalyst for sulfur-resistant methanation

Minhong Jiang[a], Baowei Wang[a,*], Yuqin Yao[a], Zhenhua Li[a], Xinbin Ma[a,1], Shaodong Qin[b], Qi Sun[b]

[a] *Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China*
[b] *National Institute of Clean-and-Low-Carbon Energy, Beijing 102209, China*

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ABSTRACT

The CeO_2-Al_2O_3 supports prepared with impregnation (IM), deposition precipitation (DP), and solution combustion (SC) methods for MoO_3/CeO_2-Al_2O_3 catalyst were investigated in the sulfur-resistant methanation. The supports and catalysts were characterized by N_2-physisorption, transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy (RS), and temperature-programmed reduction (TPR). The N_2-physisorption results indicated that the DP method was favorable for obtaining better textural properties. The TEM and RS results suggested that there is a CeO_2 layer on the surface of the support prepared with DP method. This CeO_2 layer not only prevented the interaction between MoO_3 and γ-Al_2O_3 to form $Al_2(MoO_4)_3$ species, but also improved the dispersion of MoO_3 in the catalyst. Accordingly, the catalysts whose supports were prepared with DP method exhibited the best catalytic activity. The catalysts whose supports were prepared with SC method had the worst catalytic activity. This was caused by the formation of $Al_2(MoO_4)_3$ and crystalline MoO_3. Additionally, the CeO_2 layer resulted in the instability of catalysts in reaction process. The increasing of calcination temperature of supports reduced the catalytic activity of all catalysts. The decrease extent of the catalysts whose supports were prepared with DP method was the lowest as the CeO_2 layer prevented the interaction between MoO_3 and γ-Al_2O_3.

1. Introduction

Numerous efforts have been focused on the use of effectiveness and cleanliness for existing energy sources since the present energy crisis and environmental contamination. The production of synthetic nature gas (SNG) is a reasonable and clean way to utilize the coal resources. Methanation is a key process to synthesize SNG product from coal. Generally, Ni-based catalyst is an extensive catalyst which is used in methanation reaction [1,2]. Although Ni-based catalyst exhibits higher catalytic activity and selectivity of methane, it is easy to deactivate due to sulfur-poisoning. This behavior is a limitation for Ni-based catalyst to be applied in industry. In order to solve this problem, MoS_2-based catalyst has been developed because of considerable activity and sulfur tolerant capability in methanation reaction. In fact, MoS_2-based catalyst has been widely used in many hydrotreating processes such as hydrodesulfurization (HDS), the Fischer–Topsch synthesis, and sulfur-resistant water gas shift (WGS) [3–7].

MoS_2-based catalysts are prepared from MoO_3 highly dispersed on supports. Traditional support is γ-Al_2O_3 which has higher surface area and thermal stability. As previous literature reported [8], the catalyst supported with γ-Al_2O_3 exhibits lower catalytic activities and poor stability. Hence, it is necessary to develop novel supports and catalysts for sulfur-resistant methanation. Wang et al. [9] reported that the structure and property of CeO_2-Al_2O_3 compound are suitable for MoS_2-based catalysts in sulfur-resistant methanation reaction.

In fact, CeO_2 is generally used to improve the performance of alumina. CeO_2 can affect the thermal and structural stability of alumina, the degree of dispersion of active ingredient on Al_2O_3 carrier, and the storage and release of oxygen by the catalyst [10]. Therefore, CeO_2-Al_2O_3 is used in many catalytic processes, such as combustion catalysis, catalytic reforming of methane, and catalytic removal of pollutants from automobile exhausts [11–13].

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* Corresponding author. Tel.: +86 22 27402944; fax: +86 02287401818
E-mail addresses: wangbw@tju.edu.cn, wangbw01@gmail.com (B. Wang), xbma@tju.edu.cn (X. Ma).

[1] Xinbin Ma, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China.

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Preparation method is one of the key factors in determining the properties and performance of the CeO_2-Al_2O_3 support through altering chemical and physical properties, such as surface area, particle size, particle distribution, and electronic structure [14]. A variety of preparation methods for CeO_2-Al_2O_3 support have been developed. In this paper, impregnation (IM), deposition precipitation (DP), and solution combustion (SC) methods were adopted to investigate the effect of CeO_2-Al_2O_3 support on MoO_3/CeO_2-Al_2O_3 catalyst for sulfur-resistant methanation.

As a conventional material preparation method, impregnation is the most extensive and convenient method to prepare the CeO_2-Al_2O_3 support [15]. It exhibits a considerable interaction between CeO_2 and Al_2O_3, but this interaction strongly depends on the Ce loading and calcination temperature [16]. However, there are two intrinsic disadvantages resulting from the impregnation method: (1) the lack of uniform particle and active species distribution because of the forced condensation of precursors on the support surface during the drying process and (2) limited loading of active components on the support surface [14].

The deposition precipitation method is a soft-chemical route to synthesize CeO_2-Al_2O_3. Reddy et al. [17] reported that the CeO_2 in CeO_2-Al_2O_3 support is generally located on the surface of Al_2O_3, this is beneficial for improving the dispersion of active metals on support.

Solution combustion is a convenient preparation method for CeO_2-Al_2O_3. The support prepared with solution combustion method can be used in the high temperature and strong exothermic reaction [18] because of the higher combustion temperature in preparation process. Solution combustion is also an available method to synthesize $CeAlO_3$ compound. As literatures [10,16,19] reported, the formation of $CeAlO_3$ is favorable for retarding the transformation of transitional alumina (γ-Al_2O_3) to its stable phase (α-Al_2O_3). However, it also reduces the capability of storage and release of oxygen for CeO_2 [20,21]. Up to now, no similar work on the sulfur-resistant methanation over Mo-based catalysts prepared with solution combustion method has been reported.

Present investigation was undertaken based on the aforesaid ideas to explore the effect of preparation methods of CeO_2-Al_2O_3 support on MoO_3/CeO_2-Al_2O_3 for sulfur-resistant methanation. For this purpose, CeO_2-Al_2O_3 support prepared with different methods and their respective catalysts were characterized with N_2-physisorption, transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy (RS), and temperature-programmed reduction (TPR). The prepared catalysts were evaluated for sulfur-resistant methanation of syngas at 3 MPa pressure and 550 °C.

2. Experimental

2.1. Sample preparation

The commercial powdery γ-Al_2O_3 material (Yixing Qianye Non-metallic material Co. Ltd., China) was used in this study. For the CeO_2-Al_2O_3 support with 25 wt% CeO_2 prepared by IM method, an incipient wetness technique was used. In this preparation procedure, the commercial powdery γ-Al_2O_3 was added into appropriate volume of solution which had dissolved exact amount cerium nitrate in it. After impregnation, the materials were dried for 48 h at 30 °C, then calcined at 600 °C or 800 °C with a heating rate of 5 °C/min, and kept at the desired temperature for 4 h. For clarity, supports were indicated as CA-IM-600 or CA-IM-800.

For the CeO_2-Al_2O_3 support with 25 wt% CeO_2 prepared by DP method, an ammonia solution was added to a continuously stirred solution of cerium nitrate and commercial powdery γ-Al_2O_3 at 40 °C. The suspension (C (Ce^{3+} + Al^{3+}) = 1 mol/L) was first aged with agitation for 30 min at 40 °C and was left standing for 2 h at 40 °C. The solid, previously filtered and washed, was dried for 24 h at 40 °C. The calcination condition is the same with IM method. Supports were indicated as CA-DP-600 or CA-DP-800.

The preparation procedure of CeO_2-Al_2O_3 support with 25 wt% CeO_2 prepared with SC method was similar to literature [22]. The metal nitrates, $Ce(NO_3)_3{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$, used as oxidants in combustion reaction were the sources of Ce and Al. Ethylene glycol was used as fuel for combustion. First, a clear solution of metal-nitrate taken in a pre-determined proportion was prepared using appropriate amount of water as solvent (C(Ce^{3+} + Al^{3+}) = 3 mol/L). After complete dissolving all of metal-nitrate solid, an appropriate amount of ethylene glycol (v (water)/v (ethylene glycol) = 1:1) was added into the solution. This solution was then introduced into a muffle furnace, then heated up to 600 or 800 °C with a heating rate of 5 °C/min and kept at the desired temperature for 4 h. Combustion set in the heating process. Supports were indicated as CA-SC-600 or CA-SC-800.

MoO_3/CeO_2-Al_2O_3 catalysts were then prepared by impregnation with a solution of ammonium heptamolybdate. After impregnation, the sample was dried at 30 °C for 48 h. Then the MoO_3/CeO_2-Al_2O_3 catalysts were formed by calcination at 600 °C for 4 h with a heating rate of 5 °C/min. The amount of MoO_3 in all catalysts was about 20 wt%. For clarity, all catalysts prepared by different supports would be indicated as MCA-IM-600, MCA-IM-800, MCA-DP-600, MCA-DP-800, MCA-SC-600 and MCA-SC-800, respectively.

2.2. Catalyst characterization

2.2.1. N_2-physisorption analysis

A N_2-physisorption analysis of the prepared catalysts was performed at −196 °C on a Tristar-3000 apparatus (Micromeritics, America) to obtain the textural properties of catalysts (specific surface area and pore volume). Prior to the measurements, the sample was degassed at 300 °C for 4 h under vacuum. The specific surface areas were determined by the physical adsorption of N_2 at liquid nitrogen temperature, using the Brunauer–Emmett–Teller (BET) equation. Pore volumes were obtained from the desorption curves of the isotherms.

2.2.2. Transmission electron microscope analysis

The morphology and structure of the catalysts were characterized by a Tecnai G^2F20 (200 kV) transmission electron microscope (FEI, Holland), with a high resolution of 0.15 nm/200 kV. Sample specimens for TEM studies were prepared by ultrasonic dispersion of the catalysts in ethanol, and the suspensions were dropped onto a micro-mesh copper grid.

2.2.3. X-ray diffraction analysis

X-ray diffraction measurements were performed on a D/max-2500 X-ray diffraction apparatus (Rigaku, Japan) with a Ni-filtered Cu-Kα radiation source (λ = 1.54056 Å). The scan speed was 8 °/min, and the scanning angle ranged from 5° to 90°. The phase identification was determined by comparison with the Joint Committee on Powder Diffraction Standards (JCPDSs). The crystallite sizes (D_{XRD}) of ceria were determined with the Scherrer equation using the values of the full-width at half-maximum (FWHM) of the CeO_2 peak at $2\theta = 28.5°$.

2.2.4. Raman spectroscopy analysis

The Raman spectra were obtained on an InVia-Reflex (Renishaw, England) laser Raman spectrometer with high-sensitivity systems of integrated research grade microscopes. The emission line at 532 nm from the Ar^+ ion laser (Spectra Physics) was focused on