Applied Catalysis A: General 431–432 (2012) 144–150

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

Effects of MoO_3 loading and calcination temperature on the activity of the sulphur-resistant methanation catalyst MoO_3/γ-Al_2O_3

Baowei Wang[a], Guozhong Ding[a], Yuguang Shang[a], Jing Lv[a], Haiyang Wang[a], Erdong Wang[a], Zhenhua Li[a], Xinbin Ma[a,*], 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

ARTICLE INFO

Article history:
Received 3 February 2012
Received in revised form 20 April 2012
Accepted 21 April 2012
Available online 28 April 2012

Keywords:
Synthetic natural gas
Methanation
Alumina
MoO_3 loading
Calcination temperature

ABSTRACT

The effects of calcination temperature and MoO_3 loading on the syngas methanation performance of MoO_3/γ-Al_2O_3 catalyst prepared by the incipient-wetness impregnation method were studied. Mo–Al/25 catalyst (~4.04 Mo/nm^2) calcined at 600 °C reached maximum activity with 46.45% CO conversion. All of the experimental results demonstrated that the saturated monolayer coverage of MoO_3 over a γ-Al_2O_3 support was closet to 25 wt.% MoO_3. It was discovered that tetrahedrally coordinated Mo^{6+} (T), instead of octahedrally coordinated Mo^{6+} (O), is the active catalytic precursor in its oxidised state. Additionally, it was also confirmed that the presence of crystalline MoO_3 and $Al_2(MoO_4)_3$ species depended on not only the MoO_3 loading but also the calcination temperature.

1. Introduction

Since the crude oil crisis of the 1970s [1], the study and development of synthetic natural gas (SNG) production has increasingly gained attention and entered an era of rapid development. The production of SNG is a relatively reasonable and clean way to utilise coal. The use of SNG as an energy supply will effectively reduce the worldwide demand for oil and contribute significantly to the preservation of the environment.

Methanation is a key process for SNG production, which generally employs a nickel catalyst [1,2]. The methanation reaction occurs as follows:

$$3H_2 + CO = CH_4 + H_2O \quad (1)$$

The Ni-based catalysts have high catalytic activity only when the molar ratio of $H_2/CO = 3:1$. Because most gasifiers do not generate synthesis gas at such a high ratio of H_2/CO, processing is required to alter the composition before the methanation reaction is conducted. Thus, the adjustment of the H_2/CO ratio is performed by a water–gas-shift reaction

$$CO + H_2O = H_2 + CO_2 \quad (2)$$

which is an expensive process. Using Mo-based catalysts promotes the following methanation reaction.

$$2H_2 + 2CO = CH_4 + CO_2 \quad (3)$$

Mo-based catalysts enable methanation to operate at low H_2/CO ratios that are not possible for Ni-based catalysts unless steam is used to prevent carbon deposition. Additionally, Ni is extremely sensitive to poisoning by concentrations of sulphur compounds, which are always present in raw synthesis gas, greater than 0.1 ppm [3].

Due to the specific properties of Mo-based catalysts, supported Mo catalysts are widely used in various sulphur-resistant catalytic processes, such as hydrodesulphurisation (HDS) [4], hydrodenitrogenation (HDN) [5] and oxidative dehydrogenation (ODH) [6,7], amongst others. The surface structures of the molybdenum oxide species on different oxide supports have been extensively investigated by various characterisation techniques over the past decade [8]. It has been reported [4,9–11] that the Mo species supported on γ-Al_2O_3 might contain tetrahedrally coordinated Mo species, octahedrally coordinated Mo species [12,13], $Al_2(MoO_4)_3$ species and a crystalline MoO_3 phase [7,8,14]. The different Mo species formed on the catalyst surface result from the different interactions of MoO_3 with the support material and can catalyse different reactions [15]. Generally, their relative concentrations depend on the molybdenum oxide coverage on the support and the calcination temperature, amongst other conditions. As MoO_3 loading exceeds its saturated monolayer coverage, crystalline MoO_3 may form at

* Corresponding author. Tel.: +86 22 27406498; fax: +86 22 87401818.
E-mail addresses: xbma@tju.edu.cn, wangbw01@gmail.com (X. Ma).

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http://dx.doi.org/10.1016/j.apcata.2012.04.029