Journal of the Taiwan Institute of Chemical Engineers 000 (2016) 1–13

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Effect of CeO_2 support on the selective catalytic reduction of NO with NH_3 over P-W/CeO_2

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ARTICLE INFO

Article history:
Received 24 February 2016
Revised 8 April 2016
Accepted 14 April 2016
Available online xxx

Keywords:
CeO_2 supports
Selective catalytic reduction
Oxygen vacancies
Lewis acid sites

ABSTRACT

A series of CeO_2 supports over phosphotungstic acid doped CeO_2 (P-W/CeO_2) prepared by hydrothermal (Cat-A), sol–gel (Cat-B) and precipitation (Cat-C) methods were investigated in selective catalytic reduction of NO_x by NH_3. The catalytic activity of P-W/CeO_2 was dramatically affected by the preparation methods of CeO_2 supports. Results implied that the incorporation of W species could cause the decease of cell parameter and lattice contraction, resulting in inducing the formation of more Ce^{3+} and oxygen vacancies over the Cat-A catalyst, leading to the excellent oxidation ability and SCR activity. Furthermore, the Cat-A catalyst possessed the most amount of Lewis acid sites, resulting in the superior catalytic activity. Besides, the larger specific area and the excellent redox ability were responsible for the outstanding SCR performance. In brief, the favorable activity in NH_3 oxidation, as well as NO oxidation, contributed to the excellent catalytic activity. Therefore, the Cat-A catalyst exhibited the best SCR activity and over 90% NO_x conversion was obtained at 190–450 °C.

1. Introduction

With the sharp increase of vehicles, the issue of vehicle exhaust pollution has attracted more and more public attention. NO_x is one of main air pollutants emitted from vehicle exhaust [1]. The selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with ammonia is one of the state-of-the-art technologies for controlling NO_x from vehicle exhaust [2]. V_2O_5/TiO_2 promoted by WO_3 or MoO_3 has been extensively used for several decades to removal of NO_x. However, this V-based catalyst is only efficient at 300–400 °C, the formation of N_2O and loss of vanadium at high temperatures also restrain its further industry application [3–5]. Besides, the temperature of diesel exhaust gases is in a dynamic range of 180–440 °C [6]. Therefore, it is of great significance to develop environment-friendly NH_3-SCR catalysts with the broad operating temperature window.

Recently, CeO_2-based catalysts have received much attention due to the excellent redox property. Meanwhile, pure CeO_2 shows poor SCR activity and stability. In order to promote the SCR activity and widen the operation temperature window, some other transition metals such as Mn, Ti and W are often doped into CeO_2-based catalyst [7–11]. Gao et al. [12] compared the SCR performance of CeO_2/TiO_2 catalysts prepared by different methods, and the results indicated that the catalyst prepared by sol–gel method presented the best SCR activity due to better dispersion of active nano-crystalline ceria. Shan et al. [13] reported that a superior Ce-W-Ti catalyst prepared by a homogeneous precipitation method exhibited outstanding catalytic activity by the addition of WO_3 and nearly 100% NO_x conversion was obtained at 250–450 °C. Chen et al. [14] also found that introduction of WO_3 could increase the activity of CeO_2/TiO_2 catalyst prepared by co-impregnation method. Based on the above discussions, it is well established that the catalytic activity of catalyst is affected by the nature of support or the active components for the support catalysts. Therefore, various views concerning the relationship between different supports and catalytic activity have been reported [15–17]. It is usually accepted that, even for a same metal oxide-support catalyst, the supported catalyst can possess a variety of structures, which depends on the experimental conditions such as the different supports and the calcination temperatures. In our previous study [18], heteropoly acids modification on CeO_2 was developed, and the results implied that the catalyst activity of pure CeO_2 was remarkably improved by the introduction of solid acid for the improvement of surface acidity. However, the low-temperature SCR activity is still to improve in

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http://dx.doi.org/10.1016/j.jtice.2016.04.034
1876-1070/

Please cite this article as: Z. Song et al., Effect of CeO_2 support on the selective catalytic reduction of NO with NH_3 over P-W/CeO_2, Journal of the Taiwan Institute of Chemical Engineers (2016), http://dx.doi.org/10.1016/j.jtice.2016.04.034

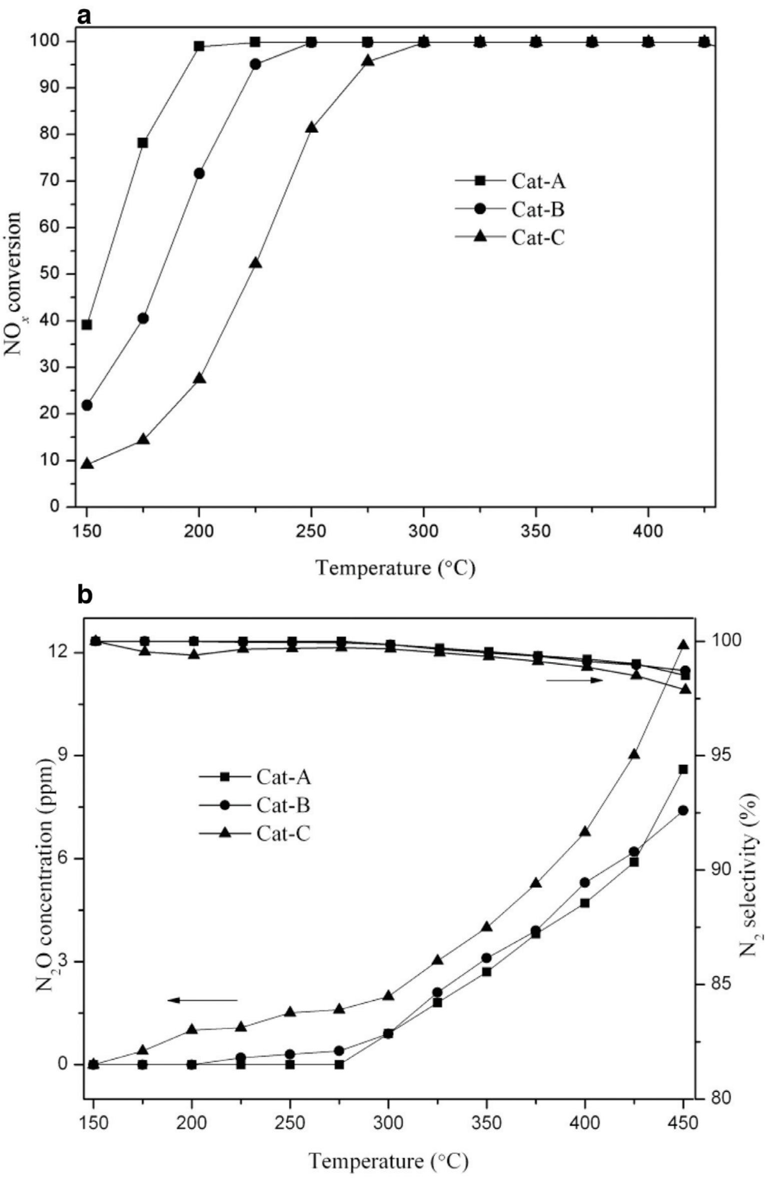

Fig. 1. The catalytic activity and N2 selectivity of P-W/CeO2 catalysts: (a): SCR activity; (b): N2 selectivity.

order to satisfy the need of industry application. Thereby, the effect of CeO_2 supports on the SCR activity is investigated over the phosphotungstic acid doped CeO_2 catalysts.

In this work, the CeO_2 supports were prepared by hydrothermal, precipitation and sol–gel methods and used for selective catalytic reduction of NO by NH_3, and the phosphotungstic acid doped CeO_2 supports (P-W/CeO_2) was prepared by impregnation. The effect of different CeO_2 supports on the structure and catalytic activity of P-W/CeO_2 was investigated. The structure and physicochemical properties of the samples were systematically characterized by XRD, N_2 physisorption, Raman, HR-TEM, H_2-TPR, NH_3-TPD and Py-IR.

2. Experimental methods

2.1. Catalyst preparation

2.1.1. Hydrothermal method

This CeO_2 supports were synthesized by the hydrothermal method. All chemicals were of analytical grate. $Ce(NO_3)_3{\cdot}6H_2O$ (0.01 mol), glucose (0.05 mol) and acrylic acid (0.03 mol) were dissolved in deionized water. Secondly, the 25 mL ammonia solution (25 wt%) was gradually dripped with vigorous stirring at room temperature. The above mixture was aged for 5 h at 20 °C, and then the above mixture was poured into a stainless autoclave and kept at 160 °C for three days. The final powder was filtered, washed, and dried at 80 °C for 12 h, and then calcined at 550 °C for 5 h in air. This catalyst was signed as CeO_2-1.

2.1.2. Sol–gel method

$Ce(NO_3)_3{\cdot}6H_2O$ (0.01 mol) and citric acid (0.02 mol) were dissolved in deionized water. The mixture was heated at 80 °C under stirring until it became a transparent yellow sol and then dried at 140 °C until the sol transformed to gel. The resulting powder was calcined at 550 °C for 5 h in air. The catalyst was labeled as CeO_2-2.

2.1.3. Precipitation method

$Ce(NO_3)_3{\cdot}6H_2O$ was dissolved in distilled water. And then $NH_3{\cdot}H_2O$ and $(NH_4)_2CO_3$ solution were dropwise added with continuous stirring until pH reached 10. The resulting precipitate was

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