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Activity and characterization of Ce–Mo–Ti mixed oxide catalysts prepared by a homogeneous precipitation method for selective catalytic reduction of NO with NH₃

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ABSTRACT

A series of Ce–Mo–Ti mixed oxide catalysts prepared by a homogeneous precipitation method were evaluated for selective catalytic reduction (SCR) of NO with NH₃. These catalysts were characterized by BET, XRD, XPS, SEM, TEM and H₂-TPR. The experimental results indicated that the optimal Ce–Mo–Ti mixed oxide catalyst (Ce₄₀Mo₁₀Ti) exhibited excellent SCR activity in a wide temperature range of 250–450 °C as well as strong resistance to high gas hourly space velocity, 10% H₂O or/and 1000 ppm SO₂. The introduction of Mo could enhance redox property and increase the amount of Ce³⁺, accompanied by the increment of oxygen vacancies and adsorbed oxygen species on the catalyst surface, which were advantageous to the SCR reaction over Ce–Mo–Ti oxide catalyst. In addition, good dispersion of Ce and Mo species on TiO₂ and their synergetic interaction also contributed to its remarkable NH₃–SCR performance.

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1. Introduction

Selective catalytic reduction (SCR) of NO with NH₃ has been regarded as one of state-of-the-art technologies for the control of NO_x emissions from stationary sources. V₂O₅–WO₃ (or MoO₃)/TiO₂ has been extensively utilized for the past few decades. Great attention is paid nowadays to environment-friendly vanadium-free catalysts for SCR applications mainly due to several inevitable drawbacks of vanadium-based catalysts, including biological toxicity of V₂O₅, relatively narrow activity temperature window (300–400 °C), high oxidation of SO₂ to SO₃ with increasing V₂O₅ loadings [1] and drop in N₂ selectivity at high temperatures [2]. Among possible substitutes, cerium-based oxides are of considerable practical concern because of the remarkable oxygen storage/release capability and redox property of CeO₂ [3]. Varieties of cerium-based oxide catalysts have been reported, such as Ce–Ti [4–6], Ce–W–Ti [7–9], Ce–Nb [10], Ce–P [11], etc.

MoO₃ has been used as a structural and chemical promoter in commercial vanadia-based catalysts [3]. In recent years, Liu et al. [12] and our group [13] added Mo to CeO₂/TiO₂ catalyst by an impregnation and single step sol–gel, respectively. Both of them showed good catalytic activity and certain resistance to H₂O

and SO₂. It is well established that the activity of a catalyst is highly dependent on its preparation method in most cases [14]. Homogeneous precipitation has been demonstrated to contribute to improving the dispersion and prevent the aggregation of metal oxide species at high content, which will be beneficial to provide more active sites [15]. This is crucial to the enhancement of the catalytic performance over mixed metal oxide catalysts. It was reported that mixed oxides of Ce–Ti [5], Ce–W–Ti [8], Ce–W [16], Co–Al [17] and V–Ce [18], prepared by a homogeneous precipitation method, showed superior SCR performances. However, to our best knowledge, there have been few reports on Ce–Mo–Ti oxide catalyst prepared by a homogeneous precipitation method for the SCR of NO with NH₃ until our present study.

In this work, a homogeneous precipitation method was employed to prepare Ce–Mo–Ti mixed oxide for the SCR of NO with NH₃. The catalysts were characterized by BET and pore size distribution measurements, XRD, XPS, SEM, TEM and H₂-TPR measurements.

2. Experimental

2.1. Catalysts preparation

Ce–Ti, Mo–Ti and Ce–Mo–Ti mixed oxides were synthesized by a homogeneous precipitation method. Cerium nitrate (Ce(NO₃)₃·6H₂O), titanium sulfate (Ti(SO₄)₂) and ammonium

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Table 1
Composition of Ce₄₀Ti and Ce₄₀Mo₁₀Ti.

Samples	Element concentrations (wt.%)		
	Ce	Mo	Ti
Ce ₄₀ Ti	22.19	–	34.76
Ce ₄₀ Mo ₁₀ Ti	20.59	3.83	32.29

molybdate ((NH₄)₆Mo₇O₂₄·4H₂O) were used as the precursors of Ce, Ti and Mo. The required amounts of precursors were added to 500 mL deionized water. Superfluous urea (35 g) was then mixed into the above solution, followed by continuously magnetic stirring at 90 °C for 8 h. The deposits were filtered and thoroughly washed with deionized water until the filtrate was neutral. The resulted precipitates were dried at 100 °C overnight and subsequently calcined at 400 °C in the air for 4 h. The obtained particles were pressed, milled and sieved out for further studies. The catalysts were denoted as Ce_mMo_nTi, in which *m* and *n* represented the weight loadings of CeO₂ and MoO₃ in 100 g TiO₂, respectively. For example, in the case of Ce₄₀Mo₁₀Ti, the weight ratio of CeO₂/MoO₃/TiO₂ was 40:10:100 and the corresponding weight ratio of their precursors was about 101:12:300. The stoichiometries of Ce₄₀Ti and Ce₄₀Mo₁₀Ti were confirmed by using an inductively coupled plasma atomic emission spectroscopy (ICP-AES) and the results are shown in Table 1.

2.2. Catalytic activity measurements

The catalytic activity measurements were carried out in a continuous-flow fixed-bed quartz reactor with required amounts of catalysts (60–100 mesh). The feed gas contained 1000 ppm NO, 1000 ppm NH₃, 3 vol.% O₂, 10 vol.% H₂O (when used), 1000 ppm SO₂ (when used) and balance N₂. The concentrations of the products, including NO, NO₂, SO₂ and O₂, were collected by the gas analyzer (350 Pro, Testo). The steady-state activity data were recorded after about 30 min at each temperature.

2.3. Characterization of catalysts

BET analysis of the catalysts was determined from N₂ adsorption/desorption at 77 K using an automated gas sorption system (Micromeritics ASAP 2020).

X-ray diffraction (XRD) patterns were recorded on an X'Pert PRO MPD system (PANalytical Corp.) with Cu K α radiation ($\lambda = 0.15406$ nm).

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Thermo ESCALAB 250 spectrometer equipped with an X-ray source with Al K α radiation (1486.6 eV). The observed spectra of Ce 3d, Mo 3d, Ti 2p and O 1s were calibrated using C 1s peak (BE = 284.6 eV) as standard.

The scanning electron microscopic (SEM) images were graphed with a Helios NanoLab 600i Dual Beam System (FEI Company) and the transmission electron microscopic (TEM) images were performed on a JEM-2010 microscope (JEOL Company).

The hydrogen temperature-programmed reduction experiments (H₂-TPR) were measured on FINESORB-3010 chemisorption analyzer (FINETEC Instruments Corp.) with 0.1 g of the catalysts with a thermal conductivity detector (TCD).

3. Results and discussion

3.1. NH₃-SCR activity

3.1.1. Effect of CeO₂ loadings

To find the optimal CeO₂ loading, MoO₃ loading was kept at 10 wt.% TiO₂. Fig. 1 shows the NO conversions as a function of reac-

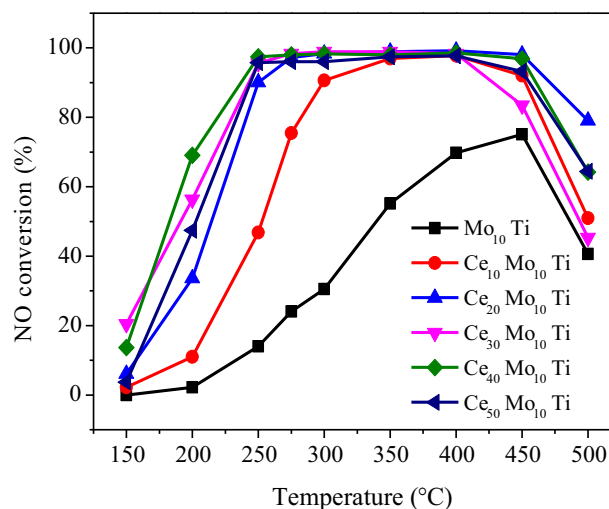


Fig. 1. NH₃-SCR activities over various catalysts with different CeO₂ loadings. Reaction conditions: [NO]=[NH₃]=1000 ppm, [O₂]=3 vol.%, balance N₂ and GHSV=90,000 h⁻¹.

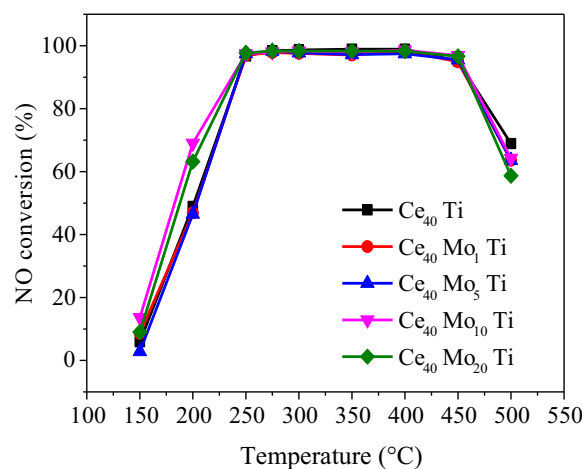


Fig. 2. NH₃-SCR activities over various catalysts with different MoO₃ loadings. Reaction conditions: [NO]=[NH₃]=1000 ppm, [O₂]=3 vol.%, balance N₂ and GHSV=90,000 h⁻¹.

tion temperature over various catalysts. As for Mo₁₀Ti, a maximum NO conversion of 75.1% was obtained at 450 °C. The introduction of CeO₂ led to the remarkable increase in NO conversions and broadened the activity temperature windows until the mass ratio of CeO₂/TiO₂ was up to 40%. In a wide temperature range of 250–450 °C, NO conversions approximately reached 100% over Ce₄₀Mo₁₀Ti at the GHSV of 90,000 h⁻¹. Further increase in CeO₂ loading resulted in the decrease of NO conversions at low and high temperatures.

3.1.2. Effect of MoO₃ loadings

The effect of MoO₃ loadings on the SCR activity of Ce–Ti oxides is presented in Fig. 2. It was found that the MoO₃ loadings had almost no effect on NO conversion (nearly 100%) at 250–450 °C. The similar results were also observed over CeO₂–WO₃/TiO₂ [9] and V₂O₅–WO₃/TiO₂ catalysts [19]. MoO₃ or WO₃ supported on TiO₂ was not highly active for the SCR reaction. MoO₃ and WO₃ primarily act as structural and chemical promoters rather than main active species [9,19]. Compared with the other mixed oxides, the catalytic activity of Ce₄₀Mo₁₀Ti was higher at temperatures below 250 °C. Therefore, Ce₄₀Mo₁₀Ti was elected as an optimal catalyst for further studies.

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