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Promotional synergistic effect of Cu and Nb doping on a novel Cu/Ti-Nb ternary oxide catalyst for the selective catalytic reduction of NO_x with NH_3

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ABSTRACT

A series of Ti-Nb binary oxide were synthesized by co-precipitation as supports to prepare Cu/Ti-Nb mixed oxide catalysts through wetness impregnation. The novel catalyst 0.8%Cu/Ti_2NbO_x exhibited an excellent catalytic activity and N_2 selectivity with a broad operation temperature (250–425 °C) under a gas hourly space velocity (GHSV) of 177,000 h^{-1} for the selective catalytic reduction of NO_x with NH_3. A series of analytical techniques including high resolution transmission electron microscopy (HRTEM), N_2-physisorption, X-ray diffraction (XRD), Laser Raman spectra (LRS), X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR), NH_3 temperature-programmed desorption (NH_3-TPD), H_2 temperature-programmed reduction (H_2-TPR) and in situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) were used to investigate the correlations among catalyst structure, surface properties and catalytic performance. For the support Ti_2NbO_x, the specific surface area was larger than that of TiO_2, promoting the high dispersion of the active component. Also, the surface acid sites were increased by addition of niobium oxide species and the redox capability of the support was enhanced by doping copper species. Moreover, the introduction of copper species effectively enhanced the catalytic performance within 225–400 °C. The copper species mainly existed as isolated Cu^{2+} and non-isolated Cu^{+} and the isolated Cu^{2+} ions played a significant role in the high NH_3-SCR performance over 0.8%Cu/Ti_2NbO_x catalyst. Hydrothermal aging treatment experiment demonstrated that 0.8%Cu/Ti_2NbO_x catalyst had an excellent hydrothermal stability. In addition, water vapor or/and SO_2 had a slightly reversible inhibition influence on the catalytic performance over 0.8%Cu/Ti_2NbO_x, indicating that it was a promising candidate for NH_3-SCR catalyst in the future practical application. The reaction pathway over 0.8%Cu/Ti_2NbO_x catalyst followed both Eley-Rideal mechanism and Langmuir-Hinshelwood mechanism at 225 °C.

1. Introduction

As the atmospheric pollution is becoming more and more severe, it has attracted public awareness on environmental protection awareness. Nitrogen oxides (NO_x) are one of major air pollutants that could cause photochemical smog, acid deposition, nitrate aerosol, ozone depletion and greenhouse effect [1–3]. NO_x is mainly emitted from stationary sources and mobile sources [4,5]. Selective catalytic reduction of nitrogen oxides with ammonia (NH_3-SCR) is an effective technique that has been widely applied for the abatement of NO_x from coal-fired plants and stationary boilers. V_2O_5-WO_3(MoO_3)/TiO_2 catalyst has been commercially used for NO_x abatement due to its excellent catalytic performance. However, there are still some drawbacks, such as a narrow reaction temperature window of 300–400 °C and the biological toxicity of V_2O_5 to environment and human being [6,7]. Hence, it is necessary to develop environmental-friendly catalysts as alternatives.

Recently, TiO_2-anatase as support for the selective reduction catalyst was investigated by many researchers because of its great SO_2 resistance [6,8,9]. However, pure TiO_2 is poorly active during the SCR reaction due to its weak acidity and poor redox ability [10]. Some modifications have been investigated to overcome these defects. The addition of metal elements was commonly used to increase the activity of TiO_2. Yao found that more Lewis acid sites and NH_4NO_2 species were formed on the surface of $CuO/Ti_{0.95}Ce_{0.05}O_2$ catalyst, resulting in the best NO conversion

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of 90% within a reaction temperature of 250–275 °C [5]. Also, The Cu/Ti oxide catalyst for NH_3-SCR has also been investigated [11,12], and the highest activity was achieved at high temperature (about 300 °C) with an active temperature window of 340–440 °C at GHSV of 50,000 h^{-1}. Both of their reports showed an enhancement on the catalytic activity of TiO_2 with addition of Cu. However, these catalysts exhibited over 90% NO_x conversion and N_2 selectivity with a relatively narrow reacting temperature window under a comparatively low GHSV below 100,000 h^{-1}. Effects of the temperature window and GHSV on the NH_3-SCR activity of catalyst have been investigated [13,14]. And it was essential for the potential SCR catalyst with high activity under broad range of reaction temperature and high GHSV. So, more efforts must be made to develop novel TiO_2-based catalysts for the further industrial application.

The promoting effect of niobium oxides on catalytic reduction of NO_x has been frequently investigated over V_2O_5-Nb_2O_5/TiO_2 [15], Fe_2O_3-Nb_2O_5 [16], CeO_2-Nb_2O_5 [4], NbO_x-CeO_2-ZrO_2 [17], Mn_2NbO_x [18] catalysts due to its strong acidity. Also, copper species have been commonly used as the active species in SCR catalysts for their low cost, non-toxicity and good catalytic activity [19]. Cu/SSZ-13 has been commercially used as the diesel exhaust denitration catalyst since 2010 [20,21]. Moreover, many researchers pointed that the catalytic activity was significantly effect by the dispersion of copper species on the support [5,19,22]. Well dispersion of active species would lead to a higher activity. Shan et al. [13] and Yao et al. [5] reported that addition of some elements (such as W or Ce) on the support could facilitate the dispersion of active species to increase the catalytic activity. The effects of niobium oxides on the dispersion of copper species as active species on the support TiO_2 have not been investigated at present.

In this study, niobium oxide was employed for enhancing the acidity of anatase TiO_2, and the copper species were used as mainly active species. The Cu/Ti-Nb ternary oxide catalyst was studied systematically. The optimal proportion of Cu/Ti-Nb has been explored. Meanwhile, the relationship among the "performance – structure – property" was investigated. Besides, in situ DRIFTS were performed to elucidate the mechanism of NH_3-SCR reaction over the catalyst in this work.

2. Experimental

2.1. Catalyst preparation

The titanium-niobium oxides were prepared by using co-precipitation method. Aqueous solutions of $TiOSO_4{\cdot}xH_2SO_4{\cdot}xH_2O$ and $NbCl_5$ were mixed with the desired molar ratios. Sodium dodecyl benzene sulfonate and urea solution were then added into the mixed solution. Afterwards, the mixed solution was heated to 95 °C and held for 3 h under continuous magnetic stirring. The resulting suspension was naturally cooled down to room temperature and kept for 3 h and then centrifuged, washed with ultrapure water until no $SO_4{}^{2-}$ and Cl^- were detected. Then the precipitate was washed twice with anhydrous ethanol and dried at 85 °C overnight. The resulting product was subsequently calcined in air at 350 °C for 1 h and 600 °C for 3 h and finally grounded into a fine powder. The mixed oxides were denoted as $Ti_mNb_nO_x$, where m/n represents the molar ratio of Ti/Nb (m/n = 1, 2, 3, 4). The single oxides, namely Nb_2O_5 and TiO_2, were prepared by using precipitation method.

The yCu/$Ti_mNb_nO_x$ samples were prepared by incipient-wetness impregnating the $Ti_mNb_nO_x$ with $Cu(NO_3)_2{\cdot}3H_2O$ solution, where y indicated the loading amount of copper. For example, 1%Cu/$Ti_mNb_nO_x$ catalyst represents that the copper loading amount is 1 g Cu/(1 g Cu + 99 g $Ti_mNb_nO_x$). The mixture was kept under stirring for 4 h and dried at 85 °C overnight. The obtained materials were calcined in the following air at 550 °C for 4 h. Furthermore, yCu/TiO_2 catalysts were also prepared by using the same method for comparison.

2.2. Catalytic performance measurements

The catalytic performance of these catalysts for NH_3-SCR was determined under a steady state, involving a feed stream including 500 ppm NH_3, 500 ppm NO, 5% O_2, 50 ppm or 250 ppm SO_2(when used), 5% or 10% H_2O(when used), and N_2 as balance gas. 0.1–0.15 g catalysts of 40–60 mesh were placed between plugs of glass wool in a fixed bed quartz tube reactor (inner diameter = 0.6 cm) under atmospheric pressure. The reactor was placed inside a temperature-controlled furnace and a K-type thermocouple was inserted in the center of the catalyst bed for measuring the reaction temperature. Prior to catalytic tests, the catalysts were pretreated in a flow of 10% O_2/N_2 at 500 °C for 30 min to remove the residual species adsorbed on the surface and then cooled down to room temperature. After that, the simulated gas stream was fed into the reactor with a space velocity (GHSV) of 177,000 h^{-1}. The concentrations of outflow were measured by a Nicolet iS50 FTIR spectrometer equipped with a heated gas cell (Pike Technologies, optical path length = 2.4 m), which was kept 110 °C to avoid condensation during the tests. The spectra were recorded with a 0.5 cm^{-1} resolution and co-addition of 32 scans, referenced to a N_2 background. For each experiment, fresh catalysts were used and the NO_x conversion and N_2 selectivity were calculated from the following equations:

$$NO_x\text{conversion} = \frac{C_{NO_x(\text{in})} - C_{NO_x(\text{out})}}{C_{NO_x(\text{in})}} \times 100\% \tag{1}$$

$$C_{NO_x} = C_{NO} + C_{NO_2} + 2C_{N_2O} \tag{2}$$

$$N_2\ \text{selectivity} = \left(1 - \frac{2 \times C_{N_2O}}{C_{NO_x(\text{in})} + C_{NH_3(\text{in})} - C_{NO(\text{out})} - C_{NO_2(\text{out})} - C_{NH_3(\text{out})}}\right) \times 100\% \tag{3}$$

2.3. Catalysts characterization

The micro-morphology of the samples was characterized by high resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F, Japan) operated at 200 kV. And the chemical analysis was obtained by energy dispersive X-ray spectrometer (EDS).

Textural characteristics of these catalysts were measured by N_2 adsorption-desorption experiment using a Micromeritics 3Flex instrument at liquid N_2 temperature (−196 °C). Prior to each analysis, the samples were outgassed under vacuum at 150 °C for 12 h. The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) equation at p/p_0 in the range of 0.05–0.30. Pore size distributions and average pore diameters were determined by Barrett-Joyner-Halenda (BJH) method using the desorption branches in 0.01–0.995 partial pressure range.

Powder X-ray diffraction (XRD) patterns of samples were carried out using a X-ray diffractometer (PANalytical X′ Pert PRO, Holland) with Cu-Kα radiation (λ = 0.15406 nm) at 40 kv and 40 mA. The X-ray diffractogram was recorded in a 2θ range of 10°-90° with the step size of 0.026°.

Laser Raman spectra (LRS) were collected on a Lab. HR800 Laser Raman spectrometer (Jobin Yvon Co., France) with a shot of LMPlanFI 50*/0.50 JAPAN using Ar^+ laser beam. A wavelength of 514.532 nm was used for the exciting source and the laser power was 10 mV. The wavenumber values of the spectra were accurate to 1 cm^{-1}. And the samples were grounded before every measurement.

X-ray photoelectron spectroscopy (XPS) data were obtained with experiments on Thermo Scientific Escalab 250Xi instrument