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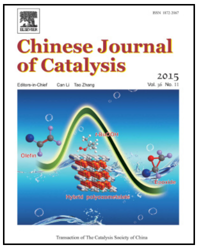

Article

Highly dispersed V_2O_5/TiO_2 modified with transition metals (Cu, Fe, Mn, Co) as efficient catalysts for the selective reduction of NO with NH_3

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ABSTRACT

Different transition metals were used to modify V_2O_5-based catalysts (M-V, M = Cu, Fe, Mn, Co) on TiO_2 via impregnation, for the selective reduction of NO with NH_3. The introduced metals induced high dispersion in the vanadium species and the formation of vanadates on the TiO_2 support, and increased the amount of surface acid sites and the strength of these acids. The strong acid sites might be responsible for the high N_2 selectivity at higher temperatures. Among these catalysts, Cu-V/TiO_2 showed the highest activity and N_2 selectivity at 225–375 °C. The results of X-ray photoelectron spectroscopy, NH_3-temperature-programmed desorption, and *in-situ* diffuse reflectance infrared Fourier transform spectroscopy suggested that the improved performance was probably due to more active surface oxygen species and increased strong surface acid sites. The outstanding activity, stability, and SO_2/H_2O durability of Cu-V/TiO_2 make it a candidate to be a NO$_x$ removal catalyst for stationary flue gas.

1. Introduction

Selective catalytic reduction (SCR) has proved to be the most effective technology in the control of NO$_x$ emissions from both stationary and mobile sources, such as coal-fired power plants and heavy duty diesel engines [1–6]. The most widely used SCR catalyst is a V_2O_5-based catalyst, which is very active when operating at 300–400 °C and highly tolerant to sulfur [7,8]. However, the V_2O_5-based catalyst still suffers from a low N_2 selectivity, narrow temperature window, and sublimation of V_2O_5 at high temperatures even after modification with molybdenum and tungsten species [9–15]. The prices of tungsten and molybdenum resources have also increased recently. Therefore, improving the V_2O_5-based catalyst with a low cost composition is still of great importance in industrial applications [16–18].

In recent years, many non-noble metals (Cu, Fe, Mn, Co, Ce, Zr, Nb, Sn, La, etc.) have been explored to promote the selectivity, operational temperature window, and stability of the V_2O_5-based catalyst [7,19–23]. Normally, the introduced metals are in the form of oxides or vanadates, which have many effects on the active V species [13,17,24,25]. The redox properties and

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dispersion of the vanadium species, the surface acid sites, and the inhibition of phase transfer from anatase to rutile are those most commonly targeted for improvement by introducing the metals. For example, the introduction of Fe_2O_3 improves the adsorption and activation of NH_3 [26], or the oxidation of NO to NO_2 [19]. Liu and co-workers [27] studied the effect of Mn on V_2O_5/TiO_2 for NH_3-SCR. They found that adding Mn significantly enhanced the activity, redox cycle, and the reactive intermediates, thus promoting the NH_3-SCR performance. Recently, some studies have shown that introducing the metals as vanadates can significantly improve the activity and N_2 selectivity, and especially the stability [28–30]. He and co-workers [29] have reported iron vanadates on TiO_2, which showed high activity, N_2 selectivity, and H_2O/SO_2 durability in NH_3-SCR reactions, which was due to the electronic inductive effect between the Fe^{3+} and V^{5+} species. Therefore, modifying the V_2O_5-based catalysts with low cost metals is possible and could be of great importance in industrial applications.

In this work, we introduced abundant, low cost transition metals (Cu, Fe, Mn, Co) into V_2O_5/TiO_2, forming highly dispersed M-V/TiO_2 catalysts for SCR reactions. The activity, N_2 selectivity, and SO_2/H_2O resistance of the different M-V/TiO_2 catalysts were studied. Both Cu-V/TiO_2 and Fe-V/TiO_2 performed excellently. The crystal structures and morphologies were characterised by X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and energy-dispersive X-ray analysis and element mapping (EDX mapping). Redox properties, surface active oxygen species and acid sites were studied by hydrogen temperature-programmed reduction (H_2-TPR), X-ray photoelectron spectroscopy (XPS), ammonia temperature-programmed desorption (NH_3-TPD), and *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (*in-situ* DRIFTS). The relationship between the catalytic performance and the physical and chemical properties of the catalysts was studied.

2. Experimental

2.1. Catalyst preparation

Titanium (IV) oxide (99.8%, anatase) with a particle size of about 25 nm was purchased from Aladdin. All other chemicals were purchased from Sinopharm Chemical Regent Company and all were used without further purification.

The M-V/TiO_2 catalysts were prepared by a co-impregnation method. In a typical process, the desired amounts of the nitrates of the different metals (Cu, Fe, Mn, Co) were first dissolved in deionised water. The amounts of $Cu(NO_3)_2\cdot 3H_2O$, $Fe(NO_3)_3\cdot 9H_2O$, $Mn(NO_3)_2$ (50 wt% aq.), and $Co(NO_3)_2\cdot 6H_2O$ were 0.23 g, 0.05 g, 0.28 g, and 0.23 g, respectively. The desired amount of ammonium metavanadate (NH_4VO_3) was dissolved in an aqueous solution of HNO_3. These amounts were 0.16 g, 0.25 g, 0.18 g, and 0.18 g, respectively. The total amount of all the M-V oxides was kept at 10% (mass fraction) of TiO_2 to achieve approximately monolayer coverage [29]. These two solutions were then mixed by magnetic stirring. TiO_2 (2.0 g) was then added to the mixed solution and dispersed with ultrasound and stirred for 1 h before being dried in a rotary evaporator at 48 °C with the help of a vacuum pump. These mixtures gave molar ratios of the metal to vanadium of 1:1.5, 1:17, 1:2, and 1:2, respectively, which were designed to favour the formation of vanadates, namely $CuV_2O_6/Cu_2V_2O_7$, $Fe_{0.12}V_2O_5$, MnV_2O_6, and CoV_2O_6. Finally, the so obtained samples were dried at 80 °C for 12 h and calcined at 400 °C for 6 h in air. For comparison, the V_2O_5/TiO_2 catalyst was also prepared by the same impregnation method without the addition of a nitrate.

For the comparative studies on the structure and the physical and chemical properties, the pure metal (Cu, Fe, Mn, Co) vanadates and corresponding metal (Cu, Fe, Mn, Co) oxides, namely 10% MO_x/TiO_2, were also prepared by the same impregnation method. The TiO_2 support and the ammonium metavanadate (NH_4VO_3) was absent from the preparation of these catalysts.

2.2. Characterisation

XRD was performed on a Rigaku D/MAX-RB X-ray diffractometer using Cu K_α (40 kV, 40 mA) radiation and a secondary beam graphite monochromator. Nitrogen adsorption-desorption isotherms of the samples were measured at −196 °C using a Micromeritics ASAP 2010 instrument, and the corresponding pore size distribution curves were calculated from desorption branches by the BJH method. The specific surface areas of the samples were calculated by the Brunauer-Emmett-Teller (BET) method. TEM and HRTEM were recorded on a JEM-200CX and JEM-2100F microscope, respectively. EDX mapping was obtained using an Inca Energy 200 TEM system from Oxford Instruments. To prepare the (HR)TEM and EDX-mapping samples, the M-V/TiO_2 samples were first dispersed in ethanol by ultrasonication for 30 min and a Cu grid was dipped into the solution (a Mo grid was used instead of a Cu grid to avoid disturbing the copper in the Cu-V/TiO_2 catalyst) and dried under the irradiation of infrared lamp before analysis. XPS of all the elements was recorded on a Perkin-Elmer PHI 5000C ESCA system equipped with a dual X-ray source, using a Mg-K_α (1253.6 eV) anode and a hemispherical energy analyser. The background pressure during data acquisition was kept below 10^{-6} Pa. All the binding energies were calibrated using contaminant carbon (C 1*s* = 284.6 eV) as a reference. The visible Raman spectra were recorded on an inVia-reflex Renishaw spectrometer equipped with a holographic notch filter, a CCD detector, and irradiated with a laser at 514 nm. The UV Raman spectra were recorded on a home-assembled UV Raman system equipped with a Jobin-Yvon T64000 triple-stage spectrograph. A He-Cd laser at 325 nm was used as the excitation source.

H_2-TPR and NH_3-TPD were conducted on a TianjinXQ TP-5080 auto-adsorption apparatus, and NH_3 and H_2 were monitored by a TCD. Each sample (80 mg) was pre-treated with high-purity N_2 (99.999%, 30 mL/min) at 300 °C for 30 min before either test. For H_2-TPR, after cooling to room temperature, the flowing gas was switched to 10% H_2-90% N_2 and the reactor temperature was raised to 800 or 900 °C at a rate of 10 °C/min. For NH_3-TPD, after cooling to 100 °C, the samples were