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ARTICLE

WO_3 Modification of MnO_x/TiO_2 Catalysts for Low Temperature Selective Catalytic Reduction of NO with Ammonia

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Abstract: A series of WO_3-modified MnO_x/TiO_2 catalysts were prepared by three different impregnation methods and were investigated by specific surface area measurement, X-ray diffraction, laser Raman spectroscopy, H_2 temperature-programmed reduction, high-resolution transmission electron microscopy, and in situ Fourier transform infrared spectroscopy. The three-component catalysts obtained with the one-step impregnation exhibited the best catalytic activity. The characterization data revealed that a synergism between tungsten and manganese oxide existed in the catalysts when tungsten was loaded either prior to or simultaneously with manganese, which made the active components better dispersed and blocked the transformation of TiO_2 from the anatase to rutile structure. The manganese oxide existed in the form of Mn_2O_3 on all the samples but was accompanied by a small amount of MnO_2 for $15\%MnO_x$-$5\%WO_3/TiO_2$. WO_3 improved the reducibility and enhanced the amount and strength of the surface acid sites, especially the Brönsted acid sites and promoted the formation of the active intermediate ($-NH_2$). Lewis acid sites had the major role in the low temperature selective catalytic reduction reaction while surface $-NH_2$ was an important intermediate species.

Key words: tungsten oxide; modification; manganese oxide; low-temperature selective catalytic reduction; surface acidity; active intermediate

There is interest in developing a low temperature (353–533 K) selective catalytic reduction (SCR) catalyst so that the catalyst bed can be placed downstream of the desulfurization scrubber and/or particulate control device where most of sulfur dioxide and dust is removed to have less deactivation. Some transition metal containing catalysts, including Cr/TiO_2 [1], $NiSO_4/Al_2O_3$ [2], MnO_x/Al_2O_3 [3], V_2O_5/activated carbon [4], CuO/Al_2O_3 [5], CuO/TiO_2 [6], Fe_2O_3/TiO_2 [7], iron-silica aerogels [8], MnO_x/NaY [9], and other oxides [10], had been investigated and shown to be active for medium temperature SCR of NO with NH_3 in the presence of excess oxygen. Peña et al. [11] investigated a series of catalysts prepared from various transition metal oxides (V, Cr, Mn, Fe, Co, Ni, and Cu) on titania and reported that MnO_x/TiO_2 catalysts can be used below 423 K with both high NO conversion and N_2 selectivity.

Manganese oxide has attracted interest for its higher SCR activity at low temperature. It contains various types of labile oxygen, which are necessary in the catalytic cycle [12]. Mn-based low temperature catalysts that have been investigated can be divided into three categories: unsupported, supported, and binary metal oxide-based catalysts. The activity and selectivity of pure manganese oxide in SCR was investigated by Kapteijn et al. [12], and 90% NO conversion was obtained at 450 K. For the supported catalysts, carriers like Al_2O_3 [3], TiO_2 [13,14], USY [15], MnO_x/AC [16], and MnO_x/ACF [17] have been widely studied. Among these, MnO_x/TiO_2 catalysts gave a higher catalytic activity at low temperature [11]. The other kind of Mn-based catalysts are mixed oxides doped with a transitional metal to make use of a synergistic effect between the two metal oxides. Mn-Fe com-

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posite oxides have been investigated. Chen et al. [18] reported that a Fe(0.4)-MnO_x catalyst showed the best activity, yielding 98.8% NO_x conversion and 100% selectivity for N_2 at 393 K and a space velocity of 30000 h^{-1}. This may be due to the formation of the active center $Fe_3Mn_3O_8$. Liu et al. [19] reported that the interaction of iron, manganese, and titanium species in $Fe_{0.5}Mn_{0.5}TiO_2$ catalyst gave the highest SCR activity. Some researchers have suggested that adding other metal oxides into MnO_x/TiO_2 can give it a higher low temperature activity. For examples, Li et al. [20] prepared a series of Cr-Mn catalysts by co-precipitation and found that Cr(0.4)-MnO_x had a high low temperature SCR activity due to the formation of $CrMn_{1.5}O_4$. Wu et al. [21] studied the effect of various transition metals (Fe, Cu, Ni, and Cr) on the catalytic activity of a Mn/TiO_2 catalyst and reported that the ternary oxides exhibited better catalytic performance than the double oxide counterparts. In particular, Cu (0.1)-Mn(0.6)/TiO_2 and Cr(0.1)-Mn(0.6)/TiO_2 gave 95% NO reduction at 413 K and Ni(0.1)-Mn(0.6)/TiO_2 gave 99% conversion. In addition, the carrier-free Cr(0.4)-MnO_x catalyst prepared by Chen et al. [22] gave 98.5% NO conversion at 393 K. Wu et al. [23] investigated TiO_2-supported MnO_x catalysts doped with a second metal, e.g., Fe_2O_3, WO_3, MoO_3, and Cr_2O_3 and found that the catalytic performance at low temperatures decreased in the order of Mn-W/TiO_2 > Mn-Fe/TiO_2 > Mn-Cr/TiO_2 > Mn-Mo/TiO_2, but the N_2 selectivity decreased in the order of Mn-Fe/TiO_2 > Mn-W/TiO_2 > Mn-Mo/TiO_2 > Mn-Cr/TiO_2. In our previous studies [24], it was also confirmed that Mo improved the catalytic activity and SO_2 resistance of MnO_x/TiO_2.

WO_3 is widely used as a promoter in the commercial V_2O_5-WO_3/TiO_2 catalyst. WO_3 provides high thermal stability to the catalyst by forming W–Ti–O chemical bonds on the TiO_2 surface [25], which inhibited the sintering of anatase TiO_2 and the anatase to rutile transition. In addition, WO_3 was reported to give a wider temperature window of SCR, increased the poison resistance to alkali metal oxides and arsenic oxide, and reduced ammonia oxidation and SO_2 oxidation [26]. With some SO_2 remaining even after the desulfurizer, both TiO_2 and WO_3 were more resistant to sulfur poisoning. Therefore, the ternary WO_3-MnO_x/TiO_2 catalyst can be a good catalyst for the low temperature SCR system.

In our previous report [27], the effect of WO_3 modification on a MnO_x/TiO_2 catalyst was studied. In this report, our research was focused on the comparative study of MnO_x-WO_3/TiO_2 catalysts synthesized by a one-step impregnation method with two different step-by-step preparation methods [27]. The catalysts were characterized by specific surface area measurement, X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), laser Raman spectroscopy (LRS), H_2 temperature-programmed reduction (H_2-TPR), and in situ FT-IR.

1 Experimental

1.1 Preparation of catalysts

The MnO_x/TiO_2 samples were prepared by the impregnation of TiO_2 (Degussa, P25) with manganese acetate. The deionized water (50 ml) was added to an 80 ml beaker containing 2.0 g of TiO_2 with steady stirring. Then, the appropriate amount of manganese acetate precursor was added.

WO_3/TiO_2 catalysts were also prepared by impregnating the same titania support with a water solution of ammonium paratungstate and oxalic acid. $MnO_x/WO_3/TiO_2$ catalysts were synthesized by a step-by-step impregnation of WO_3/TiO_2 with the solution of manganese acetate. $WO_3/MnO_x/TiO_2$ catalyst was also prepared by the step-by-step impregnation of MnO_x/TiO_2 with a solution of ammonium paratungstate and oxalic acid. The MnO_x-WO_3/TiO_2 catalyst was prepared by a one-step impregnation method. The required amount of hydrated ammonium paratungstate was added and dissolved in the solution of oxalic acid. Then, manganese acetate was added and the carrier titania was added to the mixture with continuously stirring. All the mixtures obtained after impregnation were stirred for 2 h at 25 °C and then at 85 °C for 4 h before they were dried overnight at 110 °C and calcined at 500 °C for 2 h. The loadings of MnO_x and WO_3 were 15 wt% and 5 wt%, respectively.

1.2 Catalytic activity

SCR activity measurements were carried out in a fixed bed reactor (i.d. 6 mm) at 80–300 °C containing 0.3 g of catalyst with a gas hourly space velocity (GHSV) of 24,000 h^{-1}. The total gas flow was 100 ml/min, which was premixed in a gas mixer to give the simulated gas of 0.08% of NO, 0.08% of NH_3, 5% of O_2 and balanced by N_2. Then the gas mixture was fed into the reactor. The NO and NO_2, concentrations were continuously monitored by a flue gas analyzer (Testo 330-2 LL).

1.3 Characterization of catalysts

Specific surface areas of the catalysts were measured by nitrogen adsorption at liquid N_2 temperature (−196 °C), using a Micromeritics F-sorb 3400 (Beijing Jinaipu, China) adsorption apparatus. An XD-3 diffractometer (Beijing PEPSEE, China) was employed with Cu K_α radiation (λ = 0.15406 nm) to get the XRD patterns of the catalysts. H_2-TPR was carried out in a quartz U-tube reactor connected to a thermal conduction detector (TCD) using a H_2-Ar mixture (7.3% H_2 by volume) as reductant. TPR was started from room temperature to 700 °C at a rate of 10 °C/min. Raman analysis was carried out on a Renishaw RM 2000 confocal microscope Raman spectrometer. A visible laser was used as the excitation light source with the following analysis parameters: output light intensity at 100% and 50%, scanning from 1200 to 100 cm^{-1} with a resolution of