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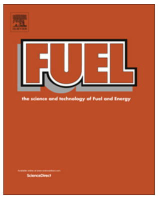

Full Length Article

Acidity, surface species, and catalytic activity study on V_2O_5-WO_3/TiO_2 nanotube catalysts for selective NO reduction by NH_3

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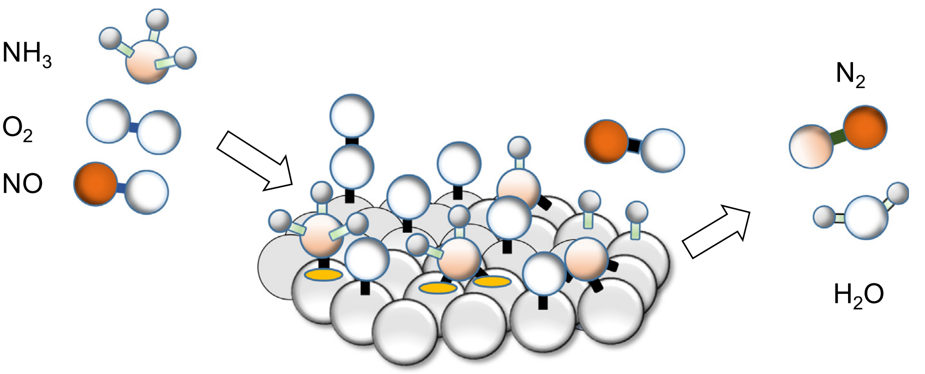
HIGHLIGHTS

- We analyze the acidity, redox properties and catalytic activity of V-W/NT catalysts.
- Reduced V^{4+}/V^{5+} species and Lewis and Brønsted acid sites promote the NO conversion.
- V_2O_5 increases Brønsted and Lewis acid sites. Lewis acid sites are promoted by WO_3.
- V-W/NT presents higher catalytic activity than W/NT and V/NT catalysts.
- NO conversion is not affected by SO_2, but water inhibits the catalytic activity.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we report the catalytic activity of V_2O_5/TiO_2, V_2O_5-WO_3/TiO_2 and WO_3/TiO_2-nanotube model catalysts in removing NO with NH_3 via the SCR process. The catalytic activity includes the effect of SO_2 and H_2O. We also analyze the effect of WO_3 and V_2O_5 loading upon the surface acidity of the nanotubes, and the effect of WO_3 on the V^{4+}/V^{5+} ratio, and its correlation with the catalytic activity. TiO_2-nanotubes (NT), employed as support, were prepared by hydrothermal treatment of TiO_2 with NaOH. The catalysts were characterized by X-ray diffraction, HR-TEM microscopy, N_2 physisorption, FTIR, H_2-TPR, Raman and XPS.

In general, we found that ternary catalysts (V_2O_5-WO_3/NT) showed a higher NO conversion versus V_2O_5/NT and WO_3/NT model catalysts. In fact, we found a high NO conversion (93%) over 3V-10W/NT catalyst at low temperature (380 °C). In the presence of SO_2 (50 ppm) and H_2O (5 vol.%), NO conversion slightly decreases (from 93 to 80% at 380 °C).

The surface acidity (Brønsted and Lewis) of the nanotubes is the main parameter improved by adding V_2O_5. WO_3 preferably modifies the Lewis acid sites of the nanotubes. Additionally, the structure and morphology of the nanotubes as well as the V^{4+}/V^{5+} ratio, which depend on the metal loading, play an important role in the removal of NO at intermediate temperatures even in the presence of SO_2 and H_2O.

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1. Introduction

The Selective Catalytic Reduction (SCR) with NH_3 is probably the best available technology to remove NOx from the stack gases of power plants and other stationary sources [1]. As for the catalysts used in SCR, V_2O_5/TiO_2 and V_2O_5-WO_3/TiO_2-based materials are the most active and probably the most commonly used because of their high activity, good thermal stability, and resistance to poisoning by SO_2 [2–7]. V_2O_5 is the active material for the catalytic activity in NO reduction. However, catalysts with V_2O_5 are usually limited at 2 wt.% in order to avoid the undesired SO_2 oxidation to SO_3. The addition of WO_3 promotes the catalytic activity, improves the acid properties of TiO_2, extend the operating temperature window for SCR, and stabilizes the anatase phase [8–10].

The interaction between TiO_2 and supported vanadium oxide results in surface oxide phases with structures that are remarkably different from those of the corresponding bulk oxides [11,12]. In the case of vanadium oxides, for instance, a low content of species with a strongly distorted tetrahedral geometry was observed; likewise, for higher contents of vanadium oxide, oligomeric or polymeric metavanadate species were formed [11,12]. Furthermore, a direct correlation between high surface $V^{3+} + V^{4+}/V^{n+}$ and V^{4+}/V^{5+} ratio and the SCR activity has been reported [13,14]. However, the behavior of the oxygen species attached to the vanadium and the dispersion of the active species are influenced by the support [13]. Well-dispersed and isolated vanadium oxide species show low activity for the SCR reaction but present a high selectivity towards N_2 [15]. The addition of tungsten modifies the surface acidity, which improves the ammonia supply for the SCR reaction and promotes the NO conversion [7]. However, the mechanistic aspects, such as the intrinsic nature of active sites and the reactive adsorbed NH_3 species (bounded to Brønsted or Lewis acid sites) involved in the SCR process, are not clear yet [16,17].

In this sense of investigation, different transition metal oxides and supports have been used to modify the properties of the V_2O_5-based catalysts in order to improve the catalytic activity. The main goal is to obtain a high dispersion of vanadium and the formation of vanadate species on the support, as well as to modify the surface acidity and the strength of the acid sites [18]. Several catalysts such as CeO_2/TiO_2 [19], Mn/TiO_2 [20], and NT structured catalysts such as Ce–carbon nanotubes [21]; Ce–titanium nanotubes [22], Cu/NT [23], and microspheres based on V_2O_5-$WO_3/Fe_2O_3/TiO_2$ [24] have been reported. The results consistently show that the combination of metal oxide catalysts modify the redox and acid properties of the catalytic materials to improve the NO reduction.

It has been reported [7] that the redox properties of the catalysts are involved with the catalytic activity at low temperature. The surface acidity seems to be involved with the absorption and activation of NH_3 at high temperature. However, the observed parallelism in the catalytic behavior of the catalysts reported in the literature (where the classic peak profile of the NO conversion reaches a maximum at a given temperature), and the competition of SCR and the ammonia oxidation reactions, suggest that the basic mechanism features of the reactions reported by different catalysts are probably the same [25]. In this case, the basic mechanism of the SCR system could be determined by the chemistry of the reactants [25].

The chemistry involved in the SCR process is complex and includes the typical stoichiometric reaction (1). The SCR process occurs when the selectivity to N_2 is close to 100% and the NH_3/NO ratio is close to 1. Oxygen does participate in the reaction (1), and NO is the main reactant. Adsorbed ammonia (molecularly adsorbed as unsaturated cations on Lewis acid sites or as ammonium ions over Brønsted acid sites) represents the active species.

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$

The two atoms of nitrogen arise, one from the ammonia and the other from the NO [25]. Water produced by the SCR process interacts with the surface of the catalysts and remains adsorbed on the reaction sites; avoiding the adsorption of ammonia. In fact, the presence of water, and SO_2 in the gas stream not only modifies the chemistry involved in the SCR system but also the activity of the catalysts is severely affected [25].

In this work, we report the NO conversion on V_2O_5, WO_3, and WO_3/V_2O_5-supported on TiO_2 nanotube model catalysts. The catalytic tests also include the presence of SO_2 and H_2O in the feed stream. We analyze the effect of 3 wt.% of V_2O_5, 3 wt.% of WO_3, and 3 wt.% of the WO_3/V_2O_5 ratio upon the surface acidity of the nanotubes. We also explore the redox properties and the vanadium species of the catalysts. Our main objective is to correlate the acid and redox properties of our catalysts with the catalytic activity of the SCR process. In general, we found that Brønsted and Lewis acid sites promotes the NO conversion at low temperature, up to 300 °C, but Lewis acid sites remains above 300 °C. Besides, the maximum NO conversion was reached when the ratio of the reduced V^{4+}/V^{5+} species is close to 0.75.

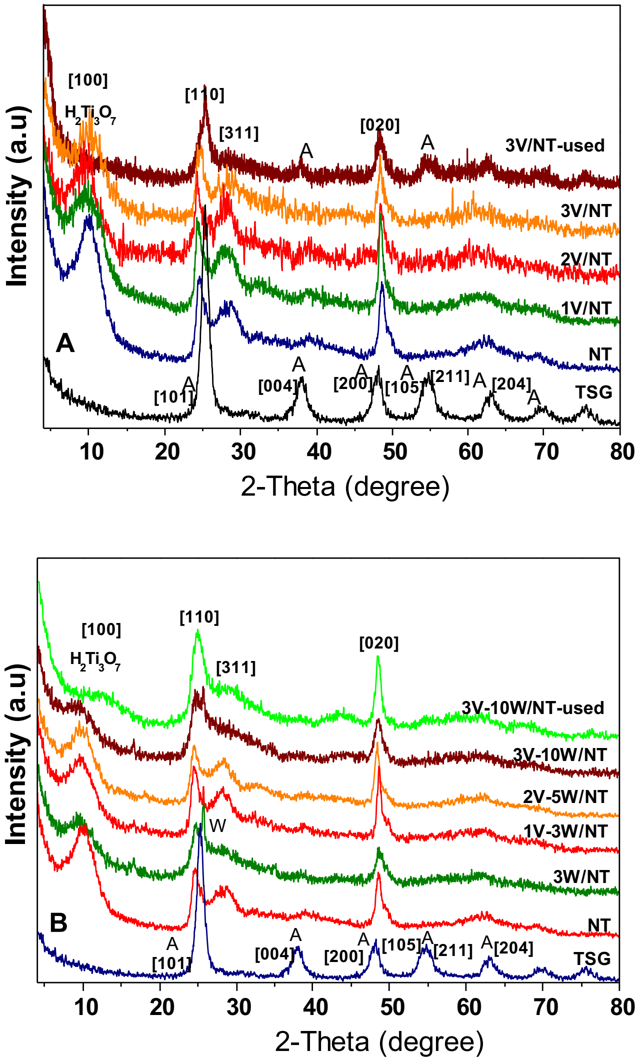

Fig. 1. XRD patterns for (A) V/NT and (B) V-W/NT catalysts. $H_2Ti_3O_7$ means the trititanic acid phase and A means anatase phase. TSG means titania obtained by sol-gel. NT means titania nanotubes.

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