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Water in the ball-milling process affects the dispersion of vanadia species on V₂O₅/TiO₂ catalysts for NH₃-SCR†

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Due to the formation of abundant hydroxyl groups on the TiO₂ support, water in the ball-milling process promoted the dispersion of vanadia species on V₂O₅/TiO₂ catalysts. Therefore, a high ratio of polymeric vanadyl species and strong redox capability were obtained for the vanadia-based catalyst, which led to good NH₃-SCR activity.

Nitrogen oxides (NO_x), mainly emitted from diesel vehicles and power plants, are important precursor pollutants resulting in the formation of acid rain, PM_{2.5}, and ozone.^{1–3} Selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) over V₂O₅-WO₃(MoO₃)/TiO₂ has been widely applied in the process of de-NO_x from stationary sources.^{4–6} Due to the high operating temperature window of vanadia-based catalysts, the de-NO_x unit for coal-fired power plants is usually placed upstream of the particle removal device and desulfurizer.⁷ However, the low temperature of the flue gas from other industries, such as cement, coking, ceramics, and industrial boilers, makes the control of NO_x emissions from these industries a challenge.⁸ Therefore, many efforts have been devoted to improving the

SCR activity of vanadia-based catalysts and lowering the temperature of the NH₃-SCR reaction.

Many techniques such as adding promoters, regulating the morphology, and modifying the support have been applied to promote the SCR activity of vanadia-based catalysts. A V₂O₅-WO₃/TiO₂ catalyst decorated with a highly dispersed sub-monolayer of Mo exhibited excellent catalytic activity at 230–400 °C and presented strong resistance to H₂O and SO₂.⁹ In our previous study, treatment by sulfate can promote the NH₃-SCR reaction over V₂O₅/TiO₂, and the activity increases with the sulfur content, resulting from the abundant polymeric vanadyl species formed.¹⁰ In addition, a vanadia-based catalyst with a TiO₂ support pretreated at a high temperature presented outstanding NH₃-SCR performance at low temperatures.¹¹

However, the preparation methods used in these studies are mainly the traditional solution-based methods (wet impregnation, co-precipitation, *etc.*), which need a large amount of water or other solvents. The solid ball-milling method has the advantages of high energy efficiency, solvent-free reaction, and environment-friendly processes, so it has been used in environmental catalysis. Ag/Al₂O₃ catalysts synthesized by wet impregnation and a semiwet ball-milling method showed similar reduction efficiency of NO_x by ethanol.¹² CeO₂/TiO₂ synthesized by ligand-assisted ball milling presented higher catalytic activity than that prepared by the impregnation method, owing to higher reducibility of cerium species, better dispersion, and a higher Ce³⁺ ratio resulting from the interaction between ligand molecules and cerium ions.¹³ Compared to the catalysts prepared by the wet impregnation method, V₂O₅/TiO₂ catalysts synthesised by the ball-milling method include a great amount of non-stoichiometric chemical species V^{x+}, and show high SCR activity in mid/low temperature ranges.¹⁴ In addition, the dry ball-milling method has also been proven to be able to induce a structural transformation from V₂O₅ crystallites to monomeric species, leading to an increase in the SCR reactivity of V₂O₅/TiO₂ catalysts.¹⁵ Therefore, the simple ball-milling method has good application prospects and would have an important effect

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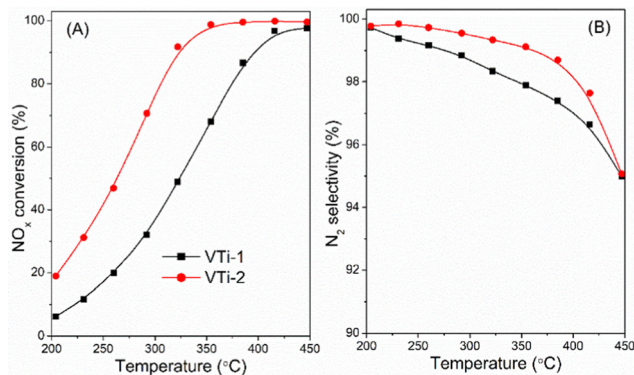


Fig. 1 NO_x conversion (A) and N_2 selectivity (B) over vanadia-based catalysts. Reaction conditions: $[\text{NO}] = 500$ ppm, $[\text{NH}_3] = 500$ ppm, $[\text{O}_2] = 5\%$, balance N_2 , GHSV = $100\,000\text{ h}^{-1}$.

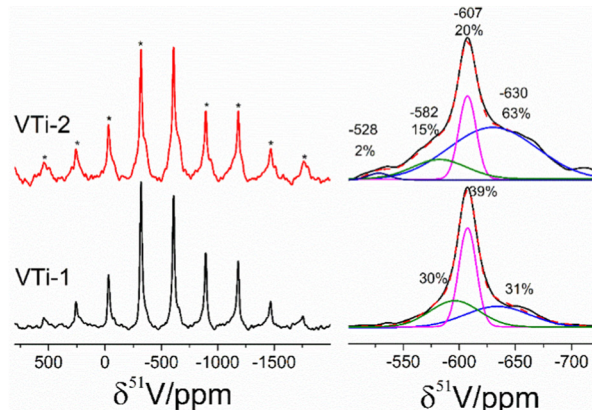


Fig. 2 Solid-state ^{51}V MAS NMR spectra of vanadia-based catalysts (left), and expansion of the corresponding isotropic regions (right).

on the physical-chemical properties and NH_3 -SCR activity of vanadia-based catalysts.

In this work, the ball-milling method was applied to synthesized vanadia-based catalysts, and it was found that the addition of a tiny amount of water in the ball milling process enhanced the NH_3 -SCR activity of $\text{V}_2\text{O}_5/\text{TiO}_2$ at low temperature.

Fig. 1 exhibits the SCR activity of vanadia-based catalysts with or without water in the preparation process. VTi-2, which was prepared in the presence of a tiny amount of water (1 mL $\text{H}_2\text{O}/6$ g support), presented much higher NH_3 -SCR activity than VTi-1, which was synthesized in the absence of water. 92% and 49% NO_x conversion were obtained at 320°C over VTi-2 and VTi-1, respectively. Better N_2 selectivity was exhibited on VTi-2 than VTi-1. Fig. S1 (ESI †) also shows that in the presence of water, V/Ti-2 has higher catalytic activity than V/Ti-1. Different amounts of water in the preparation process all improved the SCR activity (Fig. S2, ESI †). These results indicated that the addition of a tiny amount of water in the ball-milling process can promote the NH_3 -SCR reaction over vanadia-based catalysts at low temperatures.

The X-ray diffraction patterns (Fig. S3, ESI †) only show diffraction peaks attributed to anatase TiO_2 (JCPDS 21-1272) for both vanadia-based catalysts. In our previous study,¹⁶ part of anatase TiO_2 transformed into the rutile phase after pre-treatment, resulting in an increase in the proportion of the rutile phase, and the catalyst showed good SCR activity. However, in this study, the addition of water in the process of ball milling did not have an influence on the crystal structure of the catalyst. In addition, no diffraction peaks attributed to vanadia species were detected, illustrating that vanadium species are highly dispersed on TiO_2 or that the size and concentration of the V_2O_5 particles are lower than the detection limit. From N_2 physisorption results of vanadia-based catalysts (Table S1, ESI †), VTi-1 and VTi-2 presented similar specific surface areas. There is also not much difference in the pore diameters and pore volumes. TEM images show that the morphology and particle size of VTi-1 were similar to that of VTi-2 (Fig. S4, ESI †). Therefore, it can be concluded that the different

preparation processes don't affect the physical properties of the vanadia/titania catalysts.

Solid-state NMR spectroscopy is a feasible technique to investigate the state of vanadia species¹⁷ and the ^{51}V magic-angle spinning (MAS) NMR spectra are shown in Fig. 2. Several peaks at about -528 , -582 , -607 and -630 ppm were observed in the isotropic regions for these two catalysts. According to the literature,^{17,18} the peaks attributed to polymeric vanadyl species were shown at -582 and -630 ppm, while the peaks at -528 ppm and -607 ppm were assigned to monomeric vanadyl species and V_2O_5 -like nanoparticles, respectively. The deconvolution results in Fig. 2 indicated that the proportion of polymeric vanadyl species on VTi-2 was 78%, higher than that (61%) on VTi-1. Also, VTi-2 presented a lower proportion of bulk V_2O_5 than VTi-1. In our previous study,¹¹ crystalline V_2O_5 on the impregnated $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst could be transformed into polymeric vanadyl species when NH_3 was introduced, facilitating the NH_3 -SCR reaction. However, in this study, the vanadia-based catalysts were prepared by the ball-milling method, and the transformation from crystalline V_2O_5 into polymeric vanadyl species was not observed (Fig. S5, ESI †).

In the ball-milling process, the difference of VTi-1 and VTi-2 was the absence or presence of water. Fig. 3 presents the larger amount of hydroxyl groups on VTi-2 (prepared in the presence of H_2O) than VTi-1. According to the literature,^{19,20} H_2O can adsorb and dissociate on the surface of TiO_2 to form hydroxyls. Therefore, the addition of water in the preparation process can lead to the formation of lots of hydroxyl groups on TiO_2 . Low loading of vanadium preferably anchors at the surface Ti-OH sites of the TiO_2 support, while further increasing the vanadium content consumes almost all the remaining bridging Ti-(OH)-Ti sites.²¹ This indicates the interaction of vanadia and titania through the hydroxyl groups. Therefore, the existence of hydroxyl groups was beneficial to the dispersion of vanadia species, inhibited the formation of crystalline V_2O_5 and enhanced the interaction of titania and vanadia. As a result, NMR spectra show that VTi-2 presents more polymeric vanadyl species and less crystalline V_2O_5 . In our previous study,¹⁰ polymeric vanadyl was regarded as the main active species of

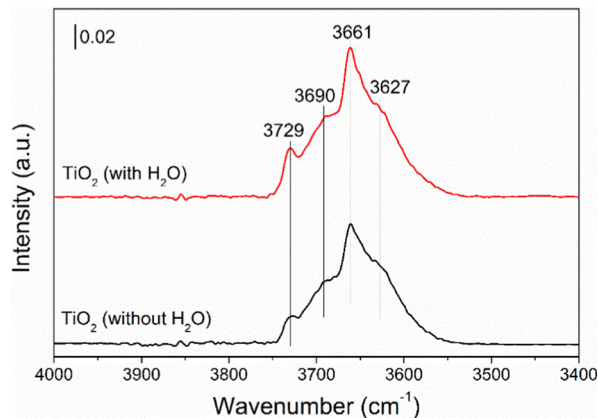


Fig. 3 IR spectra of the hydroxyl region of dehydrated TiO₂ after the ball-milling process with or without water.

NH₃-SCR at low temperature. Therefore, the higher ratio of polymeric vanadyl on VTi-2 resulted in higher SCR catalytic activity.

H₂-TPR results are exhibited in Fig. 4. Both catalysts showed a reduction peak around 400–500 °C, which was ascribed to the reduction of surface V or Ti species.^{11,22} The reduction temperature of VTi-2 by H₂ (424 °C) was lower than that of VTi-1 (476 °C), illustrating that V/Ti-2 presented stronger redox ability at low temperatures than V/Ti-1. The dispersed vanadia was easily reduced by H₂ and the reduction of V₂O₅ crystallites occurred at higher temperature.²³ Therefore, better dispersion of vanadia species of VTi-2 than VTi-1 on account of the existence of water in the preparation process (from NMR results) leads to the lower reduction temperature of V/Ti-2. The stronger redox capability over VTi-2 can be beneficial to the NH₃-SCR reaction at low temperatures.

The XPS results of the O 1s signals are shown in Fig. S6 (ESI†). The primary peaks centered at 530 eV were ascribed to the lattice oxygen species (denoted as O_β), while the shoulder peaks centered at 531 and 533 eV were assigned to the surface adsorbed oxygen (O_α) and adsorbed water or other hydroxyl species (O_γ), respectively.²⁴ Surface adsorbed oxygen is more

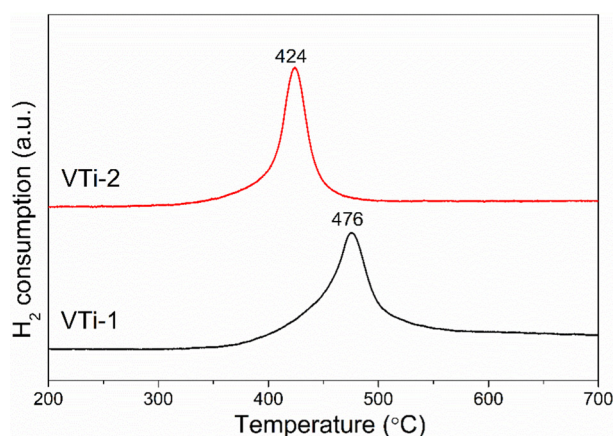


Fig. 4 H₂-TPR results of vanadia-based catalysts.

active in the oxidation of NO to NO₂ due to its higher mobility.²⁵ Fig. S6 (ESI†) also lists the relative surface concentration ratios of O_α for VTi-1 and VTi-2. The O_α/O_{all} ratio on VTi-2 was higher than that on VTi-1, which could promote the NO oxidation and then enhance the fast SCR reaction.

It is well accepted that the acidity of catalysts is a key parameter affecting NH₃-SCR catalytic activity. The NH₃-TPD results are shown in Fig. S7 (ESI†). The desorption peaks at 200–500 °C are ascribed to the desorption of NH₃ linked to various acid sites.^{26,27} It was found that VTi-2 presented a larger amount of acid sites than VTi-1. The presence of more abundant acid sites on VTi-2 than VTi-1 was beneficial to the adsorption and activation of NH₃, leading to higher NO_x conversion and N₂ selectivity.

In this study, environment-friendly ball-milling methods were used to prepare V₂O₅/TiO₂ catalysts. Water in the preparation process has an important influence on the physicochemical properties of the catalysts. The presence of trace amounts of water in the synthesis process resulted in the formation of abundant surface hydroxyl groups on TiO₂, which contributed to the dispersion of vanadium species. Therefore, fewer crystalline V₂O₅ and greater polymeric vanadyl species formed on the catalyst. Furthermore, the catalyst also presented stronger redox capability owing to the good dispersion of V species. All these factors favoured the NH₃-SCR reaction of the catalyst prepared by ball milling with a tiny amount of water. This work provides an environment-friendly method for preparing deNO_x catalysts and a simple method to increase the active sites of vanadia-based catalysts.

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Conflicts of interest

There are no conflicts to declare.

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