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Effect of preparation methods on VO_x/CoO_2 catalysts for the selective catalytic reduction of NO_x with $NH₃$

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Figure S1 exhibits the NH₃-SCR activity over VO_x/CoO_2 with different loadings prepared by the homogeneous precipitation method. With the increase of VO*^x* loading, NO_x conversion increased obviously, especially in the temperature window of 150-300 °C. 3% wt.% VO_x/Co_2 showed higher catalytic activity than 1%, 0.5%, and 0.1%. Due to the toxicity of vanadium to the human body, a vanadium-based catalyst with too high loading was not preferred. Therefore, we chose the 3% VO_x/CeO₂ catalyst to investigate rather than catalysts with higher loading.

Figure S1 NH_3 -SCR activity over VO_x/Co_2 with different loadings.

Reaction conditions: $[NO] = [NH₃] = 500$ ppm, $[O₂] = 5$ vol. %, N₂ balance, total flow rate 500 ml/min and GHSV = 50 000 h⁻¹.

The N_2 selectivity of VO_x/Co_2 catalysts prepared by different methods is shown in Figure S2. All the catalysts presented higher than 90% N₂ selectivity and only a little N₂O was produced at the temperatures we investigated.

Figure S2. The N_2 selectivity in NH_3 -SCR reaction over VO_x/CoO_2 catalysts

prepared by different methods.

The NH₃-SCR performance of VO_x/Co_2 catalysts after SO_2 poisoning for 24 h is shown in Figure S3. After SO_2 poisoning, the activity of all the catalysts decreased noticeably. However, the activity of $VO_x/CO_2(P)$ was still higher than that of other catalysts. 100% NO_x conversion could be obtained on the $VO_x/Co_2(P)$ catalyst at 250 °C and 70% on $\text{VO}_x/\text{CeO}_2(S)$. This proved again that the $\text{VO}_x/\text{CeO}_2(P)$ catalyst showed the strongest $SO₂$ resistance.

Figure S3. NH₃-SCR activity of $VO_x/Co_2(P)$ and $VO_x/Co_2(S)$ catalysts after 100

ppm SO² poisoning for 24 h.

Reaction conditions: $[NO] = [NH₃] = 500$ ppm, $[O₂] = 5$ vol. %, N₂ balance, total flow rate 500 ml/min and GHSV = 50 000 h⁻¹.

The separate oxidation activities of NO and NH_3 on VO_x/CeO_2 catalysts are shown in Figure S4. The NO oxidation activity of $VO_x/Co_2(P)$ was a little higher than that of $VO_x/Co_2(S)$. It has been reported that the enhancement of NO oxidation to $NO₂$ could significantly promote the low temperature SCR activity due to the occurrence of "fast SCR": NO and NO₂ react with NH₃ to form N₂ and H₂O.¹⁻² Higher catalytic activity over the $VO_x/CoO_2(P)$ catalyst could be related to its slightly higher NO oxidation activity.

The $VO_x/Co_2(P)$ catalyst showed a bit higher NH_3 oxidation activity than $VO_x/CeO_2(S)$ in the temperature range investigated. This indicates that the VO_x/CeO₂(P) catalyst adsorbed and activated NH₃ more easily and therefore achieved higher NH_3 -SCR activity than the $VO_x/CeO_2(S)$ catalyst.

Figure S4. NH₃/NO conversion in separate NH₃ or NO oxidation reactions over

 $VO_x/CoO_2(P)$ and $VO_x/CoO_2(S)$ catalysts.

Reaction conditions: $[NO] = 500$ ppm or $[NH_3] = 500$ ppm, $[O_2] = 5$ vol. %, N₂

balance, total flow rate 500 ml/min and GHSV = 50000 h⁻¹.

The changes in band intensities of nitrate species on NO*^x* pre-adsorbed catalysts during the introduction of NH_3 are shown in Figure S5. When NH_3 was introduced, the intensity of the bands attributed to monodentate nitrate and bridging nitrate species decreased slightly. The amount of bidentate nitrate species increased markedly, which may be due to the transformation of monodentate and bridging nitrate to bidentate nitrate.

Figure S5.The band intensities of nitrate species calculated from DRIFT spectra

(Figure 9) centered at 1542 cm^{-1} (monodentate nitrate), 1203 cm^{-1} (bridging nitrate)

and 1245 cm⁻¹ (bidentate nitrate) of $VO_x/Co_2(P)$ (A) and $VO_x/Co_2(S)$ (B).

References

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