Support shape effect on the catalytic performance of VO\textsubscript{x}/CeO\textsubscript{2} catalysts for the selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3}

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Abstract: VO\textsubscript{x}/CeO\textsubscript{2} catalysts, employing CeO\textsubscript{2} nanocubes (NCs), nanorods (NRs), and nanopolyhedrons (NPs) with predominately exposed \{100\}, \{110\}, and \{111\} facets as the supports, were prepared by an incipient wetness impregnation method. The catalysts were characterized in detail and applied to the selective catalytic reduction (SCR) of NO\textsubscript{x} with NH\textsubscript{3}. The catalytic tests showed that V-CeO\textsubscript{2}-NPs could achieve significantly higher NO conversion than V-CeO\textsubscript{2}-NCs and V-CeO\textsubscript{2}-NRs across the entire temperature range. The characterization results confirmed that the redox and acidic properties of VO\textsubscript{x}/CeO\textsubscript{2} catalysts were closely related to the exposed facets of corresponding CeO\textsubscript{2} supports.

Keywords: CeO\textsubscript{2} support, facets, VO\textsubscript{x} species.

1. Introduction (11-point boldface)
Currently, nitrogen oxides (NO\textsubscript{x}, including NO and NO\textsubscript{2}) from stationary and mobile sources have been regarded as major air pollutants. Ceria (CeO\textsubscript{2}) has been attracted much attention due to its high oxygen storage capacity and nice redox property. Recently, CeO\textsubscript{2} nanocrystals with well-defined morphologies were successfully synthesized and used as catalysts or supports for various catalytic reactions, in which the shape-dependent catalytic performances were observed clearly. Here, VO\textsubscript{x}/CeO\textsubscript{2} catalysts employing CeO\textsubscript{2} nanocubes (NCs), nanorods (NRs) and nanopolyhedrons (NPs) as the supports were prepared (denoted as V-CeO\textsubscript{2}-NCs, V-CeO\textsubscript{2}-NRs, V-CeO\textsubscript{2}-NPs) and applied to the NH\textsubscript{3}-SCR reaction. The catalytic performances of these catalysts were found to be quite different. To elucidate this difference, the surface structure, redox and acidic properties of VO\textsubscript{x}/CeO\textsubscript{2} catalysts were investigated using various characterization techniques. The results indicated that the catalysts displayed significant support-morphology-dependent SCR activity.

2. Experimental (or Theoretical)
CeO\textsubscript{2} supports with various morphologies were prepared by a hydrothermal method according to the previous report. The V-CeO\textsubscript{2}-NCs catalyst with a vanadia (VO\textsubscript{x}) loading of 5 wt% was prepared by an incipient wetness impregnation method. The CeO\textsubscript{2}-CNs support was impregnated with an aqueous solution of NH\textsubscript{4}VO\textsubscript{3} in oxalic acid (\(n\text{NH}_4\text{VO}_3: n\text{oxalic acid} = 1:2\)). Then, the sample was dried at 100 °C overnight and calcined at 500 °C for 4 h. The V-CeO\textsubscript{2}-NRs and V-CeO\textsubscript{2}-NPs catalysts were prepared by a similar method.

3. Results and discussion
The TEM and HRTEM images of CeO\textsubscript{2} supports are collected in Figure 1. Furthermore, the schematic illustrations of the idealized support shapes are also shown in Figure 1. As shown in the Figure 1, we could see that CeO\textsubscript{2}-NCs only exposes \{100\} facets, while CeO\textsubscript{2}-NRs and CeO\textsubscript{2}-NPs mainly expose \{110\} and \{111\} facets, respectively.

Figure 2 shows the NH\textsubscript{3}-SCR performance of VO\textsubscript{x}/CeO\textsubscript{2} catalysts at temperature ranging from 150 to 400 °C under a GHSV of 120, 000 mL g\textsuperscript{-1} h\textsuperscript{-1}. A significant difference on the catalytic performance is observed over the three catalysts. V-CeO\textsubscript{2}-NPs displays the best SCR activity, followed by V-CeO\textsubscript{2}-NCs, and V-CeO\textsubscript{2}-NRs shows negligible NO conversion. Furthermore, more than 90% N\textsubscript{2} selectivity is obtained over V-CeO\textsubscript{2}-CPs in the whole temperature range investigated (Figure 2b).
Figure 1. TEM images, HRTEM images, and schematic illustrations for CeO2-NCs (a1, a2, a3), CeO2-NRs (b1, b2, b3), CeO2-NPs (c1, c2, c3).

Figure 2. NO conversion (a) and N2 selectivity (b) as a function of temperature in the NH3-SCR reaction. Reaction conditions: [NO] = [NH3] = 500 ppm, [O2] = 5%, [H2O]= 5.5% (when used), [SO2]=110 ppm (when used), N2 balance, total flow rate 200 mL min⁻¹ and GHSV = 120,000 mL g⁻¹ h⁻¹.

4. Conclusions

In summary, VOₓ/CeO₂ catalysts with same VOₓ loading with tunable CeO₂ morphology/facet were prepared, and then the catalytic properties of such catalysts were further investigated in the NH3-SCR reaction. The combination of characterization techniques and activity test demonstrated that VOₓ/CeO₂ catalysts displayed significantly support-morphology-dependent catalytic activity. This study not only provides a facile method for the preparation of highly efficient CeO₂-based SCR catalysts, but also enables a better understanding of the relationship between the support morphology and catalytic performance of supported vanadium catalysts.

References