Preparation and Denitrifying Performance of V_2O_5 - MoO_3 / TiO_2 - CeO_2 /H-Mordenite[†]

RUJUN XUE*, CHUNYANG CHEN, QINGCHAO WANG, MIN ZHOU and SHUFEN CHEN

School of Chemical Engineering and Technology, Anhui University of Science and Technology, Huainan 232001, P.R. China

*Corresponding author: Tel: +86 554 6631981; E-mail: klzhu@aust.edu.cn

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With MoO_3 as additive, V_2O_5 coatings was loaded to H-mordenite zeolite- TiO_2 composite carrier to prepare V_2O_5 - MoO_3 / TiO_2 - CeO_2 /HM as NO_x SCR catalyst. X-Ray diffraction, N_2 adsorption-desorption and NH_3 temperature programmed desorption (NH_3 -TPD) techniques were used to characterize the structure, surface area, acidity of the catalyst. Denitration performance of the catalyst was investigated using fixed-bed micro-reactor. The effect of V_2O_5 content on denitrification performance was studied extensively. Experimental results show that H-mordenite zeolite is beneficial to increase the specific surface area of the TiO_2 support and improve V_2O_5 dispersing on the carrier in a monolayer state. The catalyst with 8 % V_2O_5 load displays optimal denitration performance. When the V_2O_5 load $\geq$ 8 % V_2O_5 , the catalytic activity decrease. MoO_3 has help to vanadium-base catalyst and the denitration performance of the V_2O_5 / CeO_2 - TiO_2 /HM with MoO_3 additive increased and NO conversion reached to 92 %.

Keywords: V_2O_5 - MoO_3 / TiO_2 - CeO_2 /H-mordenite catalyst, Denitration performance, Preparation.

INTRODUCTION

Nitrogen oxides are the main component of air pollution. At present, the main NO_x elimination technologies are to use flue gas denitrification method. Within them selective catalytic reduction (SCR) is the most widely used manner due to its high efficiency and high selectivity. The catalyst can be divided into three types, namely supported noble metal, composite metal oxide and zeolite catalyst. In the early times, precious metal-based catalyst was the main catalyst of SCR¹. In recent years, of metal oxide such as V_2O_5 - WO_3 and V_2O_5 - MoO_3 loaded on TiO_2 have replaced noble metal catalysts to be used in traditional SCR². And molecular sieve catalyst replaced the noble metal catalysts for SCR purification of high temperature combustion exhaust gas due to its good thermal stability. But the catalyst activity of the zeolite catalyst is poor, studies referred to various metal ions exchanged onto zeolite to strengthen the SCR catalytic activity were conducted^{3,4}.

Vanadium based catalyst having a moderate oxidation-reduction capacity is widely used in selective catalytic reduction of NO_x and in elimination of SO_x and NO_x . But the presence form of vanadium oxide, surface acidity and oxidation-reduction capacity of the catalyst and the like were affected greatly by the carrier². Titanium dioxide has greater surface

area and pore size than γ - Al_2O_3 , is either beneficial to the diffusion of reactants or conducive to loading high content V_2O_5 which making TiO_2 -base catalysts with higher SCR activity⁵. But V_2O_5 / TiO_2 catalyst also has its drawbacks *i.e.*, its disabled effect by alkali metal⁶; easy to be sintered for the poor thermal stability of TiO_2 support and tendency of existing in polycrystalline form⁷. These confine the operating temperature of the catalyst lower than 420 °C. At higher temperatures the selectivity of the catalyst would drop down.

In view of the disadvantages of the existing SCR catalysts for NO_x , this study prepare the catalyst with zeolite and TiO_2 as composite carrier, V_2O_5 coating as a active component which convert NO_x and by introducing MoO_3 into V_2O_5 as the additive to enhance its SCR activity and selectivity. Furthermore modifying the TiO_2 with CeO_2 to stabilize the crystal phase and grain size of TiO_2 for increasing its surface area. Cerium dioxide also has an excellent ability to store and release oxygen, which is helpful to improve the catalytic activity and selectivity. Dispersing TiO_2 onto the zeolite could increase the acidity of TiO_2 carrier and avoid its pore structure collapsed during the heat treatment by the aid of the acidity and the heat stability of zeolite, thus ensuring the pore structure and specific surface area of the TiO_2 .

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EXPERIMENTAL

Catalyst preparation: H-mordenite (HM) was obtained with Na-mordenite (NaM, Dalian catalyst plant) by means of ion exchange with NH_4Cl solution and calcined at 550°C for 4 h subsequently.

With cyclohexane, Triton X-100 and *n*-butanol constituted the oil solution. Then TiCl_4 and aqueous solution of cerium nitrate were added into half oil solution and stirred to obtain microemulsion I. Aqueous solution of ammonia was added to other half oil solution to formulate microemulsion II, in which 5.5 g HM was uniformly dispersed. Under continuously stirring, microemulsion I was mixed with microemulsion II slowly and reacted for 1 h at the pH 8.5 value. Following this, the catalyst precursor was filtered, washed thoroughly with ethanol-acetone solvent and dried for 4 h at 105°C , calcined at 500°C for 3 h. Thus $\text{CeO}_2\text{-TiO}_2\text{/HM}$ catalyst carrier was obtained.

Using deionized water as solvent, oxalic acid, ammonium metavanadate and ammonium molybdate were dissolved. Then $\text{CeO}_2\text{-TiO}_2\text{/HM}$ catalyst carrier was added in under stirring. Evaporate the solvent slowly till the materials become sticky shape with 90°C water bath. The viscous material was dried at 120°C for 3 h, calcined at 450°C for 3h to achieve the catalyst.

Catalyst characterization: X-Ray diffraction patterns were collected using a Shimadzu XRD-6100 X-ray diffractometer equipped with a graphite monochromator, operating at 40 kV and 40 mA and employing nickel-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$).

Nitrogen adsorption/desorption at 77 K were measured using a Micromeritics TriStar3000 equipment after the samples were degassed ($1.33 \times 10^{-2} \text{ Pa}$) at 300°C overnight. The specific surface area was calculated following the method of Brunauer, Emmet and Teller (BET).

NH_3 temperature programmed desorption ($\text{NH}_3\text{-TPD}$) were measured using a Tianjin Xianquan TP-5000 adsorption instrument.

Evaluation of catalytic activity: The catalytic experiments were carried out in a fixed bed quartz tubular flow reactor (i.d. 6 mm, length 400 mm) at atmospheric pressure. The amount of the catalyst was 300 mg. The feed consisted of a mixture of $\text{CH}_4/\text{NO}/\text{O}_2/\text{He}$ with a volume ratio of 1/1/20/78. The flow rate was 300 mL/min. Experiments were carried out at $300\text{--}550^\circ\text{C}$, program heating rate $2^\circ\text{C}/\text{min}$. The feed and the reaction products were analyzed on-line by online gas chromatograph (Type GC-122, Shanghai). The nitrogen oxides were measured with a NOVA 300 CLD Chemiluminescent NO and NO_x analyzer.

Catalytic activity is calculated by the following formula: Conversion of NO = moles of (NO introduced – NO in exit gas) $\times 100 \%$ / moles of NO introduced

RESULTS AND DISCUSSION

XRD characterization of the sample: Fig. 1 is the XRD patterns of 0.5 % $\text{CeO}_2\text{-}20 \%$ $\text{TiO}_2\text{/HM}$. The diffraction peaks between $5\text{--}32^\circ$ range attribute to zeolite, the peaks are sharp and well-defined, implying that good crystallinity of the mordenite. The diffraction peaks at 25° and beyond 35°

Fig. 1. XRD pattern of $\text{CeO}_2\text{-TiO}_2\text{/HM}$

attribute to anatase TiO_2 , the peaks are lower and wider, indicating a very small grain size of TiO_2 . There is no characteristic diffraction peak of CeO_2 in Fig. 1. The reason is small amounts of CeO_2 doped into the TiO_2 crystal phase cannot be detected *via* XRD.

Influence of TiO_2 loading on Specific surface area of $\text{CeO}_2\text{-TiO}_2\text{/HM}$: The specific surface area data of the $\text{CeO}_2\text{-TiO}_2\text{/HM}$ samples with different TiO_2 load measured in the experiments are shown in Table-1.

HM	10 % $\text{TiO}_2\text{/HM}$	20 % $\text{TiO}_2\text{/HM}$	30 % $\text{TiO}_2\text{/HM}$	40 % $\text{TiO}_2\text{/HM}$	50 % $\text{TiO}_2\text{/HM}$
307	132	151	139	126	126

It can be seen from the data in Table-1 that profiting from the higher specific surface area of the mordenite, a higher TiO_2 load could be carried on HM. Furthermore, the zeolite added during the preparation of TiO_2 could effectively reduce the free energy of the TiO_2 crystal nucleation, which helped to generate smaller grains, therefore would increase the specific surface area of TiO_2 . However, the data in Table-1 also shown that after the load of $\text{TiO}_2 > 20 \%$, the specific surface area of $\text{CeO}_2\text{-TiO}_2\text{/HM}$ decreased, this was because that at this time TiO_2 not only deposited on the surface of the zeolite, also caused the zeolite pore blockage. Therefore, the optimum load of TiO_2 on zeolite is 20 % preferably, which could give the largest surface area of $\text{CeO}_2\text{-TiO}_2\text{/HM}$. The higher of TiO_2 specific surface area, the larger V_2O_5 load could reach on the one hand, more favorable of vanadium oxide species well dispersed on the carrier surface on the other hand, which would form more V_2O_5 active sites so that the SCR catalyst may provide a higher activity.

Surface acidity of the catalysts: The surface acidity of the catalysts was analyzed *via* $\text{NH}_3\text{-TPD}$ (Fig. 2).

Fig. 2. $\text{NH}_3\text{-TPD}$ curves of catalysts. (1) $\text{V}_2\text{O}_5/\text{TiO}_2$; (2) $\text{V}_2\text{O}_5/\text{CeO}_2\text{-TiO}_2\text{/HM}$; (3) $\text{MoO}_3\text{-V}_2\text{O}_5/\text{CeO}_2\text{-TiO}_2\text{/HM}$

Generally, low-temperature desorption peak ($< 400\text{ }^{\circ}\text{C}$) corresponds to the weak acid site, the middle-temperature desorption peak ($400\text{--}500\text{ }^{\circ}\text{C}$) corresponds to the moderate acid sites and the high-temperature peak ($> 500\text{ }^{\circ}\text{C}$) corresponds to the strong acid sites. As can be seen from Fig. 2, all catalysts at *ca.* $150\text{ }^{\circ}\text{C}$ have a desorption peak corresponding to the weak acid sites on the catalyst; V_2O_5 /CeO₂-TiO₂/HM at about $400\text{ }^{\circ}\text{C}$ emerged a broad peak, indicating that the catalyst was rich in moderate acid site; the NH_3 -desorption amount of MoO_3 - V_2O_5 /CeO₂-TiO₂/HM in the whole temperature ranges significantly increased, implying that the catalyst was rich in acidity and acidic site amount.

Denitrification performance of the catalysts with different V_2O_5 content: It can be seen from Fig. 3 that the active ingredient V_2O_5 content has a great influence on catalytic activity and MoO_3 - V_2O_5 (8 %)/CeO₂-TiO₂/HM possesses the best low-temperature catalytic activity. When compared to MoO_3 - V_2O_5 (5 %)/CeO₂-TiO₂/HM and MoO_3 - V_2O_5 (10 %)/CeO₂-TiO₂/HM, its NO conversion at $350\text{ }^{\circ}\text{C}$ was higher 16 and 12 %, respectively. The high-temperature activities of MoO_3 - V_2O_5 (5 %)/CeO₂-TiO₂/HM and MoO_3 - V_2O_5 (8 %)/CeO₂-TiO₂/HM were comparable both larger than that of MoO_3 - V_2O_5 (10 %)/CeO₂-TiO₂/HM and their NO conversion at $550\text{ }^{\circ}\text{C}$ closed 82 % while that of MoO_3 - V_2O_5 (10 %)/CeO₂-TiO₂/HM was approximately 42 %. On the other hand, high-temperature activity of the catalyst would decrease due to the enhanced V_2O_5 polymerization degree under high temperature. Fig. 3 showed the operating temperature window (NO conversion $\geq 80\text{ }%$) of MoO_3 - V_2O_5 (8 %)/CeO₂-TiO₂/HM is more wider ($320\text{--}550\text{ }^{\circ}\text{C}$) than that of the other catalysts, so the 8 % V_2O_5 content in the coating is the most suitable content of the active ingredient. The reason is as follows: when the V_2O_5 load on the support is low ($< 8\text{ }%$), vanadia can be well dispersed to form isolated tetrahedral vanadate species, which is the active center of the catalyst. With the increase of V_2O_5 load, the active center of the catalyst increases and catalytic ability raise. Vanadia species may form polymeric two-dimensional network in distorted tetrahedral and square-pyramidal coordination accompanying the increase of V_2O_5 load and the increased polymerization degree would reduce the number of active sites and decrease activity of the catalyst. Finally, at higher load ($> 15\text{ }%$), the main present form of V_2O_5 was three dimensional crystallites in octahedral coordination⁷, the catalysis of such a crystalline phase is very limited and makes the catalytic activity decrease.

Fig. 3. Influence of V_2O_5 content on denitrification performance of catalysts. (1) MoO_3 - V_2O_5 (8 %)/CeO₂-TiO₂/HM; (2) MoO_3 - V_2O_5 (5 %)/CeO₂-TiO₂/HM; (3) MoO_3 - V_2O_5 (10 %)/CeO₂-TiO₂/HM; (4) MoO_3 - V_2O_5 (15 %)/CeO₂-TiO₂/HM

Conclusion

Using molecular sieve as support, TiO₂ as the carrier to prepare V_2O_5 -based multi-component catalyst, the molecular sieve-TiO₂ composite carrier provided a larger surface area for loading more V_2O_5 active component. High V_2O_5 load and dispersion are helpful to increase acid active-sites so that the catalyst has a high activity. When V_2O_5 content is more than 8 %, the increased V_2O_5 polymerization degree makes the catalytic activity decrease. Catalyst MoO_3 - V_2O_5 (8 %)/CeO₂-TiO₂/HM displays the best denitration activity ($320\text{--}550\text{ }^{\circ}\text{C}$).

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