Preparation and Denitrifying Performance of V$_2$O$_5$-MoO$_3$/TiO$_2$-CeO$_2$/H-Mordenite†

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With MoO$_3$ as additive, V$_2$O$_5$ coatings was loaded to H-mordenite zeolite-TiO$_2$ composite carrier to prepare V$_2$O$_5$-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$_2$O$_5$ 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$_2$O$_5$ dispersing on the carrier in a monolayer state. The catalyst with 8 % V$_2$O$_5$ load displays optimal denitration performance. When the V$_2$O$_5$ load ≥ 8 % V$_2$O$_5$, the catalytic activity decrease. MoO$_3$ has help to vanadium-base catalyst and the denitration performance of the V$_2$O$_5$/CeO$_2$-TiO$_2$/HM with MoO$_3$ additive increased and NO conversion reached to 92 %.

Keywords: V$_2$O$_5$-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 SCR[1]. In recent years, of metal oxide such as V$_2$O$_5$-WO$_3$ and V$_2$O$_5$-MoO$_3$ loaded on TiO$_2$ have replaced noble metal catalysts to be used in traditional SCR[2]. 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 carrier[2]. Titanium dioxide has greater surface area and pore size than γ-Al$_2$O$_3$, is either beneficial to the diffusion of reactants or conducive to loading high content V$_2$O$_5$ which making TiO$_2$-base catalysts with higher SCR activity[5]. But V$_2$O$_5$/TiO$_2$ catalyst also has its drawbacks *i.e.*, its disabled effect by alkali metal[6]; easy to be sintered for the poor thermal stability of TiO$_2$ support and tendency of existing in poly-crystalline form[7]. These confine the operating temperature of the catalyst lower than 420 ºC. 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$_2$O$_5$ coating as a active component which convert NO$_x$ and by introducing MoO$_3$ into V$_2$O$_5$ 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$_2$.

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 ºC 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 with ethanol-acetone solvent and dried for 4 h at 105 ºC, calcined at 500 ºC for 3 h. Thus CeO_2-TiO_2/HM catalyst carrier was obtained.

Using deionized water as solvent, oxalic acid, ammonium metavanadate and ammonium molybdate were dissolved. Then CeO_2-TiO_2/HM catalyst carrier was added in under stirring. Evaporate the solvent slowly till the materials become sticky shape with 90 ºC water bath. The viscous material was dried at 120 ºC for 3 h, calcined at 450 ºC 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 CuK_α radiation (λ =1.5418 Å).

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

NH_3 temperature programmed desorption (NH_3-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 CH_4/NO/O_2/He with a volume ratio of 1/1/20/78. The flow rate was 300 mL/min. Experiments were carried out at 300-550 ºC, program heating rate 2 ºC/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) × 100 %/ moles of NO introduced

RESULTS AND DISCUSSION

XRD characterization of the sample: Fig. 1 is the XRD patterns of 0.5 %CeO_2-20 % TiO_2/HM. The diffraction peaks between 5-32º range attribute to zeolite, the peaks are sharp and well-defined, implying that good crystallinity of the mordenite. The diffraction peaks at 25º and beyond 35º
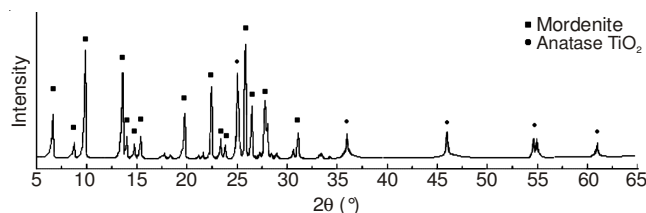

Fig. 1. XRD pattern of CeO_2-TiO_2/HM

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 CeO_2-TiO_2/HM: The specific surface area data of the CeO_2-TiO_2/HM samples with different TiO_2 load measured in the experiments are shown in Table-1.

TABLE-1 SPECIFIC SURFACE AREA OF CeO_2-TiO_2/HM WITH DIFFERENT TiO_2 LOAD, m^2/g					
HM	10 % TiO_2/HM	20 % TiO_2/HM	30 % TiO_2/HM	40 % TiO_2/HM	50 % TiO_2/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 TiO_2 > 20 %, the specific surface area of CeO_2-TiO_2/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 CeO_2-TiO_2/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.

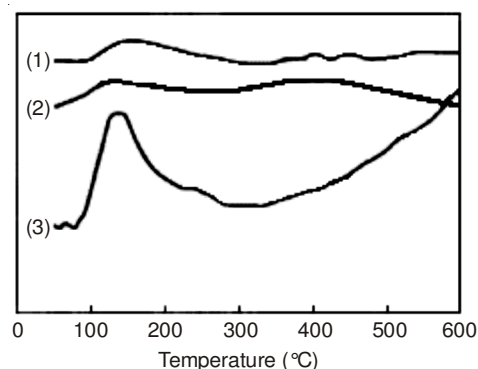**Surface acidity of the catalysts:** The surface acidity of the catalysts was analyzed *via* NH_3-TPD (Fig. 2).

Fig. 2. NH_3-TPD curves of catalysts. (1) V_2O_5/TiO_2; (2) V_2O_5/CeO_2-TiO_2/HM; (3) MoO_3-V_2O_5/CeO_2-TiO_2/HM

Generally, low-temperature desorption peak (< 400 ℃) corresponds to the weak acid site, the middle-temperature desorption peak (400-500 ℃) corresponds to the moderate acid sites and the high-temperature peak (> 500 ℃) corresponds to the strong acid sites. As can be seen from Fig. 2, all catalysts at *ca.* 150 ℃ have a desorption peak corresponding to the weak acid sites on the catalyst; V_2O_5/CeO_2-TiO_2/HM at about 400 ℃ 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/CeO_2-TiO_2/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 %)/CeO_2-TiO_2/HM possesses the best low-temperature catalytic activity. When compared to MoO_3-V_2O_5 (5 %)/CeO_2-TiO_2/HM and MoO_3-V_2O_5(10 %)/ CeO_2-TiO_2/HM, it's NO conversion at 350 ℃ was higher 16 and 12 %, respectively. The high-temperature activities of MoO_3-V_2O_5 (5 %)/CeO_2-TiO_2/HM and MoO_3-V_2O_5 (8 %)/ CeO_2-TiO_2/HM were comparable both larger than that of MoO_3-V_2O_5(10 %)/CeO_2-TiO_2/HM and their NO conversion at 550 ℃ closed 82 % while that of MoO_3-V_2O_5(10 %)/CeO_2-TiO_2/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 ≥ 80 %) of MoO_3-V_2O_5(8 %)/CeO_2-TiO_2/HM is more wider (320-550 ℃) 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 %), 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 %), the main present form of V_2O_5 was three dimensional crystallites in octahedral coordination[7], the catalysis of such a crystalline phase is very limited and makes the catalytic activity decrease.
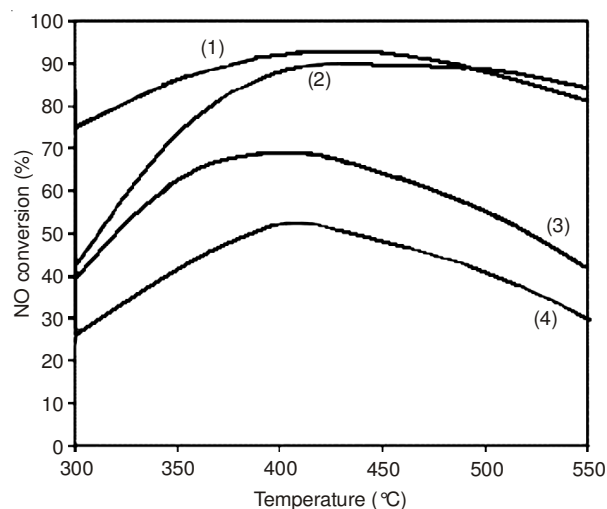

Fig. 3.　Influence of V_2O_5 content on denitrification performance of catalysts. (1) MoO_3-V_2O_5(8 %)/CeO_2-TiO_2/HM; (2) MoO_3-V_2O_5(5 %)/CeO_2-TiO_2/HM; (3) MoO_3-V_2O_5(10 %)/CeO_2-TiO_2/HM; (4) MoO_3-V_2O_5(15 %)/CeO_2-TiO_2/HM

Conclusion

Using molecular sieve as support, TiO_2 as the carrier to prepare V_2O_5-based multi-component catalyst, the molecular sieve-TiO_2 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 %)/CeO_2-TiO_2/HM displays the best denitration activity (320-550 ℃).

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