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Novel Approach for a Cerium-Base High-Efficient Catalyst with Excellent NH_3-SCR Performance

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A high-efficient NH_3-SCR catalyst, CeO_2/WO_3-TiO_2, was prepared by a novel stepwise precipitation approach. This catalyst showed excellent catalytic performance, with superior low-temperature activity, high N_2 selectivity and broad operation temperature window. Furthermore, the CeO_2/WO_3-TiO_2 catalyst could perform well even under an extremely high space velocity condition of 1,000,000 h^{-1}.

Selective catalytic reduction of NO_x with NH_3 (NH_3-SCR), using V_2O_5-WO_3/TiO_2 or V_2O_5-MoO_3/TiO_2 as catalyst, has been widely used for the removal of NO_x from stationary sources.[1] This technology has also been introduced into the market for diesel vehicles and is thought to be one of the best technologies for meeting the increasingly stringent standards for NO_x emissions.[2]

There have been strong interests to develop highly active catalysts, such as the manganese-based oxides, for low-temperature SCR.[3-5] Such a catalyst would be placed downstream the de-sulfurizer and electrostatic precipitator for stationary applications. The low-temperature activity of SCR catalyst is also very important for reducing NO_x emission from diesel vehicles, for example, during cold startup and on traveling short distances. To promote the NO_x reduction at low temperature, an upstream diesel oxidation catalyst (DOC) was often used to increase the NO_2/NO molar feed ratio and thus promote the fast SCR reaction. However, the optimal NO_2/NO molar ratio cannot be guaranteed due to the complex engine operating conditions.[6] Moreover, the installation of DOC, containing precious metals, will definitely increase the cost of NO_x reduction system and occupy more space on the vehicle. Due to the limited space onboard, one of the main challenges for diesel vehicles is the reduction of catalyst volume, which means that the SCR catalyst is demanded to have good performance under high space velocity condition in wide temperature range.[2]

Owing to the toxicity of active vanadium species and large N_2O formation of vanadium-based catalysts, great efforts have been made to develop substitutional environmentally-benign NH_3-SCR catalysts. Due to its unique redox, oxygen storage, and acid-base properties, ceria recently has attracted much attention for its applications in NH_3-SCR catalysts as support,[7] promoter,[8,9] or main active component. [10]

Pure CeO_2 oxides usually just possess poor NH_3-SCR activity. However, CeO_2-zeolites, obtained by the combination of CeO_2 with zeolites using simple physical mixing method, could achieve excellent NO_x conversions at very high space velocities.[11] The catalytic performance of CeO_2 could also be greatly improved by surface sulfation.[12] Ce-based composite oxide catalysts, such as Ce-Ti,[13] Ce-W,[14] Ce-Mo,[15] Ce-W-Ti,[16] and Ce-Cu-Ti[17] oxides, are more attractive than single oxide catalysts because other metal elements can promote the catalytic properties of CeO_2. In this study, a high efficient CeO_2/WO_3-TiO_2 catalyst was prepared using a novel stepwise precipitation approach, and the catalyst showed excellent catalytic performance.

The CeO_2/WO_3-TiO_2 catalyst was prepared by an optimized precipitation method. $Ce(NO_3)_3{\cdot}6H_2O$, $(NH_4)_{10}W_{12}O_{41}$ and $Ti(SO_4)_2$ dissolved to distilled water together, with a Ce/W/Ti molar ratio of 0.2/0.1/1.0. Excessive urea was added into the mixed solution and then heated to 90 °C. After vigorous stirring for 12 h (some samples with different precipitation time were also prepared), the precipitated solids were collected by filtration and then washed with distilled water, dried at 100 °C for 12 h and calcinated at 500 °C for 5 h, orderly. In order to comprehensively evaluate the activity of CeO_2/WO_3-TiO_2 catalyst, V_2O_5-WO_3/TiO_2, Mn/TiO_2 and Cu-SAPO-34 catalysts were prepared as reference materials (see the ESI[†] for details of the preparation of these catalysts).

The SCR activity tests of the sieved powder catalysts were carried out in a fixed-bed quartz flow reactor at atmospheric pressure. The reaction conditions were controlled as follows: 500 ppm NO, 500 ppm NH_3, 5 vol.% O_2, 5 vol.% H_2O (when used), 5 vol.% CO_2 (when used), N_2 balance, and 400 mL/min total flow rate. Different GHSV were obtained by changing the volume of catalyst. The effluent gas, including NO, NH_3, NO_2 and N_2O was continuously analyzed by an online FTIR gas analyzer (Nicolet Antaris IGS analyzer). The concentration data were collected after 0.5 h when the SCR reaction reached a steady state. N_2 physisorption, XRD, XPS, H_2-TPR, SEM-EDX and NO_x-TPD were used for catalyst characterizations (see the ESI† for details of the characterizations).

The pH variation of the mixed solution during the preparation of the catalyst was shown in Fig. 1. The initial pH of the mixed solution was nearly zero due to the strong acidity of $Ti(SO_4)_2$. After heating of the solution, the pH increased gradually due to the hydrolysis of urea, and some white suspended particles were produced in the first 2 hour. After 3 hours of reaction, the pH of the solution increased to be nearly 3.0 and the suspended particles turned to be a little light yellow. Then, the pH showed a sharp increase and the particles turned to be yellow gradually. After twelve hours of reaction, the pH reached *ca.* 7.0 and kept to be stable in there, while the colour of the suspended particles was still yellow.

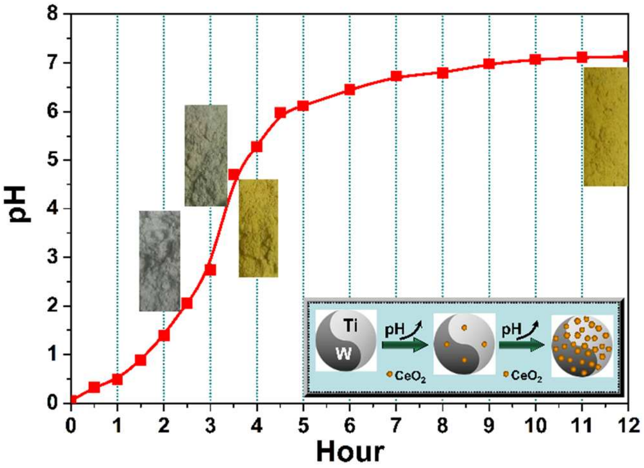

Fig. 1 The pH variation of the mixed solution during the preparation of the catalyst. Photos of the obtained samples with different precipitation time (2 h, 3 h, 4 h, and 12 h) and a diagram showing the formation process of the CeO_2/WO_3-TiO_2 catalyst were both inserted.

Table 1 Surface atomic concentrations (according to XPS and SEM-EDX analysis) and the BET surface areas of the samples with different precipitation time.

Analysis	Sample	2 h	3 h	4 h	12 h
XPS	Ce (%)	0	0.8	5.8	8.0
	W (%)	1.9	2.1	1.7	1.4
	Ti (%)	17.0	20.1	18.1	16.5
	O (%)	81.1	77.0	74.4	74.1
EDX	Ce (%)	0.0	0.9	4.3	5.3
	W (%)	4.1	3.9	3.8	3.2
	Ti (%)	27.4	27.0	28.8	22.3
	O (%)	68.5	68.6	63.1	69.2
BET surface area (m^2/g)		86.9	116.9	131.5	173.6

The XPS analysis of the surface atomic concentrations of the samples showed a gradually increase of surface Ce species with precipitation time (Table 1). Combining with the variation of pH, the formation process of the CeO_2/WO_3-TiO_2 catalyst could be proposed. The Ti and W species were firstly co-precipitated when the pH of the mixed solution firstly increased, and then the Ce species was precipitated uniformly onto the precipitated W-Ti species following the further increase of pH. This homogenous precipitation process is very important for the production of highly dispersed CeO_2 on WO_3-TiO_2.

Although no obvious difference of the samples could be found in the SEM images (Fig. S1), the EDX analysis confirmed the proposed formation process of the CeO_2/WO_3-TiO_2 catalyst, with a gradually increase of Ce atomic concentration (Table 1). The differences of the atomic concentration results obtained by XPS and SEM-EDX were induced by the different analysis depths of the two methods. The BET surface area of the samples showed a gradually increase with the precipitation time from 86.9 to 173.6 m^2/g (Table 1). In a XRD analysis of the samples with different precipitation time, only anatase TiO_2 was detected, confirming that CeO_2 was highly dispersed (Fig. S2). It was reported that nano-crystalline CeO_2 is the main active phase over Ce-Ti based catalyst, thus the highly dispersed CeO_2 structure produced by the homogenous precipitation process is probably a main reason for its excellent NH_3-SCR performance.[13,18] H_2-TPR analysis suggested that the presence of Ce species on the catalyst could significantly enhance its redox property, which is very important for the NH_3-SCR reactivity in the low-temperature region (Fig. S3).

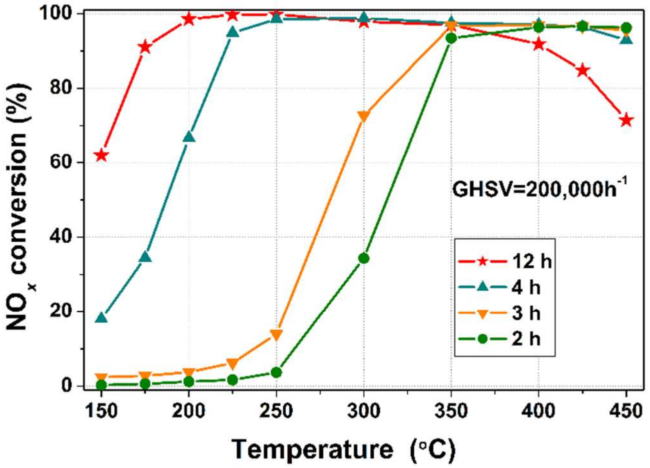

Fig. 2 NO_x conversion over the samples with different precipitation time.

Fig. 2 shows the NO_x conversion over the samples with different precipitation time under a GHSV of 200,000 h^{-1}. There is a clear enhance trend of the NO_x conversion with the increase of precipitation time for the samples. The sample of 2 h, without Ce on the surface, did not present any low-temperature SCR activity, and the sample of 3 h, with little Ce on the surface, just showed an insignificant low-temperature activity. However, the samples of 4 h and 12 h, with relatively high Ce on their surfaces, exhibited remarkable promoted low-temperature activities. Particularly, the sample of 12 h (CeO_2/WO_3-TiO_2) presented superior low-temperature NO_x conversion under this relatively high space velocity condition, with over 80% NO_x conversion being achieved in a wide temperature range from 175 to 425 °C. The NH_3 conversion over the samples was shown in Fig. S4. Below 350 °C, the NH_3 conversion of each sample was very similar to the corresponding NO_x conversion, indicating that the NO and NH_3 were almost consumed with a molar ratio of 1:1. Above 350 °C, the NH_3 conversions kept to be 100%, which is associated with the oxidation of NH_3 in addition to SCR reaction. The N_2O production over the samples was shown in Fig. S5. The samples of 4 h and 12 h induced remarkably lower N_2O production, indicating that surface Ce species were effective for N_2O inhibition.

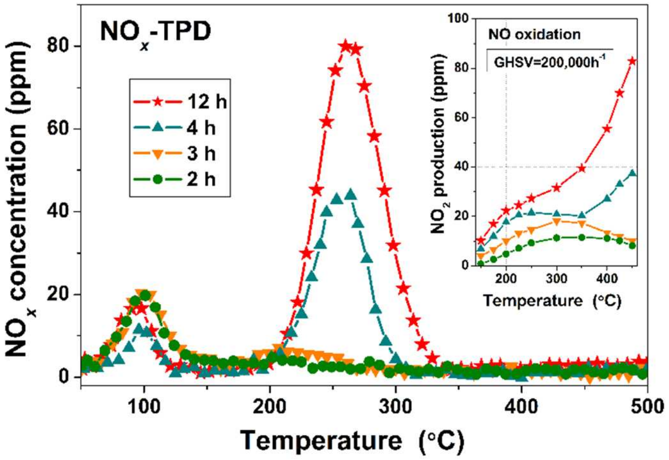

Fig. 3 NO$_x$-TPD profiles and the NO_2 productions during separated NO oxidations (inserted) of the samples with different precipitation time.

Previous studies have shown that, NO$_x$ adsorption behavior is very important for the low-temperature SCR over oxide catalysts. To investigate the influence of CeO_2 on the NO$_x$ adsorption/desorption of the catalyst, NO$_x$-TPD were performed on the samples with different precipitation time (Fig. 3). The first peak at *ca.* 100 °C is due to the desorption of physisorbed NO$_x$, while the second peak at *ca.* 250 °C was mainly related to the decomposition of chemsorbed NO$_x$ species.[19-20] The chemsorbed NO$_x$ species showed an evident increase with the increase of surface Ce amount, indicating that NO$_x$ species mainly adsorb on Ce sites of the CeO_2/WO_3-TiO_2 catalyst during NH_3-SCR reaction. Many studies have shown that, if the SCR catalyst can effectively oxidize NO to NO_2 *in situ*, its low-temperature SCR activity will be significantly enhanced due to the "fast SCR" effects. In this study, separated NO oxidation tests were carried out over these samples, and the NO_2 production during the tests were shown in Fig. 3. The NO_2 production presented an obvious increase with the increase of surface Ce amount, implying that the highly dispersed Ce species on WO_3-TiO_2 could act as the adsorption and oxidation sites for NO during NH_3-SCR reaction at low temperature and thereby remarkably enhance the low-temperature SCR activity.

To better evaluate the NH_3-SCR performance of CeO_2/WO_3-TiO_2 catalyst, a comparative SCR activity test over V_2O_5-WO_3/TiO_2, Mn/TiO_2, and Cu-SAPO-34 catalysts was carried out (Fig. 4). Mn/TiO_2 catalyst has been widely studied for its outstanding low-temperature SCR activity. However, in this study under the relatively high GHSV of 200,000 h^{-1}, Mn/TiO_2 just presented relatively low NO$_x$ conversion in a narrow temperature range, together with high N_2O production. Under the same GHSV condition, the active temperature of CeO_2/WO_3-TiO_2 was lower than that of the widely used V_2O_5-WO_3/TiO_2 for more than 50 °C. In addition, the N_2O production over CeO_2/WO_3-TiO_2 was quite low, even in the high temperature range. Cu-SAPO-34 is a very promising NH_3-SCR catalyst for diesel vehicles. Compared with Cu-SAPO-34, the CeO_2/WO_3-TiO_2 showed a similar catalytic performance. The wide operation temperature window and less formation of nitrogenous by-products are both important merits of the CeO_2/WO_3-TiO_2 catalyst for its practical utilization, especially on diesel vehicles.

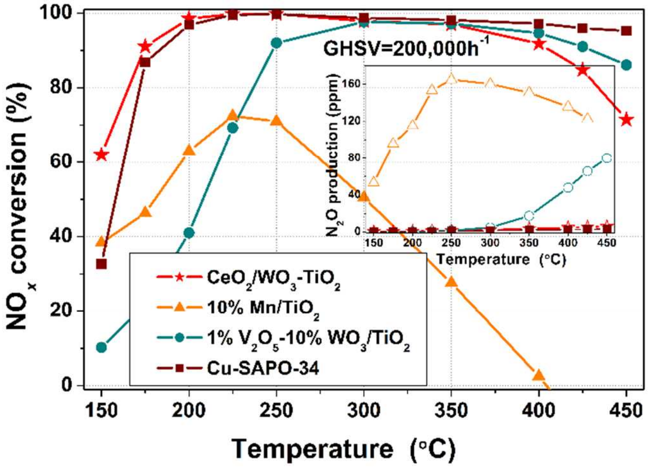

Fig. 4 Comparisons of the NO$_x$ conversion and N_2O prodction (inserted) over CeO_2/WO_3-TiO_2 catalyst with those over V_2O_5-WO_3/TiO_2, Mn/TiO_2, and Cu-SAPO-34 catalysts.

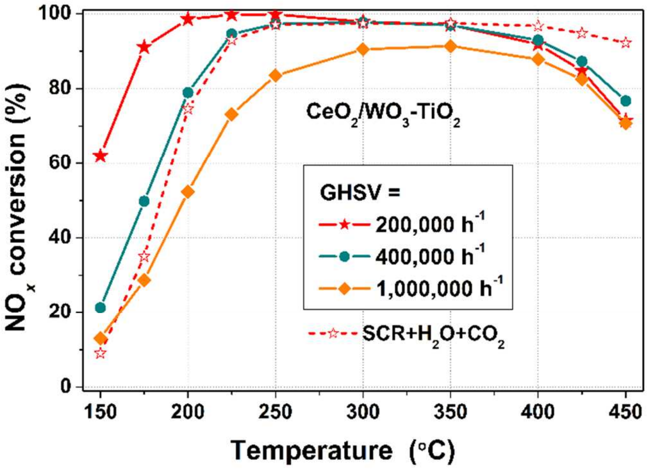

Fig. 5 NO$_x$ conversion over CeO_2/WO_3-TiO_2 catalyst under different GHSVs.

The effects of H_2O and CO_2 on NO$_x$ conversion over the CeO_2/WO_3-TiO_2 catalyst were tested under a GHSV of 200,000 h^{-1} (Fig. 5 and Fig. S6). The existence of 5% H_2O and coexistence of 5% H_2O and 5% CO_2 both induced a decrease of low temperature activity while an enhancement of high temperature activity. Over 90% NO$_x$ conversion could still be obtained from 225 to 450 °C. The influence of GHSV on NO$_x$ conversion was also investigated (Fig. 5). With the increase of GHSV, the low-temperature SCR activity of the catalyst decreased obviously. However, it still exhibited excellent SCR performance even under an extremely high GHSV of 1,000,000 h^{-1}, with over 80% NO$_x$ conversion still being achieved in the temperature range of 250-425 °C. The high-efficient characteristic of the CeO_2/WO_3-TiO_2 catalyst is important for its practical use on diesel vehicles to reduce the volume of the SCR catalytic converter.

In conclusion, we prepared a high efficient NH_3-SCR catalyst, CeO_2/WO_3-TiO_2, using a novel stepwise precipitation approach. This catalyst showed excellent catalytic performance with outstanding low-temperature activity, high N_2 selectivity and broad operation temperature window under high space velocity condition.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Catalyst preparation, activity test and some characterizations. See DOI: 10.1039/c000000x/

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