



Short Communication

Selective catalytic reduction of NO_x by NH₃ over MoO₃-promoted CeO₂/TiO₂ catalyst



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ABSTRACT

The addition of MoO₃ enhanced the activity of CeO₂/TiO₂ catalyst for the selective reduction of NO_x with NH₃. The MoO₃-promoted CeO₂/TiO₂ exhibited higher activity than CeO₂/TiO₂ even in the co-presence of H₂O and SO₂. This is because the introduction of Mo to the Ce10Ti catalyst can inhibit the adsorption of H₂O and SO₂ as well as the formation of sulfate species on the catalyst surface, thus alleviating the poisoning effect of H₂O and SO₂.

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1. Introduction

Nitrogen oxides (NO_x) are serious pollutants that cause not only the formation of acid rain but also photochemical smog. Selective catalytic reduction of NO_x with NH₃ (NH₃-SCR), using V₂O₅-WO₃(MoO₃)/TiO₂ as catalyst, has attracted much attention as a practical method to remove NO_x emitted from stationary sources [1]. However, the toxicity of vanadium and the narrow temperature window (300–400 °C) has restrained the practical application of V-based catalyst [2]. For the above reasons, it is desirable for developing novel NH₃-SCR catalyst with no vanadium but high deNO_x performance.

Recently, Ce-based catalyst seems to be promising for the NH₃-SCR of NO_x [3–5]. Ce/TiO₂ catalyst prepared by impregnation method was reported to be active for the NH₃-SCR of NO_x [6]. Gao et al. [7] also found that Ce/TiO₂ is active for this reaction. However, the presence of SO₂ leads to a noticeable decrease of the deNO_x activity [7,8]. From a practical point of view, the ability of resistance against H₂O and SO₂ is important for any catalyst with potential deNO_x application. Chen et al. [9] found that the addition of W results in the enhancement of the activity of Ce/TiO₂ catalyst. Moreover, its resistance against H₂O and SO₂ was also improved due to the existence of W. Recently we found that the addition of MoO₃ can improve the activity of Ce/TiO₂ catalyst in the absence of H₂O and SO₂ [10]. However, the effects of the H₂O and SO₂ as well as the impregnation preparation procedure on the catalytic performance of MoO₃-promoted Ce/TiO₂ catalyst remain unclear.

In this study, it was found that CeO₂-MoO₃/TiO₂ is more active than CeO₂/TiO₂ even in the co-presence of H₂O and SO₂. The impregnation preparation procedure also influences the catalytic performance. On the basis of the characterization results, the cause of the promoting effect of MoO₃ has been proposed.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by the impregnation method, and Degussa AEROSIL TiO₂ P25 was used as support. 10 wt.% CeO₂/TiO₂ (Ce10Ti) catalyst was prepared by impregnating TiO₂ with a proper amount of cerium nitrate (Ce(NO₃)₃·6H₂O) solution, then stirred for 4 h, followed by drying at 120 °C and calcinations at 500 °C for 4 h in the air. 5 wt.% MoO₃/TiO₂ (Mo5Ti) catalyst was prepared by the same method as described above using ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O) and oxalic acid (H₂C₂O₄·2H₂O) solution instead. Ce10Mo5Ti catalyst was prepared by impregnating Mo5Ti powder with an aqueous solution of cerium nitrate, stirred for 4 h, then dried at 120 °C and calcined at 500 °C for 4 h in air. Mo5Ce10Ti catalyst was prepared according to the opposite procedure, where Ce10Ti powder was impregnated with ammonium molybdate and oxalic acid solution.

2.2. Catalytic activity measurement

The activity measurements were carried out in a fixed-bed quartz reactor using a 0.12 g catalyst of 40–60 meshes. The feed gas mixture

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contained 500 ppm NO, 500 ppm NH₃, 5% O₂ and helium as the balance gas. The total flow rate of the feed gas was 300 cm³·min⁻¹, corresponding to a GHSV of 128,000 h⁻¹. In order to investigate the effects of H₂O and SO₂ on the activity of the catalyst, 5% H₂O and/or 50 ppm SO₂ was introduced into the reaction gas mixture. The reaction temperature was increased from 200 to 400 °C. The composition of the product gas was analyzed by a chemiluminescence NO/NO₂ analyzer (Thermal Scientific, model 42i-HL) and gas chromatograph (Shimadzu GC 2014 equipped with Porapak Q and Molecular sieve 5A columns). The activity data were collected when the catalytic reaction practically reached steady-state condition at each temperature.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) measurements were recorded on a Bruker D8 ADVANCE system with Cu K α radiation at 45 kV and 200 mA. XPS measurements were conducted on an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Mg K α radiation, calibrated internally by carbon deposit C 1s binding energy (BE) at 284.8 eV. A least-square routine of peak fitting was used for the analysis of XPS spectra.

In-situ DRIFTS spectra were recorded using a thermo Nicolet 6700 spectrometer equipped with a high temperature environmental cell fitted with ZnSe window and an MCT detector cooled with liquid N₂. The catalyst was loaded in the Harrick IR cell and heated to 400 °C under helium at a total flow rate of 100 cm³·min⁻¹ for 60 min to remove adsorbed impurities. A background spectrum was collected under a flowing helium atmosphere and was subtracted from the sample spectra. The DRIFTS spectra were recorded by accumulating 100 scans with a resolution of 4 cm⁻¹.

3. Results and discussion

3.1. Effect of MoO₃ addition on the catalytic performance

Fig. 1 shows the catalytic performance of Ce10Ti, Ce10Mo5Ti and Mo5Ce10Ti catalysts for the selective catalytic reduction of NO_x with NH₃ in the presence of oxygen. It is evident that the addition of MoO₃ considerably promoted the activity of Ce10Ti catalyst below 325 °C and that Ce10Mo5Ti showed higher activity than Mo5Ce10Ti. For Ce10Ti catalyst, the NO_x conversion was only 37% at 250 °C. Even lower NO_x conversion (14%) was obtained at this temperature over Mo5Ti catalyst [10]. In contrast, 75% and 66% NO_x conversion was

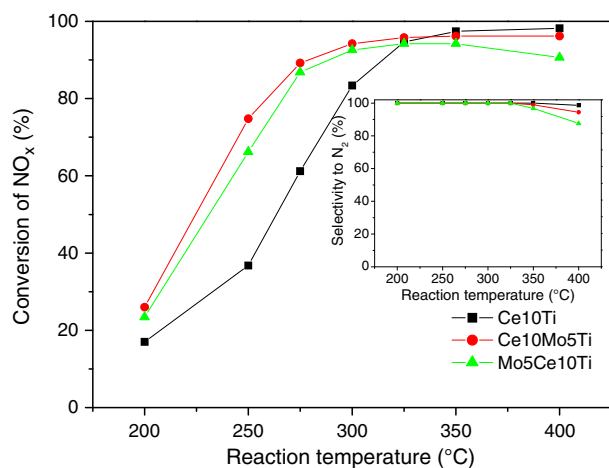


Fig. 1. The NH₃-SCR activity and N₂ selectivity (inserted) of Ce10Ti, Ce10Mo5Ti and Mo5Ce10Ti catalysts for the selective catalytic reduction of NO_x with NH₃ in the presence of oxygen. Reaction conditions: [NO] = [NH₃] = 500 ppm, [O₂] = 5%, GHSV = 128,000 h⁻¹.

achieved at 250 °C over Ce10Mo5Ti and Mo5Ce10Ti, respectively. This fact indicates that the synergistic effect between Ce and Mo could exist over the MoO₃-promoted Ce10Ti catalyst. The N₂ selectivity over Ce10Mo5Ti catalyst exhibited a slight decrease above 350 °C, but it is still higher than that of Mo5Ce10Ti catalyst (see the inserted figure). The decrease of the N₂ selectivity is due to the formation of N₂O, which was produced by the reaction of NH₃ with nitrate at high temperatures [3]. Consequently, the addition of MoO₃ showed a promoting effect on the activity and the change in impregnation preparation procedure affected the catalytic performance of MoO₃-promoted Ce10Ti catalyst.

3.2. Effect of H₂O and SO₂

The effect of H₂O and SO₂ on the activities of Ce10Ti, Ce10Mo5Ti and Mo5Ce10Ti catalysts was investigated and the results are shown in Fig. 2A. Compared with Fig. 1, it can be seen that the activity of Ce10Ti catalyst was seriously suppressed by the presence of H₂O and SO₂. Only about 50% NO_x conversion was obtained in the presence of H₂O (or H₂O and SO₂) at 300 °C. Although the presence of H₂O and SO₂ also leads to the decrease of the NO_x conversion over Ce10Mo5Ti catalyst, the conversion is much higher than that obtained over Ce10Ti catalyst. At 300 °C, 84% and 75% NO_x conversions were obtained in the presence of H₂O and co-presence of H₂O and SO₂, respectively.

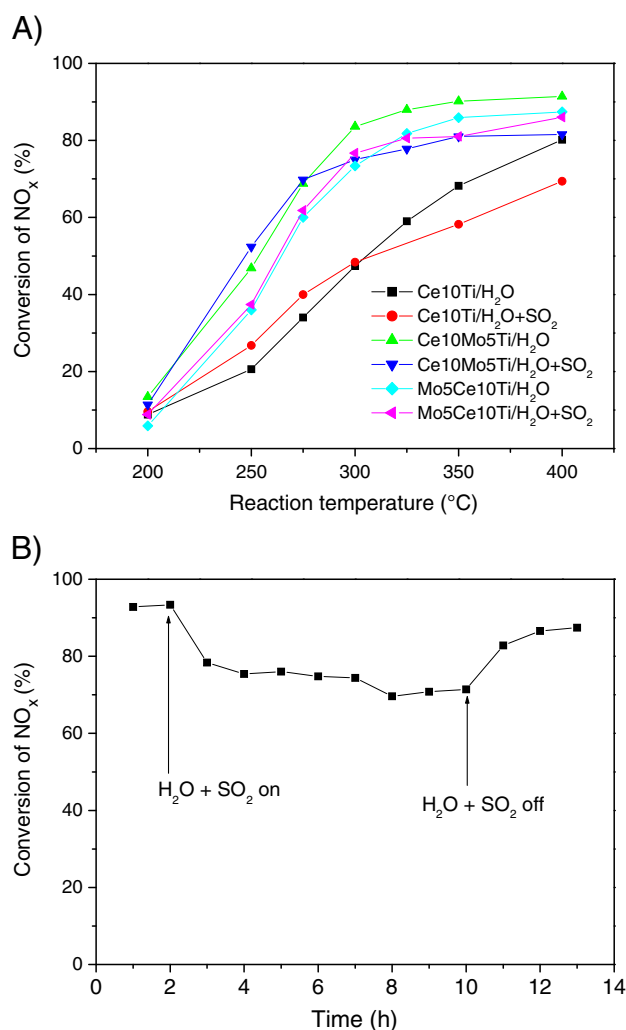


Fig. 2. (A) Effect of H₂O and SO₂ on the NO_x conversion over Ce10Ti, Ce10Mo5Ti and Mo5Ce10Ti catalysts. (B) The response of the NO_x conversion over Ce10Mo5Ti catalyst at 300 °C to the intermittent feed of H₂O and SO₂. Reaction conditions: [NO] = [NH₃] = 500 ppm, [O₂] = 5%, [H₂O] = 5%, [SO₂] = 50 ppm, GHSV = 128,000 h⁻¹.

Ce10Mo5Ti exhibited noticeably higher activity than Mo5Ce10Ti catalyst in the presence of H₂O. And below 300 °C the NO_x conversion over Ce10Mo5Ti in the presence of H₂O is even higher than that of Ce10Ti catalyst in the absence of H₂O. In the co-presence of H₂O and SO₂ 100% N₂ selectivity can be obtained over these catalysts (see Fig. S1).

Fig. 2B illustrated the response of the NO_x conversion over Ce10Mo5Ti catalyst at 300 °C to the intermittent feed of H₂O and SO₂. The coexistence of H₂O and SO₂ induced a gradually decrease of NO_x conversion and the conversion was decreased to 71% from 93% in 10 h. After stopping H₂O and SO₂, the NO_x conversion was increased to 87%. The loss of SCR activity could be ascribed to the deposit of sulfate on the catalyst surface [11].

3.3. Effect of O₂

It is well recognized that oxygen plays an important role in the NH₃-SCR of NO_x [12]. The effect of oxygen on catalytic activity was studied in this work. As shown in Fig. S2, the NO_x conversion is only 34% over Ce10Mo5Ti catalyst at 300 °C in the absence of oxygen. However, the conversion was increased significantly when 1% oxygen was introduced into the reactants. With the oxygen concentration further increasing, the NO_x conversion was seldom changed. This indicates that oxygen plays a significant promoting role in the SCR reaction. Similar promoting effect was also observed over MnO_x-CeO₂ catalyst by Qi and Yang [12]. The presence of oxygen can be adsorbed and activated on the surface of Ce10Mo5Ti catalyst thus forming the surface chemisorbed oxygen species, which was reported to be highly active for the NH₃-SCR of NO_x [13].

3.4. Catalyst characterization

Fig. 3 showed the XRD patterns of Ce10Ti, Ce10Mo5Ti and Mo5Ce10Ti catalysts. For all the catalysts, the anatase phase was the main phase [2], and only a little rutile phase appeared [14]. The peak ascribed to crystalline MoO₃ was not observed for Ce10Mo5Ti and Mo5Ce10Ti catalysts, indicating that the molybdenum oxide was highly dispersed on the surface of TiO₂. A weak peak of cubic CeO₂ crystallites was observed over Ce10Ti catalyst [15]. This peak becomes a little bit higher over Mo5Ce10Ti catalyst, and the most noticeable peak ascribed to CeO₂ appeared over Ce10Mo5Ti catalyst, indicating that the introduction of Mo could induce the crystallite of CeO₂ and over Ce10Mo5Ti catalyst the crystallization is more apparent. The cubic CeO₂ can contribute to the activation of NH₃ [16], thereby enhancing the SCR activity. On the other hand, it could be more susceptible to H₂O and SO₂ than the highly dispersed CeO₂. Therefore, Ce10Mo5Ti is more sensitive to the presence of H₂O and SO₂ than Ce10Ti at 200 °C (see Figs. 1 and 2A).

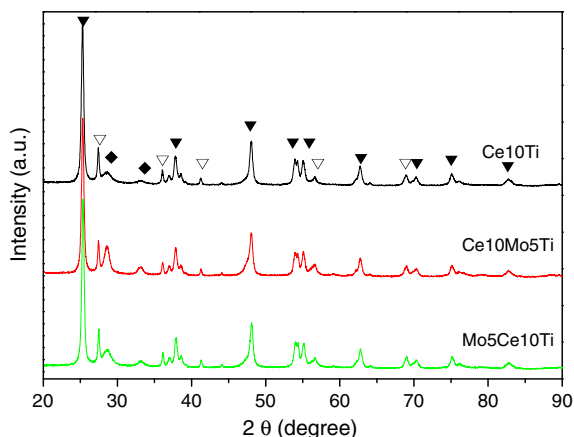


Fig. 3. XRD patterns of Ce10Ti, Ce10Mo5Ti and Mo5Ce10Ti catalysts. (▼) Anatase TiO₂; (▽) Rutile TiO₂; (◆) Cubic CeO₂.

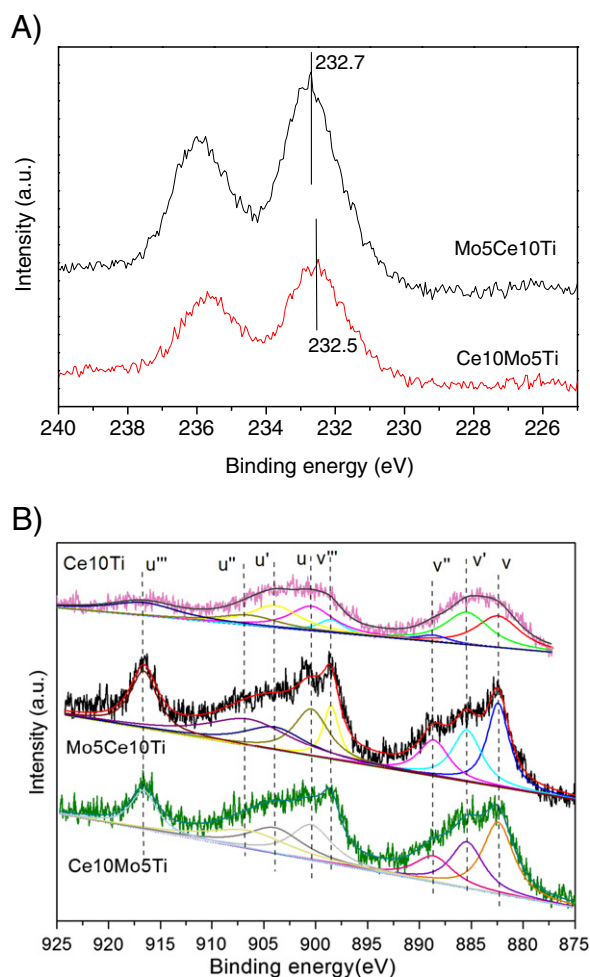


Fig. 4. (A) Mo 3d XP spectra of Mo5Ce10Ti and Ce10Mo5Ti catalysts. (B) Ce 3d XP spectra of Ce10Ti, Mo5Ce10Ti and Ce10Mo5Ti catalysts.

X-ray photoelectron spectra (XPS) analysis was conducted to elucidate the surface nature of the active sites over the catalyst systems. As shown in Fig. 4A, the Mo 3d_{5/2} peak was centered at 232.7 and 232.5 eV for Mo5Ce10Ti and Ce10Mo5Ti catalysts respectively, corresponding to Mo⁶⁺ state [17]. The complex spectrum of Ce 3d was decomposed into eight components with the assignment defined in Fig. 4B. The sub-bands labeled u' and v' represent the 3d¹⁰4f¹ initial electronic state corresponding to Ce³⁺, and those labeled u'', u''', v'', v''', v' and v''' represent the 3d¹⁰4f⁰ initial electronic state corresponding to Ce⁴⁺ [2]. It can be seen that the redox pair of Ce³⁺/Ce⁴⁺ exists in the three catalysts. For Ce10Mo5Ti catalyst, the surface concentration of Ce is 2.4%, which is higher than that of Mo5Ce10Ti (2.0%) and Ce10Ti (2.3%) catalysts. More amount of Ce exists on the surface could contribute to improving the NH₃-SCR activity.

3.5. In situ DRIFTS

Previous studies have shown that the adsorption of NH₃ on the catalyst surface plays an important role in the NH₃-SCR process [11,12]. Therefore, the adsorption of NH₃ on Ce10Ti and Ce10Mo5Ti catalysts in the co-presence of H₂O and SO₂ was studied by in situ DRIFTS. Fig. 5A showed the DRIFT spectra of NH₃ adsorption over Ce10Ti catalyst in the co-presence of H₂O and SO₂ at different temperatures. Compared with the DRIFT spectra of NH₃ adsorption in the absence of H₂O and SO₂ [10], it can be seen that two new peaks centering at 1608 and 1363 cm⁻¹ appear, which can be assigned to the adsorption of H₂O [18,19] and the deposited sulfate species [18],

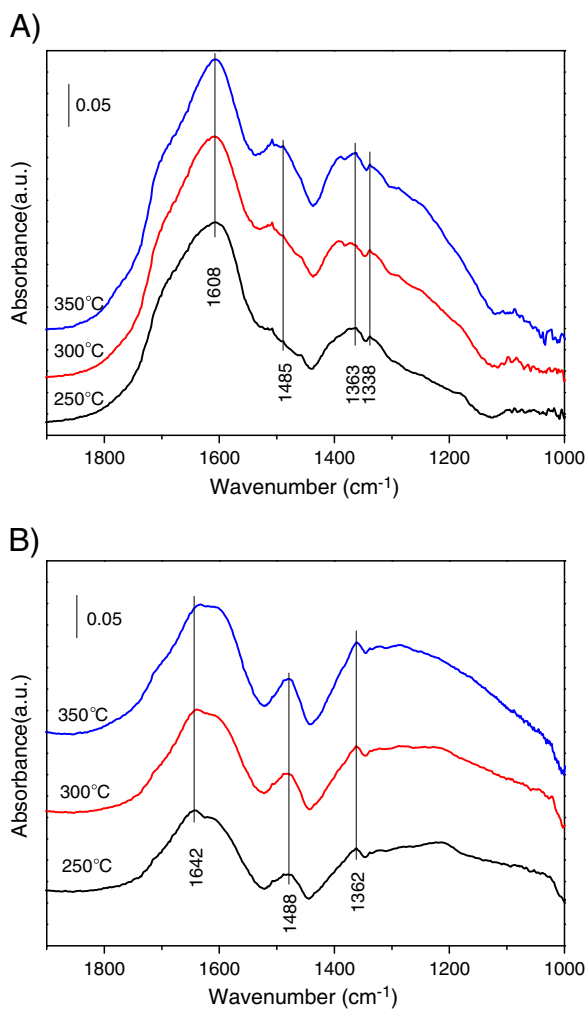


Fig. 5. DRIFT spectra of Ce10Ti (A) and Ce10Mo5Ti (B) in the flow of 500 ppm NH₃ + 5% H₂O + 50 ppm SO₂ at different temperatures.

respectively. The adsorbed H₂O can block the active sites thus leading to the decrease of the NH₃-SCR activity [20]. The sulfate species can also cover the active sites thus poisoning the deNO_x catalyst [1]. In our previous report [10], the peaks (1595 and 1170 cm⁻¹) ascribed to asymmetric and symmetric bending vibrations of the coordinated NH₃ linked to Lewis acid sites [21,22] were observed over Ce10Ti catalyst in the absence of H₂O and SO₂. It is evident that these peaks were absent in the co-presence of H₂O and SO₂ (see Fig. 5A). Therefore, the co-presence of H₂O and SO₂ inhibits the formation of coordinated NH₃ on Lewis acid sites, which was reactive species in the NH₃-SCR process, resulting in the decrease of the NO_x conversion.

By the comparison of Fig. 5A and B, it can be seen that the intensity of the peaks ascribed to the adsorption of H₂O and sulfate species over Ce10Mo5Ti catalyst were weaker than those over Ce10Ti catalyst. This fact indicates that the introduction of Mo to the Ce10Ti catalyst could inhibit the adsorption of H₂O and SO₂ as well as the formation of sulfate species on the catalyst surface, thus alleviating the poisoning effect of

H₂O and SO₂ as shown in Fig. 2A. In addition, more noticeable adsorption band of NH₃ on Brønsted acid sites (1488 cm⁻¹) [2,23] can be observed over Ce10Mo5Ti catalyst (see Fig. 5B). Previous research showed that Brønsted acid site is beneficial for the adsorption of NH₃ thus promoting the SCR activity [24,25]. All these are the mechanistic cause of the higher activity of Ce10Mo5Ti catalyst than Ce10Ti catalyst in the co-presence of H₂O and SO₂.

4. Conclusions

CeO₂-MoO₃/TiO₂ showed higher activity than CeO₂/TiO₂ for the selective catalytic reduction of NO_x with NH₃. More importantly, the resistance against H₂O and SO₂ was also improved due to the addition of MoO₃. It was suggested that the role of added MoO₃ is to inhibit the adsorption of H₂O and SO₂ as well as the formation of sulfate species on the catalyst surface, thus alleviating the poisoning effect of H₂O and SO₂. In addition, it leads to the formation of Brønsted acid sites and the crystallization of CeO₂, which contribute to the adsorption and activation of NH₃, respectively, thus promoting the NH₃-SCR to proceed.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catcom.2013.11.032>.

References

- [1] Z.M. Liu, S.I. Woo, Catal. Rev. Sci. Eng. 48 (2006) 43–89.
- [2] W. Shan, F. Liu, H. He, X. Shi, C. Zhang, Appl. Catal. B 115/116 (2012) 100–106.
- [3] G. Qi, R.T. Yang, R. Chang, Appl. Catal. B 51 (2004) 93–106.
- [4] W. Shan, F. Liu, H. He, X. Shi, C. Zhang, ChemCatChem. 3 (2011) 1286–1289.
- [5] Y. Peng, J.H. Li, L. Chen, J.H. Chen, J. Han, H. Zhang, W. Han, Environ. Sci. Technol. 46 (2012) 2864–2869.
- [6] W.Q. Xu, Y.B. Yu, C.B. Zhang, H. He, Catal. Commun. 9 (2008) 1453–1457.
- [7] X. Gao, Y. Jiang, Y.C. Fu, Y. Zhong, Z.Y. Luo, K.F. Cen, Catal. Commun. 11 (2010) 465–469.
- [8] W.Q. Xu, H. He, Y.B. Yu, J. Phys. Chem. C 113 (2009) 4426–4432.
- [9] L. Chen, J.H. Li, M.F. Ge, R.H. Zhu, Catal. Today 153 (2010) 77–83.
- [10] Z.M. Liu, S.X. Zhang, J.H. Li, L.L. Ma, Appl. Catal. B 144 (2014) 90–95.
- [11] G. Qi, R.T. Yang, Appl. Catal. B 44 (2003) 217–225.
- [12] G. Qi, R.T. Yang, J. Catal. 217 (2003) 434–441.
- [13] F. Liu, H. He, Y. Ding, C. Zhang, Appl. Catal. B 93 (2009) 194–204.
- [14] Z.B. Wu, R.B. Jin, H.Q. Wang, Y. Liu, Catal. Commun. 10 (2009) 935–939.
- [15] P. Li, Y. Xin, Q. Li, Z.P. Wang, Z.L. Zhang, L.R. Zheng, Environ. Sci. Technol. 46 (2012) 9600–9605.
- [16] Y. Peng, K.Z. Li, J.H. Li, Appl. Catal. B 140–141 (2013) 483–492.
- [17] D. Soogunda, P. Lecoura, A. Daudin, B. Guichard, C. Legens, C. Lamonier, E. Payen, Appl. Catal. B 98 (2010) 39–48.
- [18] F. Liu, H. He, Catal. Today 153 (2010) 70–76.
- [19] A.L. Goodman, E.T. Bernard, V.H. Grassian, J. Phys. Chem. A 105 (2001) 6443–6457.
- [20] X. Mou, B. Zhang, Y. Li, L. Yao, X. Wei, D.S. Su, W. Shen, Angew. Chem. Int. Ed. 51 (2012) 2989–2993.
- [21] L. Lietti, I. Nova, G. Ramis, L. Dall'Acqua, G. Busca, E. Giannelo, P. Forzatti, F. Bregani, J. Catal. 187 (1999) 419–435.
- [22] M.A. Larrubia, G. Ramis, G. Busca, Appl. Catal. B 27 (2000) L145–L151.
- [23] S.D. Lin, A.C. Gluhoi, B.E. Nieuwenhuys, Catal. Today 90 (2004) 3–14.
- [24] L. Chen, J.H. Li, M.F. Ge, Environ. Sci. Technol. 44 (2010) 9590–9596.
- [25] G. Zhou, B. Zhong, W.H. Wang, X.J. Guan, B.C. Huang, D.Q. Ye, H.J. Wu, Catal. Today 175 (2011) 157–163.