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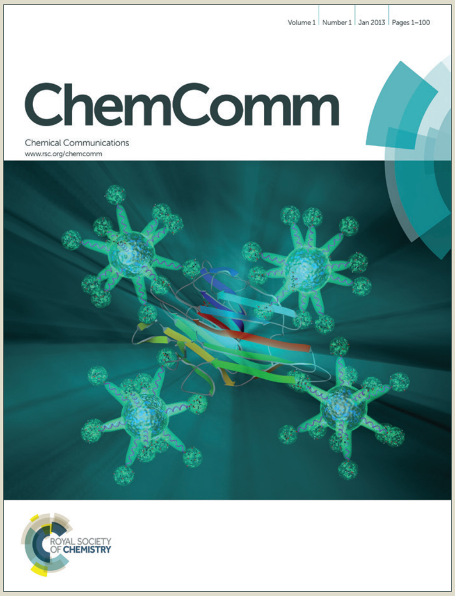

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A novel mechanism for poisoning of metal oxides SCR catalyst: base-acid explanation correlated with redox property

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Huazhen Chang[a], Junhua Li[a,b*], Wenkang Su[a], Yuankai Shao[a], Jiming Hao[a,b]

A novel mechanism is proposed for poisoning effect of acid gas and N_2O formation on SCR catalyst involving basic-acid property correlated with redox ability of M-O or M-OH (M= Ce or V) of metal oxides and the strength of their basicity responsible for resistance to HCl and SO_2 at medium and low temperatures.

An important feature in the development of SCR catalysts for stationary and automotive applications is the enhancement of resistance to toxicant and promotion of N_2 selectivity at medium and low temperatures. It is commonly recognized that acid and redox functions coexist and they are both important on SCR catalysts.[1] The acidity of catalyst is enhanced after poisoning by SO_2, but the activity decreased at low temperatures.[2] The research on correlation between basicity of catalyst and SCR performance is scarce, especially for deactivation by acid gases and N_2O formation.

The most widely used catalyst system for SCR of NO_x is the V-based catalyst supported on TiO_2.[1] It was suggested that the redox properties are the key factors for the high reactivity of V-based catalyst at low temperatures.[3] In recent decades, many neoteric catalysts were developed in medium and low temperature range, such as $FeTiO_x$, MnO_x-CeO_2, Ln-Na-Cu-O and Co/MFI.[4] In the development of novel SCR catalysts, Ce-based oxides with high oxygen storage capacity and excellent redox property attracted much attention.[5] The enhancement of acidity by Ce addition was recognized by previous study.[6]

Acids and bases related to each other. Acid and base active surface sites, in particular, can be relevant in determining the interaction mechanisms between the surface and the reagents, or between the surface and the reaction intermediates.[7] Whereas, the basicity of SCR catalyst was studied to a lesser extent as comparing with the acidity. It was reported that Ti^{4+} ions exposed on (0 0 1) and (0 1 0) faces of TiO_2 P25 particles are L acid centers and a fraction of O^{2-} ions on the surface of TiO_2 P25 behave as basic centers, actually, the behavior of Ti^{4+}-O^{2-} acid-base pairs depends on the surface structure.[8] For low-temperature SCR reaction, the active sites for NO adsorption and oxidation, act indeed as basic sites. Except for non-oxide catalysts, the basic sites are believed to be surface O atoms.[9] Furthermore consideration of the phenomena of acid and basic catalysis has contributed to the understanding of the mechanism of chemical reactions in general. Another important reason is the basic sites are easily poisoned by acidic molecules such as HCl and SO_2, characterization and understanding of the basic sites would be helpful to improve the resistance to acid gases.

Carbon dioxide is believed to adsorb on metals and basic oxides in many forms, such as the monodentate, bidentate, and bridged forms.[9] The strength and amount of basic sites are reflected in desorption temperature and the peak area, respectively, in a CO_2-TPD plot. In this study, the basicity of CeMo/Ti and VW/Ti catalysts was characterized by DRIFT spectra of CO_2 adsorption and CO_2-TPD. Based on surface basicity, the poisoning mechanism of two catalysts by HCl was revealed. The correlation between basic-acid and redox property was proposed that basic sites could convert to acid sites for SCR reaction and the redox property was inhibited after poisoning by acid gas. The later contributes mainly to deactivation effect of acid gases due to existence of strong basic sites on catalyst surface. In addition, the effect of basic sites on the formation of N_2O was also proposed.

The catalysts were prepared by impregnation method, which is similar to that reported in literature.[5] The detailed preparation procedures are described in ESI†. The CeO_2-MoO_3/TiO_2 (the molar ratio of Ce:Mo=2:1, loading 10 wt.% totally) catalyst is expressed as CeMo/Ti. The V_2O_5-WO_3/TiO_2 catalyst with 1 wt.% V_2O_5 and 5 wt.% WO_3 was denoted as VW/Ti. The V and W loading has been selected since it roughly corresponds to that of commercial catalysts. The HCl poisoning experiment was carried out by employing 250 ppm of HCl and 10 % of H_2O in inlet gas to poison the catalysts on stream at 200 °C. The NH_4Cl-poisoned catalysts (NH_4Cl content of 4.0 wt.%) were prepared by impregnating of samples in aqueous solution of NH_4Cl. The SCR activity test was estimated in a fixed-bed quartz reactor with following reaction conditions: 500 ppm NO, 500 ppm NH_3, 5 % O_2, 9 % H_2O (when used), 200 ppm HCl (when used), and balance in N_2. When investigating the effect of HCl addition on SCR activity, the sample was kept at steady state for 12h. The concentrations of NO, NO_2 (NO_x = NO + NO_2) and other components were measured with a FT-IR gas analyzer (Gasmet Dx-4000).

The basic centers of CeMo/Ti and VW/Ti catalysts were characterized by DRIFT spectra of CO_2 adsorption (see Fig. 1(a))

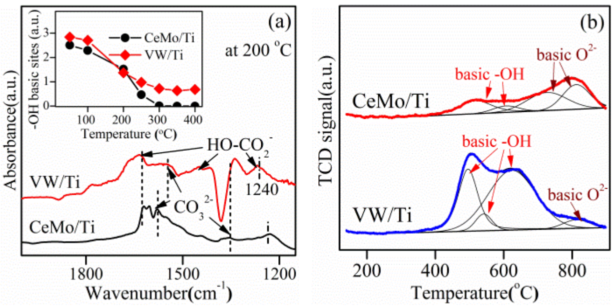


Fig. 1(a) DRIFT spectra of CO_2 adsorption on CeMo/Ti and VW/Ti catalysts and the amount of -OH basic sites vs temperature on two catalysts (insert); (b) CO_2-TPD curves of CeMo/Ti and VW/Ti catalysts.

The spectra of both catalysts show complex patterns mainly due to monodentate (bands at 1580 and ca. 1360 cm^{-1}) and bidentate (bands at 1670, 1537 and 1246 cm^{-1}) carbonate groups, produced by nucleophilic attack of basic O^{2-} ions exposed to CO_2 molecules. In addition, components at 1630, 1434 and 1230 cm^{-1} are assigned to bicarbonate species, which should be produced by reaction of CO_2 with some -OH basic groups left on sites in defect position.[10]

It is generally considered that the appearance of the characteristic band near 1230 cm^{-1} [δ(OH)] confirmed the formation of HO-CO_2^- (i.e. bicarbonate) species. The intensity of the 1230 cm^{-1} band hereby has been taken as a measure of the number of -OH basic species.[11] In this study, the amount of -OH basic groups on CeMo/Ti and VW/Ti were calculated from the peak areas of the characteristic band (shifted to 1240 cm^{-1} on VW/Ti) and they are shown in Fig. 1(a). It revealed that more -OH basic sites exist on VW/Ti catalyst and they can still be detected at 400 °C. Meanwhile, these groups decreased rapidly as temperature increasing and disappeared at 300 °C on CeMo/Ti, indicated that the interaction between -OH basic sites and CO_2 was unstable on this catalyst. But the carbonate species were stable at high temperatures on two catalysts, which means, the interaction between basic O^{2-} sites and CO_2 was much strong.

Fig. 1(b) shows the CO_2-TPD curves of CeMo/Ti and VW/Ti catalysts. The weak, medium, strong and very strong basic sites on catalyst are characterized from the peaks in the temperature range of 100-250, 250-400, 400-650, and >650 °C.[12] The CO_2-TPD spectrum of the CeMo/Ti consists of four peaks attributed to strong and very strong basic sites. The calculated area of the latter peaks is much bigger indicating that very strong basic sites are dominant on CeMo/Ti catalyst. Meanwhile, much more strong basic sites exist on VW/Ti catalyst and the total amount of basic sites (calculated from CO_2-TPD) is much higher than that on CeMo/Ti catalyst. Combining with the results from DRIFT study, we proposed that the basic O^{2-} adjacent to metal ions, which showed much strong interaction with CO_2, can be attributed to very strong basic sites; meanwhile, the -OH basic sites, which is abundant on VW/Ti catalyst and showed relatively weaker interaction with CO_2, can be considered as strong basic sites in CO_2-TPD. The existence of basic sites is supposed to facilitates the adsorption of acid gases. The different features of basic sites on two catalysts ought to represent different behavior in acid gas poisoning. The basic O^{2-}, i.e. very strong basic sites, is more likely being attacked by acid gas (i.e., HCl and SO_2).

Fig. 2(a) shows the effect of HCl on NO reaction rate of CeMo/Ti and VW/Ti catalysts at 200 °C. The reaction rate over CeMo/Ti was much higher than that of VW/Ti in the presence of H_2O. With the addition of HCl, the NO reaction rate decreased over both catalysts. Whereas, the NO reaction rate over CeMo/Ti was still higher than that of VW/Ti. The CeMo/Ti and VW/Ti samples after SCR activity test (with H_2O and HCl) were characterized by ICP-AES. The molar ratio of Cl$^-$/NH^{4+} was 1.5 and 0.056 for CeMo/Ti and VW/Ti, respectively. It indicated that more chloride formed on CeMo/Ti besides NH_4Cl; whereas, formation of large amount of NH^{4+} on VW/Ti demonstrated that more Brønsted (denotes as B) acid sites formed over VW/Ti catalysts in the presence of HCl. Literatures focused on the poisoning effect of acid gases proposed that formation of ammonium or metal salts (i.e., chloride or sulfate) are the main reasons for deactivation of SCR catalysts.[13]

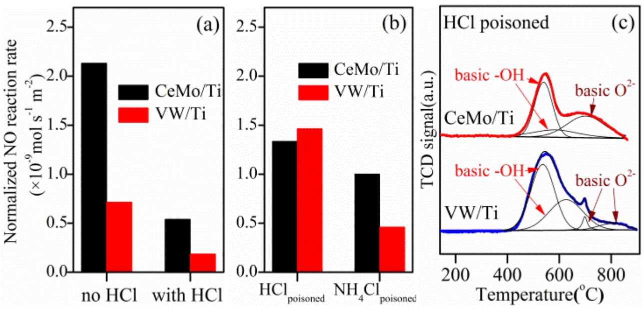


Fig. 2(a) The effect of HCl on NO reaction rate in SCR reaction, and (b) the effect of HCl and NH_4Cl-poisoning on NO reaction rate with GHSV=70, 000 h^{-1} (STP) over CeMo/Ti and VW/Ti catalysts. Reaction conditions: *T*=200 °C, 500 ppm NO, 500 ppm NH_3, 5 % O_2, 9% H_2O, 200ppm HCl (when used). (c) CO_2-TPD curves of two catalysts after HCl poisoning.

HCl and NH_4Cl poisoning were performed over two catalysts and the SCR performance were tested afterward (see Fig. 2(b)). After HCl poisoning, the NO reaction rate decreased on CeMo/Ti catalyst, indicating that HCl poisoning leads to deactivation effect for this catalyst. It is noteworthy that NO reaction rate increased in a certain extent on VW/Ti catalyst, which might due to formation of new acid sites on its surface. Poisoning by NH_4Cl restrains the reaction rate severely over both catalysts; whereas, the reaction rate was higher on poisoned CeMo/Ti than poisoned VW/Ti catalyst. The deposition of NH_4Cl on the catalysts blocks the active sites apparently at low temperatures.[13] The different behavior in HCl poisoning can be contributed to the difference in relative ratio of very strong and strong basic sites on two catalysts. The HCl prefer to react with very strong basic sites immediately, which was the main reason for deactivation of CeMo/Ti catalyst. The interaction between HCl and VW/Ti catalyst was weaker due to the weaker intensity of basic sites. As shown in Fig. 2(c), after poisoning by HCl, the intensity of peaks belongs to very strong basic sites decreased on CeMo/Ti, meanwhile, the intensity of peaks of strong basic sites increased apparently. It indicated that the amount of very strong basic sites (O^{2-}) decreased and strong basic sites (-OH) increased. It was possible that HCl adsorbs on basic O^{2-} sites and forms new -OH sites. The oxygen (maybe neighboring Ce) was so basic that HCl prefer to interact with it, thus, much less NH_4Cl could form. The intermediate, Ce-$(OH)_2Cl_2$, even though could not be detected, was much likely to form. The increase of -OH basic sites after HCl poisoning could also be detected on VW/Ti catalyst (see Fig. 2(c)).

On the other side, the -OH basic sites could also play as B acid sites for NH_3 adsorption. In order to investigate the acidity and the effect of HCl on NH_3 adsorption, DRIFT study of the effect of HCl on NH_3 adsorption was carried out on CeMo/Ti catalyst at 200 °C (see Fig. 3(a)). In the presence of HCl, the intensity of the bands assigned to B acid sites (at 1652, 1443, and 1413 cm^{-1}) and L acid sites (at 1600 and 1202 cm^{-1}) increased noticeably comparing with in the absence of HCl.[5,14] These results suggested that the addition of HCl obviously increase the quantities of both B and L acid sites on CeMo/Ti catalyst. Meanwhile, the broad bands due to the stretching vibration of NH_4^+ species are detected over VW/Ti catalyst,[15]

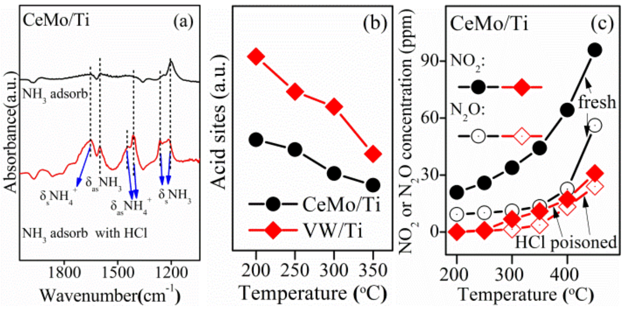


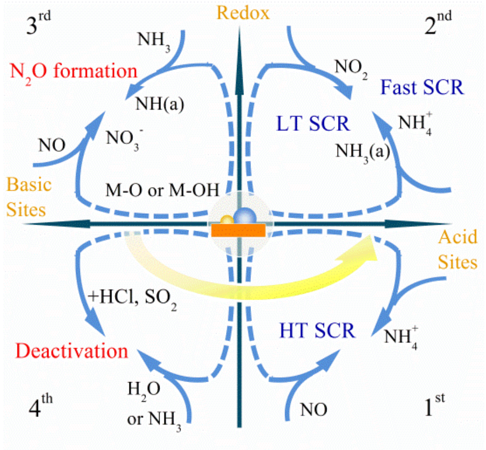
Fig. 3(a) The DRIFT spectra of the effect of HCl on NH_3 adsorption over CeMo/Ti catalyst at 200 °C; (b) the amount of surface acid sites vs temperature on CeMo/Ti and VW/Ti catalysts; and (c) the production of NO_2 vs temperature in NO oxidation and N_2O formation vs temperature in SCR reaction on CeMo/Ti catalysts.

revealing that much more B acid sites appeared on this catalyst (see Fig. S1, ESI†). Contributions of B acid sites on two catalysts at different temperatures were calculated by DRIFT spectra and the results are shown in Fig. 3(b). It showed that the amount of B acid sites on VW/Ti catalyst is larger than that of CeMo/Ti catalyst. The existing of abundant B acid sites promoted the SCR reaction and the latter showed even higher SCR activity after poisoning by HCl. Cl prefers to interact directly with surface oxygen atoms, instead of V atoms which could be available through the presence of oxygen vacancies, thus, much less chloride could be detected on VW/Ti catalyst.[16] This can also explain why much more NH^{4+} are detected on VW/Ti catalyst after activity test with HCl. On CeMo/Ti catalyst, new acid-basic sites (-OH) formed when HCl adsorbed on basic O^{2-}. These -OH sites facilitate the adsorption of NH_3, which was evidenced by DRIFT study.

In past decades, great efforts were also made to reveal the poisoning effect of SO_2 on SCR catalysts.[17] The effect of SO_2 on CeMo/Ti was also tested in this work and the SCR activity decreased after poisoning, especially at low temperatures (see Fig. S2**,** ESI†). The peak attributed to very strong basic sites shifted to lower temperature in CO_2-TPD (see Fig. S2, ESI†), indicating the basicity decreased. The -OH basic sites increased apparently at the same time after SO_2 poisoning, which will provide new B acid sites. The decrease in basicity and raise in amount of -OH sites by SO_2 poisoning are similar to HCl poisoning. The decrease in SCR activity at low temperatures was mainly related to redox property.

H_2-TPR was applied to distinguish the redox property of CeMo/Ti catalyst after HCl poisoning (see Fig. S3, ESI†). A peak at 547 °C disappeared on poisoned sample, indicating the reducibility was inhibited after HCl poisoning. Fig. 3(c) presents NO_2 production in NO oxidation before and after HCl poisoning on CeMo/Ti catalyst. At low temperature, metal ions are considered as the active sites for NO oxidation, the oxidation of NO to NO_2 is an important step in SCR reaction.[18] It showed that NO oxidation was suppressed severely over CeMo/Ti catalyst after HCl poisoning. The formation of cerium chlorides resulted in the disruption of the redox cycle of active sites ($Ce^{3+} \leftrightarrow Ce^{4+} + e$). Both of promotion in acidity and decrease in redox ability affects the SCR performance of CeMo/Ti catalysts. It is noteworthy that HCl poisoning would inhibit the over oxidation of NH_3, the formation of N_2O was suppressed and the N_2 selectivity was improved subsequently (see Fig. 3(c) and Fig. S4, ESI†). The modification of basic sites and repression of redox property which benefits the N_2 selectivity was also evidenced by MnO_x-CeO_2 catalyst (see Fig. S5, ESI†).

Based on the present work and previous study, the correlation of basic-acid and redox properties of M-O or M-OH (M= Ce or V) can be incorporated into a cross and four quadrants for the SCR reaction over metal oxides catalysts (Scheme 1). According to this scheme, there are essentially two related functions on the catalyst, that is, basic-acid and redox functions. Acidity is indispensable for NH_3 adsorption in SCR reaction. With moderate redox property, the SCR reaction could take place which is initiated by NH_3 adsorption on a B acid site at high temperatures (1st quadrant). As the redox ability increase, NO could be oxidized to NO_2 or nitrate species, and then reacts with adsorbed NH_3 or NH^{4+} at low temperatures (2nd quadrant). For the latter, the reaction involving the formation of ammonium nitrate as intermediate has been proposed as Fast SCR reaction.[18] With the acid sites, the basic sites (O^{2-} or -OH) are co-existence on the catalyst surface. In 3rd quadrant, the basic sites and strong redox property would enhance the over oxidation of NH_3 and yield N_2O, which will decrease the N_2 selectivity in SCR reaction. However, the basic sites are more likely being attacked by acid gases, i.e. HCl and SO_2. To a certain degree, these sites could transform to acid sites for SCR reaction after poisoning. But the redox cycle is always being disturbed, which contributes to deactivation of SCR catalyst. Moreover, in the presence of H_2O and NH_3, ammonium chloride or sulfate forms and therefore blocks the active sites (4th quadrant). The formation of these salts are seems inevitable and only regeneration is possible to eliminate the deposition.



Scheme 1 Proposed scheme for correlation of basic-acid and redox properties of metal oxides catalysts in SCR reaction (M= Ce or V).

In conclusion, the basic-acid property of M-O or M-OH (M= Ce or V) was correlated with redox ability of metal oxides SCR catalysts. The strength of their basicity is responsible for deactivation behaviour in HCl and SO_2 poisoning at medium and low temperatures. HCl could react with the very basic sites (O^{2-}) easily, resulting in disturbance of redox cycle on CeMo/Ti catalyst and formation of -OH basic-acid sites. The former leads to decrease of SCR activity at low temperature. Meanwhile, the over oxidation of NH_3 and N_2O formation are suppressed after poisoning.

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[a] State Key Joint Laboratory of Environment Simulation and Pollution Control (SKLESPC), School of Environment, Tsinghua University, Beijing, 100084, China.

[b] State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, Beijing 100084, China
E-mail: lijunhua@tsinghua.edu.cn

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