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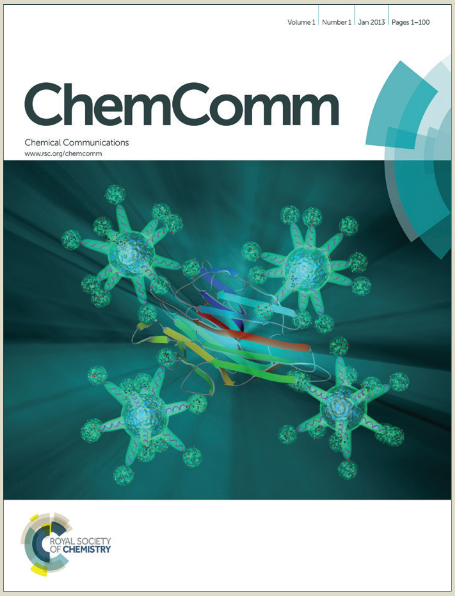

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Improved Low Temperature NH_3-SCR Performance of FeMnTiO*x* Mixed Oxide with CTAB-assisted Synthesis

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$FeMnTiO_x$ mixed oxide is prepared by CTAB-assisted co-precipitation method, and the transformation of anatase to rutile is inhibited by CTAB to some extent. The catalyst obtained in present work shows nearly 100% NO conversion at 100–350 ºC, more than 80% N_2 selectivity at 75–200 ºC, and excellent H_2O durability for the selective catalytic reduction of NO by NH_3 with a space velocity of 30000 $mL\cdot g^{-1}\cdot h^{-1}$.

Nitrogen oxides (NO_x) are one of the major pollutants in atmospheric environment, which can lead to photochemical smog, acid rain, ozone depletion and greenhouse effect, *etc*[1]. Mitigation of NO_x from the stationary and mobile sources, such as coal-burning power plants and automotive exhaust emissions, etc., has been one of the key subjects in environmental protection[2]. In recent years, many methods have been used to reduce the emission of NO_x. Among them, The selective catalytic reduction of NO by NH_3 （NH_3-SCR） is a very effective technology for denitration (*de*NO_x) in flue gas from stationary sources. The industrial operations are carried out on V_2O_5-WO_3 (MoO_3)/TiO_2 catalysts during the NH_3-SCR process[3]. Furthermore, the *de*NO_x device is placed in the upstream of electrostatic precipitator and desulfurizer, because the high-activity temperature range of the above-mentioned catalysts is 300-400 ºC. However, this arrangement causes many disadvantages, such as low N_2 selectivity in the high-temperature range, and deactivation of catalysts caused by sulfur containing compounds and dusts[4]. Therefore, it is of great significance to develop low-temperature (<200 ºC) NH_3-SCR catalysts, so that *de*NO_x unit can be placed in the downstream of electrostatic precipitator and desulfurizer where SO_2 and dusts have been removed.

Many investigations have been carried out on low-temperature NH_3-SCR catalysts. Manganese species have been demonstrated to be high NO_x conversion but low N_2 selectivity, poor H_2O durability and narrow operating temperature window[3,5,6]. Therefore, many researches have been focused on the modification of the manganese species. For instance, the performance of $(Fe_{3-x}Mn_x)_{1-\alpha}O_4$, Mn-Ce and $Fe_{0.5}Mn_{0.5}TiO_x$ mixed oxide catalysts in selectivity, activity and water resistance are improved respectively[3,7,8]. However, it is still a challenge to develop the low-temperature NH_3-SCR catalysts which has not only remarkable low-temperature activity, but also wide operating temperature window and excellent water resistance at low temperature. $FeMnTiO_x$ catalyst is considered to be a potential candidate for industrial application[3]. Anatase is considered to be more beneficial for NH_3-SCR than rutile[9]. However, whether supported catalysts prepared by impregnation method or mixed oxide prepared by co-precipitation method of $FeMnTiO_x$, the transformation of anatase to rutile will happen, which is not beneficial to improve catalytic activity in low temperature[9].

Cationic surfactant cetyltrimethyl ammonium bromide (CTAB) can release cations in aqueous solution. $FeMnTiO_x$ mixed oxide catalyst is synthesised by CTAB-assisted method (denoted as FMT(S)) in the present work. For comparison, $FeMnTiO_x$ mixed oxide catalyst is also synthesized without CTAB (denoted as FMT). The detail of preparation process is described in the supporting information. The NH_3-SCR activity and selectivity measurements over FMT and FMT(S) were performed in a fixed-bed quartz reactor, and the results are shown in Fig. 1.

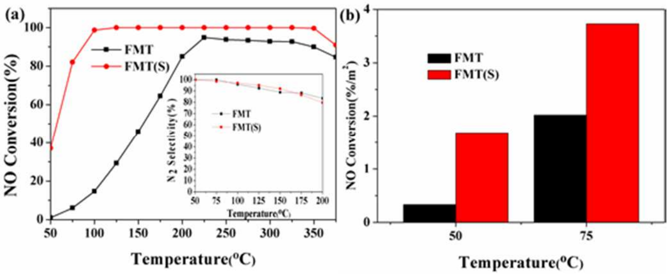

Fig. 1. (a) NO conversion and N_2 selectivity (inserted) of FMT and FMT(S) in NH_3-SCR reaction. (b) NO conversion per unit area of FMT and FMT(S) in NH_3-SCR reaction at 50 ºC and 75 ºC.

Fig. 1 shows that NO conversion is about 82% at 75 ºC, and reaches almost 100% in the range of 100-350 ºC on FMT(S). While the NO conversion is only about 6% at 75 ºC, and about 93% in the range of 225-350 ºC on FMT. In other words, the activity of FMT(S) is much better than that of FMT in low temperature range (below 200 ºC). Furthermore, the N_2 selectivity of the two catalysts is almost the same and above 80% from 75 to 200 ºC. Apparently, the addition of CTAB is beneficial to improve the low-temperature catalytic activity of FMT(S), and in order to clarify the effect of CTAB-assisted in preparation process, the physicochemical properties of these catalysts are further characterized.

The XRD patterns in Fig. 2 show that the mixed crystal configurations of anatase and rutile were detected on FMT(S), and only diffraction lines attribute to rutile were detected on FMT. There are no other diffraction lines attribute to iron or manganese species were detected on both samples. Moreover, it can be seen that the rutile diffraction peaks of the two samples are slightly shifted to high angle direction when comparing with pure rutile (inserted in Fig. 2), which suggests that the metal cations with smaller radii replace Ti^{4+} in the rutile crystal lattice. It is well known that the ionic radius of Mn^{4+} (0.53 Å) is smaller than that of Ti^{4+} (0.605 Å), while the ionic radii of Mn^{3+} (0.645 Å), Mn^{2+} (0.67 Å), Fe^{3+} (0.645 Å) and Fe^{2+} (0.78 Å) are larger than that of Ti^{4+}. It indicates that some of Ti^{4+} ions have been replaced by Mn^{4+} in the lattice of rutile.

Comparing with pure anatase (inserted in Fig. 2), the anatase diffraction peaks of FMT(S) are not shifted, which suggests that no foreign cations are incorporated into the lattice of anatase. In addition, comparing with FMT, the proportion of rutile is so small on FMT(S) that less Mn^{4+} ions are introduced into the lattice of FMT(S). It is reported that tetravalent manganese species has good low-temperature activity in NH_3-SCR reaction[10], thus more of that exposed on the surface of the catalyst, which will be beneficial to NH_3-SCR reaction.

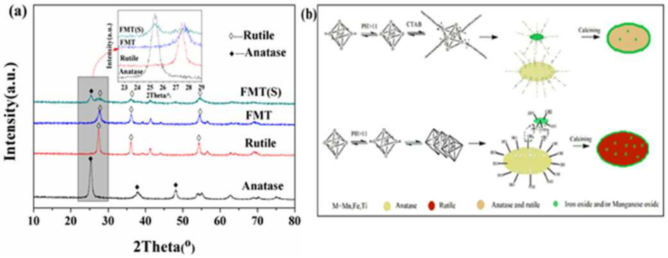

Fig. 2. (a) The XRD patterns of TiO_2 (anatase and rutile) and mixed oxide catalysts (FMT and FMT(S)), (b) Schematic diagram of preparation process of FMT and FMT(S).

According to XRD results, iron and manganese species can induce anatase into rutile in the process of preparing FMT, which is consistent with many literatures[9]. However, the transformation of anatase to rutile can be restrained by CTAB in the present work. The possible mechanism is as follows: the isoelectric point of TiO_2, Fe_2O_3 and MnO_2 are 3.9-8.2, 6.5-6.8 and 4-5, respectively, and the mixed oxides of them exhibit isoelectric point value among the corresponding pure oxides[11]; hence all metal oxides species are negative charged in condition of pH=11; the cationic surfactant molecules provide CTA^+ which combines with negative charged sites on metal oxide surface through electrostatic interaction, as shown in schematic diagram (Fig. 2); MnO_2 is rutile crystal structure, and melting point of it is 535 ºC that is far less than that of TiO_2 (1830 ºC), which is considered to promote the crystalline transition because of inducement effect[12]. While due to steric hindrance of the long chain alkane ends and no hydroxyl condensation, CTAB prevents the occurrence of this process to some extent. As we all know, this transformation of anatase to rutile will lead to a sharp decline of area. N_2-physisorption characterization is employed to determine specific surface area, and the results demonstrate that FMT(S) maintains large area (Table S1). Thus, the specific surface area may be one of the factors which leads to such a significant difference in reactivity. However, NO conversion per unit area of FMT(S) is still higher than that of FMT, the corresponding results are presented in Fig. 1(b). This indicates that there are some other factors to affect the activity of catalysts in addition to specific surface area.

As we all known, redox property is an important factor to influence NH_3-SCR reaction, and TPR results are shown in Fig. 3(a). The profile of FMT(S) exhibits two main reduction peaks at around 346 ºC and 438 ºC, and the peaks of FMT are about 410 ºC and 508 ºC. On one hand, starting reduction peak temperature of FMT(S) is much lower than that of FMT, which suggests that the redox property of FMT(S) is stronger than that of FMT. The reason may be that the interaction between active components and anatase is stronger than that between active components and rutile[13]. On the other hand, peaks area of FMT(S) is larger than that of FMT, which may be related to two factors: firstly, FMT(S) possess more surface reducible species of Mn^{4+} ions, which has been demonstrated by XRD; secondly, there are more surface adsorbed oxygen species on FMT(S) (Fig. S4 (b)). In order to further verify this results, the activities of FMT(S) and FMT for NO oxidation are also measured in present work, and the results are shown in Fig. 3(b), and the NO conversion of FMT(S) is higher than that of FMT. Koebel *et al.* demonstrated that the partial conversion of NO into NO_2 is helpful to “fast SCR”[14]. Therefore, it is reasonable that FMT(S) exhibits excellent reaction activity than FMT at low temperature in present work.

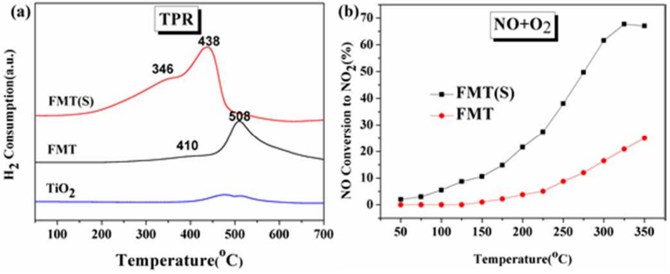

Fig. 3. (a) H_2-TPR profiles of FMT and FMT(S). (b) Oxidation activity of NO to NO_2 by O_2 on FMT and FMT(S).

Surface acid properties of catalysts plays an important role in NH_3-SCR reaction[15]. *In situ* diffuse reflectance infrared Fourier transform spectra (*In situ* DRIFTS) of NH_3 adsorption are performed at various temperatures to determine the type and quantity of acid sites, and the corresponding results are exhibited in Fig. 4. It is widely reported that the bands at about 1600 cm^{-1} and 1170 cm^{-1} are attributed to Lewis acid sites, and the bands at 1460 cm^{-1} and 1680 cm^{-1} are attributed to Brønsted acid sites[16]. The results show that FMT(S) has more Lewis acid sites and less Brønsted acid sites, while FMT is in opposite, which might be related to the more CTA^+ on FMT(S) and the more hydroxyl on FMT in the process of preparation. In addition, TPD results (Fig. S2) show that the quantity of Lewis acid sites of FMT(S) is far more than that of FMT. It is reported that NH_3 preferentially adsorbed on manganese species for MnO_x/TiO_2 catalyst[17], therefore, more surface manganese species lead to the more Lewis acid sites, which is agreement with BET and XRD results. In order to investigate the effect of Lewis acid sites on NH_3-SCR reaction at low temperature, The reaction of *in situ* DRIFTS between NO and pre-saturated NH_3+O_2 is conducted on FMT(S), and the results are exhibited in Fig. S3 (a). After the introduction of NO for 3 min, Lewis acid sites disappeared, which implies that the coordinate NH_3 on Lewis acid sites is very important to activity of NH_3-SCR reaction at low temperature, coincidentally, many literatures have also reported similar results[9,18]. For NH_3 and

O_2 co-adsorption, compared with only NH_3 adsorption in Fig. 4(a), the amount of Lewis acid increased obviously, which may be related to the oxidative abstraction of hydrogen from absorbed ammonia[19].

Nitrites are able to react with -NH_2 at temperature below 200 ºC, and the reaction rate is very quick[20], which indicates that nitrites species play an important role in NH_3-SCR reaction at low-temperature. Thus, *in situ* DRIFTS of NH_3 adsorption are carried out on FMT(S) and FMT pre-saturated with NO+O_2, the results are respectively shown in Fig. S3 (b) and Fig. S3(c). The bands at 1235 cm^{-1}, 1550 cm^{-1}, and 1610 cm^{-1} are attributed to nitrite, and 1276 cm^{-1}, 1543 cm^{-1} and 1581 cm^{-1} are attributed to nitrate[3,7]. The peak intensity of nitrite on FMT(S) is stronger than that on FMT, and nitrite disappeared quickly and part of nitrate species still existed when NH_3 was introduced into sample cell. It may be concerned that ammonium nitrite decomposes quickly into N_2 and H_2O below 100 ºC[21], hence, the results demonstrate that nitrite species are more easily formed on FMT(S) than on FMT.

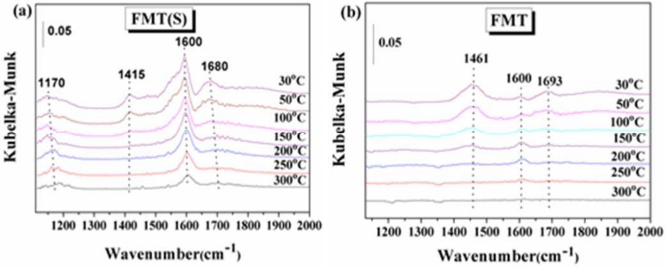

Fig. 4. *In situ* DRIFTS of NH_3 adsorption on catalysts: (a) FMT(S), (b) FMT.

X-ray photoelectron spectra (XPS) of Ti 2p and O 1s for the two catalysts are collected (Fig. S4), the value of Ti $2p_{3/2}$ XPS peak at 457.9 eV on FMT(S) is lower than 458.0 eV on FMT. Literature suggests that the shift of peaks toward lower binding energy is due to the stronger interaction of titanium with manganese[22]. Hence the interaction on FMT(S) is stronger than that on FMT, which is consistent with conclusion of TPR. The O 1s spectra after deconvolution are shown in Fig. S4 (b). The sub-bands at 529.3-529.5 eV correspond to the lattice oxygen O^{2-} (denoted as O_α), and the sub-bands at 531.4 eV correspond to the surface adsorbed oxygen (denoted as O_β), such as O_2^-, O_2^{2-}, O^- belonging to defect-oxide[23]. Generally, O_β is more reactive in oxidation reactions due to its higher mobility than O_α[24]. The ratios of $O_\beta/(O_\alpha+O_\beta)$ on the two samples are calculated and listed in Table S3, and the ratio is 38.4% on FMT(S) which is larger than that 28.8% on FMT. Combining with TPR results, it indicates that the FMT(S) is easier to adsorb oxygen than FMT. Kapteijn *et al.* pointed out that NO easily adsorbed on the active center which was oxidized by O_2[25]. Therefore, it is beneficial to further adsorption of NO and formation of nitrite and nitrate on FMT(S), which may be related to the crystal structure of anatase and rutile in TiO_6 octahedron. In rutile, the octahedron shows a slight orthorhombic distortion; in anatase, the octahedron is significantly distorted and its symmetry is lower than rutile[26]. Accordingly, anatase is easier to produce defects and dislocations, and easier to interact with manganese or iron species. Hence, it is helpful to adsorb oxygen and form nitrite on the surface of catalysts.

Since the flue gas still contain steam after electrostatic precipitation and desulfurization under practical condition, we further investigated the effect of H_2O on performance over the FMT(S). The process and results are shown in Fig. S5, and FMT(S) still exhibits excellent activity and selectivity when the water is introduced in NH_3-SCR reaction at low temperature.

In summary, CTAB can suppress the transformation of anatase to rutile during the preparation of FMT(S). According to BET specific surface area, XRD, TPR, *in situ* DRIFTS and XPS results, due to the presence of anatase, FMT(S) exhibits greater specific surface area, stronger redox property, more Lewis acid sites and more nitrite species. All of them greatly enhanced the activity of NH_3-SCR reaction at low temperature, and further research need to be done on the mechanism of CTAB action during the preparation of FMT(S).

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