

## Enhancement of $\alpha$ -oxygen formation and $N_2O$ decomposition on Fe/ZSM-5 catalysts by extraframework Al

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**The concentration of  $\alpha$ -oxygen which can oxidize methane to methanol and benzene to phenol at RT, increases linearly with the amount of introduced extraframework Al on Fe/ZSM-5 catalysts prepared by solid-state exchange of  $FeCl_3$  and  $AlCl_3$  with H-ZSM-5.**

The biomimetic catalysis of Fe/ZSM-5 (or Fe/MFI), oxidizing methane to methanol and benzene to phenol stoichiometrically by the so-called surface " $\alpha$ -oxygen" at RT,<sup>1</sup> is most fascinating among its diverse catalytic functionalities such as  $N_2O$  decomposition,<sup>2</sup> selective catalytic reduction (SCR) of nitrogen oxides.<sup>3</sup> The formation of  $\alpha$ -oxygen requires  $N_2O$  decomposition on steamed or high-temperature-treated Fe/ZSM-5.<sup>1</sup> However, the nature of the active site for  $\alpha$ -oxygen formation remains unclear.

Different extraframework Fe species, mostly mono- or binuclear iron,<sup>4,6</sup> or some specific iron clusters,<sup>7</sup> have been proposed to be the active site. However, the role of extraframework Al species, formed inevitably under pretreatment conditions, is still elusive.<sup>6,8</sup> Recent studies suggest that the solid solution formed by Fe oxide and alumina species are responsible for the higher TOF<sup>9</sup> or higher  $N_2O$  selectivity<sup>10</sup> in benzene oxidation to phenol. It is therefore of great interest to study the effect of extraframework Al on the structure of active site, and on the formation of  $\alpha$ -oxygen. In this paper extraframework Fe and Al are introduced simultaneously by solid-state exchange of  $FeCl_3$  and  $AlCl_3$  with H-ZSM-5. Both the concentration of " $\alpha$ -oxygen" and steady state  $N_2O$  decomposition increase parallel with the amount of the introduced extraframework Al.

The solid-state exchange follows the Karge group's procedure.<sup>11</sup> We calcined 2 g  $NH_4$ -ZSM-5 (Si/Al = 25, Nankai University) in pure  $O_2$  flow at 550 °C, and then ground with appropriate amounts of  $FeCl_3$  and  $AlCl_3$  in a glove box. Subsequently the mixture was heated in He flow from RT to 320 °C and kept at 320 °C for 2 h, followed by treating the solid in 0.5%  $H_2O$ -Ar flow from RT to 200 °C to hydrolysis of Al-Cl and Fe-Cl bond. Three samples with same amount of extraframework Fe (about 1.2 wt%), and with different amounts of extraframework Al were prepared. These samples are designated as Fe/ZSM-5 ( $x = 0, 1, \text{ or } 2$ ), where  $x$  in parenthesis denotes the atomic ratios of extraframework Al/Fe. UV-Raman spectra were collected on a home-made spectrometer, excited by 325 nm laser line emitted from KIMMON IK-3351R-G He-Cd laser.

A plug-flow reactor loaded with 50–55 mg catalyst was used. Before each run the catalyst was pretreated in  $O_2$  at 550 °C or in He at 900 °C for 2 h, then cooled to the studied temperature. The gas flow rate was adjusted according to the amount of loaded catalyst, corresponding to 24 000 ml  $h^{-1}$  (g catalyst)<sup>-1</sup>. A calibrated on-line mass spectrometer (Gam 200, Pfeiffer Vacuum) was used for product quantification.

The formation of surface oxygen was investigated by transient-response experiment, performed by step change from He to 5 vol%  $N_2O$  in He at 250 °C. Fig. 1 shows  $N_2$  response curves for samples treated in He at 900 °C. Only  $N_2$  appears, no  $O_2$  was detected; and the amount of released  $N_2$  increases with the increasing in the amount of added Al. For samples pretreated in  $O_2$  at 550 °C, no  $N_2$  was detected.

The detection of only  $N_2$  suggests  $N_2O$  decomposes to gaseous  $N_2$  with the formation of surface oxygen ( $O_{ad}$ ) at 250 °C. ( $O_{ad}$  concentration can thus be estimated by the amount of released  $N_2$ . For Fe/ZSM-5 ( $x = 0, 1, \text{ and } 2$ ), the obtained values are  $2.5 \times 10^{19}$ ,  $4.4 \times 10^{19}$  and  $6.4 \times 10^{19}$  site (g catalyst)<sup>-1</sup>, respectively, corresponding to O/Fe ratios of 0.20, 0.34 and 0.50, respectively. Further investigation show that once the samples has treated in He at 900 °C, subsequent treating the catalysts in  $O_2$  at 550 °C does not affect the ( $O_{ad}$ ) formation, and the ( $O_{ad}$ ) can oxidize  $CH_4$  to  $CO_2$  at 250 °C, and will be desorbed with a peak centered at 330 °C if the catalyst is heating in He flow with a ramp of 30 K  $min^{-1}$ . All these features suggest that this ( $O_{ad}$ ) is just the so-called " $\alpha$ -oxygen".<sup>3,12,13</sup>

The reactivity of the formed surface oxygen was further studied by pulsing of a  $CH_4$ -He mixture at 100 °C onto catalysts loaded with  $\alpha$ -oxygen. Since one  $CH_4$  molecule will react with two " $\alpha$ -oxygens" to form adsorbed methoxyl and hydroxyl groups,<sup>4</sup> the number of active ( $O_{ad}$ ) should be twice that of consumed  $CH_4$ . By accumulating the consumed  $CH_4$  in each pulse, we get the  $CH_4$ /Fe ratios for Fe/ZSM-5 ( $x = 0, 1, \text{ and } 2$ ) are 0.08, 0.14 and 0.19, respectively. This means about 80% of the ( $O_{ad}$ ) are active, which is in consistent with the Renken group's results that not every oxygen is active.<sup>13</sup> Linear correlations of the ( $O_{ad}$ ) concentration and the consumed  $CH_4$ , with the amount of introduced extraframework Al are evident in Fig. 2.

Two factors, the introduction of extraframework Al and high-temperature treatment in He, contribute to the increasing in ( $O_{ad}$ ) concentration. The effect of these two factors on the structure of active site was probed by  $N_2O$  decomposition.

Fig. 3 shows the steady state  $N_2O$  conversion vs. the reaction temperature over different catalysts pretreated in  $O_2$  at 550 °C and in He at 900 °C.  $N_2O$  decomposes to  $N_2$  and  $O_2$  stoichiometrically above 380 °C. Increasing in the amount of extraframework Al results in a parallel increase in  $N_2O$  conversion. The promoting effect of extraframework Al is even pronounced after pretreating the catalysts in He at 900 °C.  $N_2O$  decomposition is a first-order reaction.<sup>12</sup> The apparent activation energies and preexponential

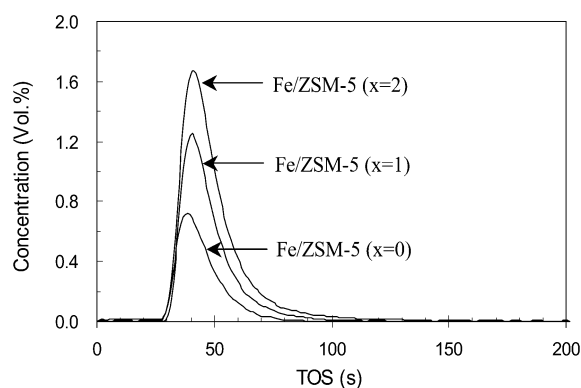
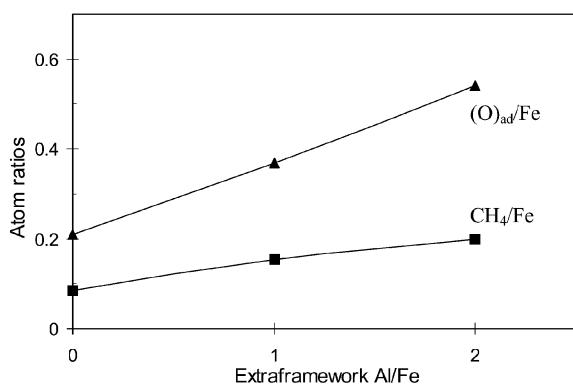
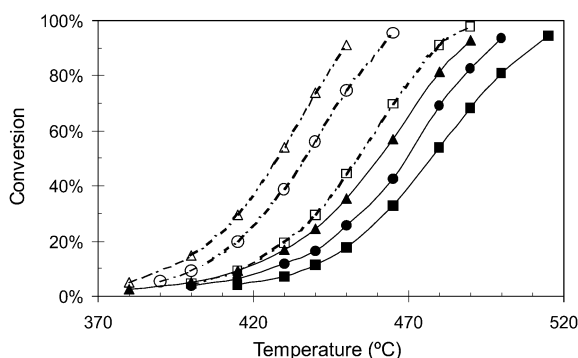


Fig. 1  $N_2$  response after step change from He to 5 vol%  $N_2O$ -He on samples. Samples are pretreated in He at 900 °C for 2 h.



**Fig. 2** Linear correlation of the surface oxygen and the consumed CH<sub>4</sub> with the amount of extraframework Al.

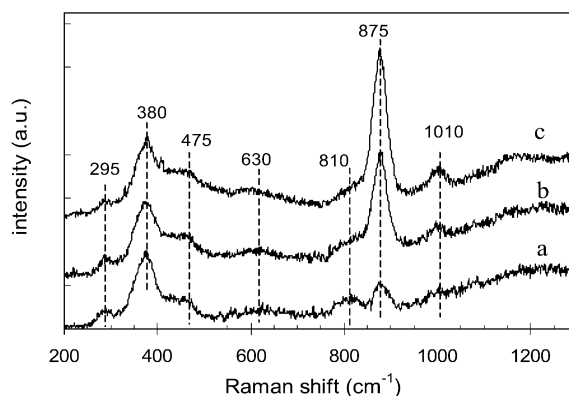


**Fig. 3** N<sub>2</sub>O decomposition over different samples. (■, □) Fe/ZSM-5 ( $x = 0$ ); (●, ○) Fe/ZSM-5 ( $x = 1$ ); (▲, △) Fe/ZSM-5 ( $x = 2$ ). Solid symbols: pretreating in O<sub>2</sub> at 550 °C; Open symbols: pretreating in He at 900 °C. Feed gas: 5 vol% N<sub>2</sub>O in He.

factors for the various catalysts are then obtained by Arrhenius plots.

For catalysts pretreated in O<sub>2</sub> at 550 °C, addition of extraframework Al remarkably lowers the apparent activation energy —  $E_a$  decreases from 186 kJ mol<sup>-1</sup> (Fe/ZSM-5 ( $x = 0$ )) to 160 kJ mol<sup>-1</sup> (Fe/ZSM-5 ( $x = 1$ )), and to 154 kJ mol<sup>-1</sup> (Fe/ZSM-5 ( $x = 2$ )), while the preexponential factors decrease from  $6.2 \times 10^7$  (Fe/ZSM-5 ( $x = 0$ )) to  $6.9 \times 10^5$  (mol N<sub>2</sub>O s<sup>-1</sup> (mol Fe)<sup>-1</sup> (Pa N<sub>2</sub>O)<sup>-1</sup>) (Fe/ZSM-5 ( $x = 2$ )). Upon treating the catalysts in He at 900 °C, all the preexponential factors increase significantly to about  $1.7 \times 10^8$  (mol N<sub>2</sub>O s<sup>-1</sup> (mol Fe)<sup>-1</sup> (Pa N<sub>2</sub>O)<sup>-1</sup>).  $E_a$  for Fe/ZSM-5 ( $x = 0$ ) remains at about 186 kJ mol<sup>-1</sup>, while apparent activation energies for samples containing extraframework Al (Fe/ZSM-5 ( $x = 1$ ) and Fe/ZSM-5 ( $x = 2$ )) are at a somewhat lower value of about 180 kJ mol<sup>-1</sup>. A blank experiment on Al/ZSM-5 prepared by the same method as the catalyst preparation shows that the activity of solely extraframework Al is negligible, thus steady state N<sub>2</sub>O decomposition reveals that the introduced extraframework Al profoundly modifies the nature of iron active site in Fe/ZSM-5.

UV-Raman spectroscopy was used to obtain structural information about the active site of Fe/ZSM-5 (Fig. 4). These samples have been treated in He flow at 900 °C. Besides the strong band at 380 cm<sup>-1</sup> and weak bands at 295 and 810 cm<sup>-1</sup> related to the vibrations of zeolite framework with MFI topology, several bands at 475, 630, 875 and 1010 cm<sup>-1</sup> can be observed. It is very interesting to note that the intensity of the strongest band at 875 cm<sup>-1</sup> parallels with the amount of introduced extraframework Al, and the band is quite sharp, with a fwhm (full width at half maximum) of about 35 cm<sup>-1</sup>. A minor feature at 1010 cm<sup>-1</sup> also shows a similar relationship with the amount of extraframework Al. A blank experiment on Al/ZSM-5 does not show any similar



**Fig. 4** UV-Raman spectra of samples after treated in He at 900 °C: (a) Fe/ZSM-5 ( $x = 0$ ); (b) Fe/ZSM-5 ( $x = 1$ ); (c) Fe/ZSM-5 ( $x = 2$ )

Raman bands, reflecting these two bands must be due to some newly formed species, most probably just the active sites formed by the close interaction between extraframework Fe and Al. Confirmative assignment of these bands requires further work and is under way.

It is probable that the active site is the mixed Fe-Al oxide cluster formed between extraframework Fe and Al, as proposed by van Santen *et al.*<sup>10</sup> and Sachtler *et al.*<sup>9</sup> However, since  $\alpha$ -oxygen can also be formed on Fe/Silicalite without any presence of Al,<sup>4</sup> it is thus most probable that some specific Fe species, *e.g.*, magnetite (Fe<sub>3</sub>O<sub>4</sub>) cluster, as proposed by Fejes *et al.*,<sup>7</sup> is the active site. It is easy to envisage that the spinel structure of aluminium oxide favors the formation of the inverse spinel structure of Fe<sub>3</sub>O<sub>4</sub> cluster.

In summary, both the concentration of “ $\alpha$ -oxygen” and the activity for steady state N<sub>2</sub>O decomposition increase linearly with the amount of introduced extraframework Al in Fe/ZSM-5 catalysts, suggesting that the interaction between extraframework Fe and Al is more efficient than solely Fe for the active site formation and for N<sub>2</sub>O decomposition. This information may also be helpful for the understanding of the active site for benzene to phenol on Fe/ZSM-5.

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