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The promotional effect of NO on N_2O decomposition over the bi-nuclear Fe sites in Fe/ZSM-5

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ABSTRACT

Combining transient response method, steady-state kinetics, in situ IR, and in situ Raman spectroscopic techniques, the effect of NO on N_2O decomposition over Fe/ZSM-5 catalyst was investigated in detail, which reveals that the active sites are bi-nuclear Fe sites. The presence of NO increases the desorption rate of O_2 and lowers the apparent activation energy of N_2O decomposition. Trace amount of water vapor can lead to the deactivation of the Fe/ZSM-5 catalyst due to the oxidation of the active Fe^{2+} sites during N_2O decomposition. On the other hand, NO treatment causes the regeneration of the inactive Fe sites by releasing O_2 at relatively low temperature. For the first time, it was found that a Raman band at 743 cm^{-1}, assigned to the bi-nuclear Fe sites, changes accordingly with the deactivation and regeneration of the Fe/ZSM-5 catalyst. The in situ IR spectroscopic study reveals that NO treatment of the deactivated catalyst can remove the hydroxyl groups bound to the inactive Fe^{3+} species. These results demonstrate that H_2O and NO play important roles in the structural transformation between the hydroxylated bi-nuclear Fe^{3+} sites and the dehydroxylated bi-nuclear Fe^{2+} sites in Fe/ZSM-5. Our conclusion is that the positive effect of NO on N_2O decomposition is due to the dehydroxylation of the hydroxylated bi-nuclear Fe sites facilitated by NO, as well as the enhancement of the O_2 desorption rate regulated by NO.

1. Introduction

N_2O is not only one of the major sources of nitrogen oxides (NO_x) depleting the ozone layer in the stratosphere, but also a strong greenhouse gas with a global warming potential approximately 300 times higher than that of CO_2 [1]. Considerable fractions of N_2O are emitted from industrial processes for the production of nitric and adipic acid. There has been increasing interest in the development of new technologies to reduce N_2O release. Noble metal containing catalysts is cost ineffective though they show very high catalytic activities for N_2O decomposition [1,2]. Fe/ZSM-5 is a relatively cheap non-noble metal containing N_2O decomposition catalyst. A peculiar behavior of Fe/ZSM-5 catalyst is that the presence of NO can significantly enhance the catalytic activity of N_2O decomposition, which is opposite to the inhibiting effect of NO observed in other catalytic systems, e.g., noble metal based catalysts [1,3,4]. This peculiar behavior could be taken as high advantages for the treatment of the exhausted gases generated in adipic and nitric acid plants since they are usually mixtures of NO and N_2O.

Numerous efforts have been made to nail the mechanism of the NO-assisted N_2O decomposition over Fe/ZSM-5 catalyst by transient response technique and theoretical calculation method. Isolated Fe ions [5,6], bi-nuclear [7], and oligo-nuclear Fe sites [8,9] were proposed to be the active Fe sites for the reaction. On the basis of transient response techniques, Peréz-Ramírez et al. studied the catalysts with higher Fe contents and suggested that added NO adsorbs on nonactive Fe sites adjacent to the active iron sites [8]. However, Sang et al. assumed that extra sites adjacent to the catalytically active site are not essential to the promotional effect of added NO [5]. Heyden et al. proposed that a $Z^-[Fe(OH)]^+$ site is responsible for N_2O decomposition based on theoretical calculation method [6]. Mul et al. reported that the NO-assisted N_2O decomposition took place on oligo-nuclear Fe sites by the formation of NO_2 that enhances the rate of O_2 desorption [9]. Pirngruber and Pieterse also found that NO_2 acted as an oxygen storage intermediate in the catalytic cycle [7]. These conflicting arguments show that the nature of the active sites and the mechanism of the NO-assisted N_2O decomposition are still quite in debate.

It is very difficult for most of the spectroscopic techniques to distinguish different Fe species since the concentration of the active Fe species is rather low and the distribution of these Fe species is heterogeneous (isolated Fe cations, bi-nuclear Fe clusters, oligo-nuclear Fe clusters, and small Fe oxide particles) in Fe/ZSM-5 [10–25]. Particularly, there are a few in situ spectroscopic techniques used

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to study the evolution of the active Fe sites under working conditions. By using in situ IR spectroscopic technique, Pirngruber and Pieterse found that NO_2 is an intermediate of the catalytic cycle and functions as intermediate oxygen storage for the decomposition of N_2O in the presence of NO [7]. However, most of the spectroscopic techniques, such as IR, cannot give detailed structural information about the active Fe sites. It has been shown that the resonance Raman spectroscopy can selectively identify these specific Fe species due to its sensitive resonance Raman effect [26–31]. In this work, the in situ Raman spectroscopic techniques are applied to further nail the nature of the active Fe sites and N_2O decomposition mechanisms.

In this work, in situ Raman spectroscopy and transient response method are used to investigate the promotional role of NO on N_2O decomposition. It was found that: (a) the dehydroxylated bi-nuclear Fe^{2+} sites are the active sites for the decomposition of N_2O in the presence of NO; (b) NO treatment can regenerate the deactivated sites by releasing O_2 at low temperatures; (c) Moreover, H_2O and NO can play key roles in the structural transformation between the hydroxylated bi-nuclear Fe^{3+} sites and the dehydroxylated bi-nuclear Fe^{2+} sites in Fe/ZSM-5.

2. Experimental

The Fe/ZSM-5 catalysts were synthesized by solid-state ion-exchange method. More details can be found in the literature [22,23,30,32,33]. The as-synthesized sample was calcined in O_2 flow at 823 K followed by the treatment in He flow at 1173 K for 2 h. The content of Fe in the catalyst is about 2.2 wt.%, corresponding to Fe/Al = 0.61.

A single-pass plug-flow quartz reactor with an inner diameter of 4 mm was used to test the catalyst performance of Fe/ZSM-5 samples for N_2O decomposition. The catalyst sample (50 mg) was retained between two quartz wool plugs. Prior to N_2O decomposition at a given temperature, the catalyst was pretreated in He flow at 1173 K for 1 h. For transient response experiments, a combination of a four-port switching valve and a six-port switching valve allowed us readily switch among the ports to the gas-phase N_2O decomposition reactor and those to the inlet pulse gases of N_2O or NO. During transient and steady-state catalytic measurements, the concentration of N_2O was 5.0 vol.% and the gas hourly space velocity was kept at 24,000 ml/g h. For N_2O decomposition in the presence of NO, the gas hourly space velocity was kept at 24,000 ml/g h and the concentrations of N_2O and NO were 5 vol.% and 1 vol.%, respectively. It should be noted the feeds contain trace amount of water (about 1–10 ppm). A well calibrated on-line mass spectrometer (GAM 200; Pfeiffer vacuum) was used for the quantification of gaseous products.

In situ visible Raman spectra were recorded on a home-made Raman spectrometer equipped with a 532-nm laser source. The samples were pressed into self-supporting wafers and placed in an in situ quartz cell equipped with gas inlet/outlet and heating system. In order to eliminate fluorescence interference (e.g., organic remnants), the wafers were pretreated in O_2 flow at 823 K for 1 h, followed by a pretreatment in He flow at 1023 K for 1 h. After these treatments, the samples were cooled to a specific temperature to record Raman spectrum at certain time intervals.

In situ DRIFTS were collected on a Nicolet Impact 410 FT-IR spectrometer in diffuse reflectance mode with an MCT detector at a resolution of 4 cm^{-1}. The samples were pressed into 20 mg self-supporting pellets, and subsequently placed into a DRIFT cell equipped with CaF_2 windows. Prior to each IR experiment in N_2 flow, the catalysts were pretreated in N_2 flow at 773 K for 1 h and then cooled to a specific reaction temperature for N_2O direct decomposition. A single beam spectrum of the catalyst before N_2O decomposition was taken as a background.

3. Results

3.1. The positive effect of NO on the decomposition of N_2O

Fig. 1 shows the decomposition of N_2O on Fe/ZSM-5 as a function of temperature in the absence and in the presence of NO. In a N_2O/He feed, the catalyst shows a substantial N_2O conversion only above 643 K. The presence of NO ($NO/N_2O = 0.2$) significantly increases the activity of N_2O decomposition. The N_2O conversion curve is shifted to a temperature about 60 K lower for the same conversion. In addition, the addition of NO in the feed leads to a significant decrease in the apparent activation energy, which is obtained by Arrhenius plot under the assumption of first-order disappearance [34]. The apparent activation energy increases from 140 kJ/mol in the presence of NO to 184 kJ/mol in the absence of NO.

3.2. Deactivation and regeneration of the active sites on Fe/ZSM-5

To investigate the effect of H_2O on N_2O decomposition at high temperature, the catalyst was pre-saturated with H_2O in He flow and deactivated through N_2O decomposition. Fig. 2A shows the response of N_2 with a sharp peak and only a small peak of O_2. This indicates that adsorbed water results in the decrease of the activity of N_2O decomposition and deposition of the surface oxygen atoms on the catalyst. Fig. 2B shows the in situ Raman spectra of N_2O decomposition on Fe/ZSM-5 pre-saturated with H_2O at 653 K. The bands at 380 and 800 cm^{-1} are characteristic Raman bands of MFI structure of ZSM-5 zeolite [26–28]. The intense band at 743 cm^{-1} is associated with the deposited oxygen species.

After the deactivation of the active sites for N_2O decomposition, a step from He to 1 vol.% NO in He was performed on the deactivated catalyst at 723 K (Fig. 3A). Interestingly, a peak of O_2 is observed, suggesting that NO treatment can efficiently regenerate

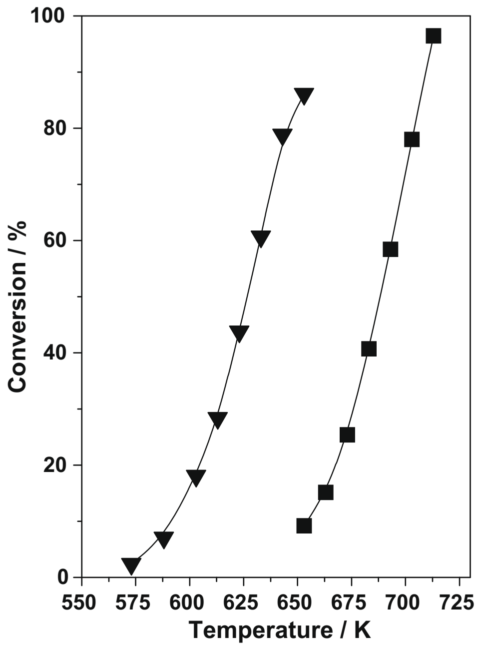

Fig. 1. Steady-state N_2O conversion on Fe/ZSM-5 as a function of temperature in different feed compositions: (▼) 1 vol.% NO and 5 vol.% N_2O in He; (■) 5 vol.% N_2O in He.

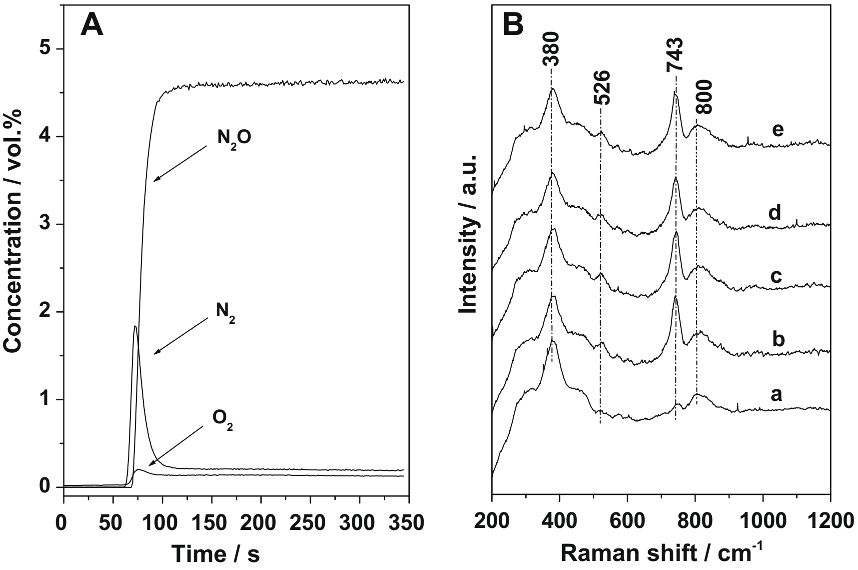

Fig. 2. (A) Response after a step from He to 5.0 vol.% N_2O/He at 653 K on Fe/ZSM-5 pre-saturated with H_2O. (B) In situ Raman spectra of Fe/ZSM-5 for direct N_2O decomposition at certain time intervals: (a) 0 min, (b) 5 min, (c) 10 min, (d) 15 min, (e) 30 min. The excitation line: 532 nm; collection time: 240 s.

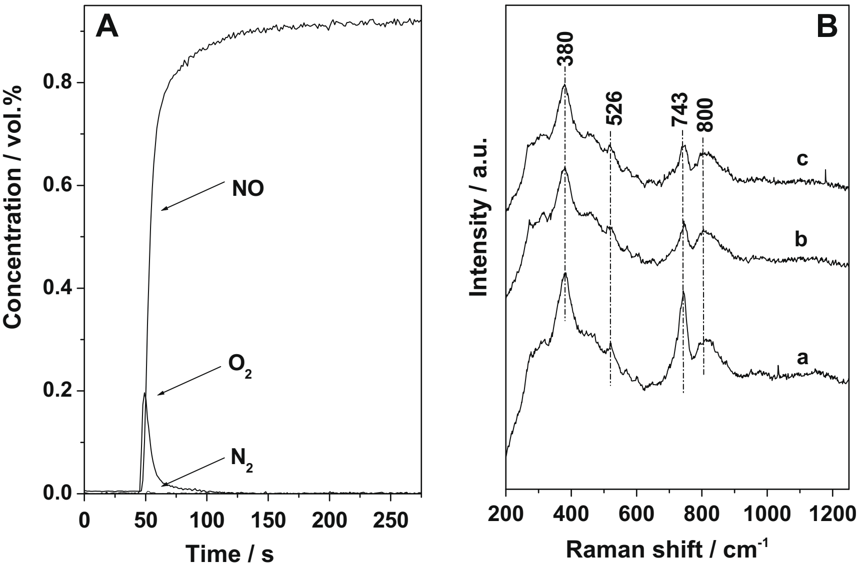

Fig. 3. (A) Response of a step from He to 1 vol.% NO/He at 723 K on Fe/ZSM-5 after the deactivation of the active sites. (B) In situ Raman spectra of Fe/ZSM-5 treated with NO after the deactivation of the active sites: (a) the deactivated catalyst, (b) treated with NO at 723 K for 10 min, (b) treated with NO at 723 K for 15 min. The excitation line: 532 nm; collection time: 240 s.

the deactivated catalyst. Accordingly, the in situ Raman spectroscopy was used to follow NO treatment of the deactivated catalyst (Fig. 3B). The intensity of the band at 743 cm^{-1} decreases after NO treatment of the deactivated catalyst at 723 K. This is in good agreement with the transient response result of the deactivated catalyst releases O_2 upon NO treatment (Fig. 3A). More importantly, these results show that the released surface oxygen atoms by NO treatment are directly related with the band at 743 cm^{-1}.

To further investigate the mechanism of NO treatment, NO pulses were performed on the deactivated catalyst at 723 K, as shown in Fig. 4A. The O_2 evolution was observed after pulsing NO, meanwhile, the amount of O_2 decreases with the increase in the NO pulse number. The amount of each NO pulse is the same, indicating that NO is not consumed in the pulse process. Surprisingly, the amount of O_2 is more than that of NO in the first pulse. Fig. 4B depicts the in situ Raman spectra of the deactivated catalyst after pulsing NO at 723 K.

3.3. N_2O decomposition on Fe/ZSM-5 in the absence and in the presence of NO

The transient response experiments were performed to further investigate the effect of NO on O_2 desorption. Fig. 5A illustrates the response of N_2O pulsed into He flow on Fe/ZSM-5 at 693 K. It should be noted that the experiment was performed after N_2O decomposition reached a steady-state. The desorption of O_2 always delays than that of N_2, which is in line with our previous work [23]. Fig. 5B shows the response of N_2O and NO mixture pulsed into He flow on Fe/ZSM-5 at 633 K. The desorption of N_2 and O_2 are almost synchronic at lower temperature during N_2O decomposition in the

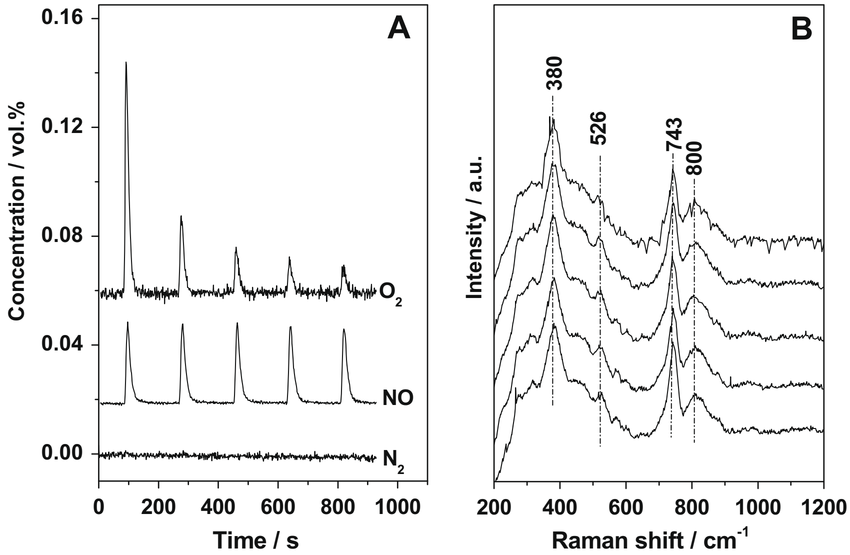

Fig. 4. (A) Response of NO pulsed into He flow on Fe/ZSM-5 at 723 K after the deactivation of the active sites. (B) In situ Raman spectra of Fe/ZSM-5 treated with increasing the pulse numbers of NO. The excitation line: 532 nm; collection time: 240 s.

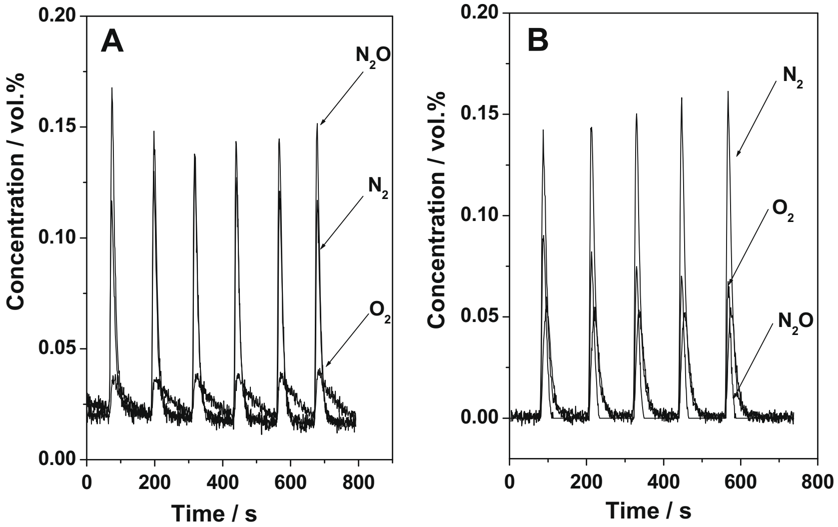

Fig. 5. (A) Response of N_2O pulsed into He flow on Fe/ZSM-5 at 693 K. (B) Response of N_2O and NO mixture pulsed into He flow on Fe/ZSM-5 at 633 K.

presence of NO. This result unambiguously indicates that the presence of NO enhances the desorption of O_2 during N_2O direct decomposition.

Fig. 6A shows the response of a step from He to mixtures of 1 vol.% NO and 5 vol.% N_2O on Fe/ZSM-5 at 633 K. It can be seen that the concentrations of N_2 and O_2 firstly reach to their maximum and then decay to a steady-state. The curve of $N_2 - 2 \times O_2$ indicates that some surface oxygen atoms are deposited on the catalyst (not shown). The deposition of surface oxygen atoms is due to trace amount of water in the feed. Fig. 6B illustrates the in situ Raman spectra of N_2O decomposition on Fe/ZSM-5 in the presence of 1 vol.% NO at 633 K as a function of time. After a step from He to the mixtures of N_2O and NO, an increase in the intensity of the band at 743 cm^{-1} is observed, furthermore, the intensity reaches a maximum after 10 min.

Fig. 7 shows the in situ DRIFT spectra of N_2O decomposition on Fe/ZSM-5 catalyst at 523 K. A strong band at 3672 cm^{-1} and a shoulder at 3628 cm^{-1} are observed with the evolution of the reaction time. After N_2O decomposition reached a steady-state, a switch from N_2O to NO was performed. It can be seen the introduction of NO leads to a significant decrease in the intensities of the bands at 3628 and 3674 cm^{-1}. Dubkov et al. [35] also observed a shoulder at 3635 cm^{-1} and a strong band at 3674 cm^{-1} after reaction of methane or H_2 with α-oxygen. Hence, the band at 3628 cm^{-1} is tentatively attributed to an OH stretching vibration in a pair of hydrogen-bonded group bound to the Fe species, whereas the band at 3672 cm^{-1} to the terminal hydroxyl groups bound to the Fe species. This result shows that the addition of NO could remove hydroxyl groups bound to Fe species. The in situ IR spectra of N_2O decomposition at 653 K and NO regeneration on Fe/ZSM-5 are similar to Fig. 7 (not shown), indicating that the active sites for N_2O decomposition could be similar.

Fig. 8 shows the in situ DRIFT spectra of N_2O decomposition on Fe/ZSM-5 in the presence of 1 vol.% NO at 633 K at certain time intervals. The two bands at 3628 and 3672 cm^{-1} are due to trace amount of water in the feed. More interestingly, it was found that

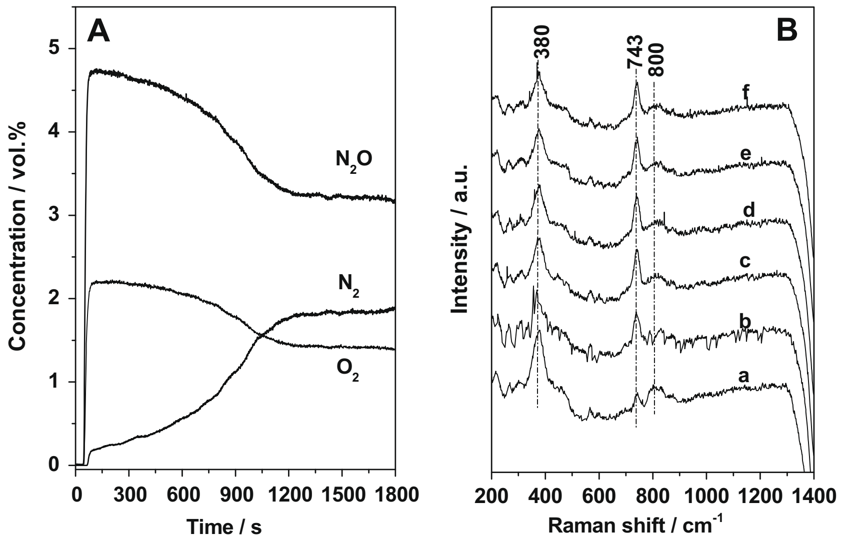

Fig. 6. (A) Response of a step from He to mixtures of 1 vol.% NO and 5 vol.% N_2O on Fe/ZSM-5 at 633 K. (B) In situ Raman spectra of Fe/ZSM-5 for 5 vol.% N_2O decomposition in the presence of 1 vol.% NO on at 633 K at certain time intervals: (a) 0 min, (b) 5 min, (c) 10 min, (d) 15 min, (e) 30 min, (f) 60 min. The excitation line: 532 nm; collection time: 240 s.

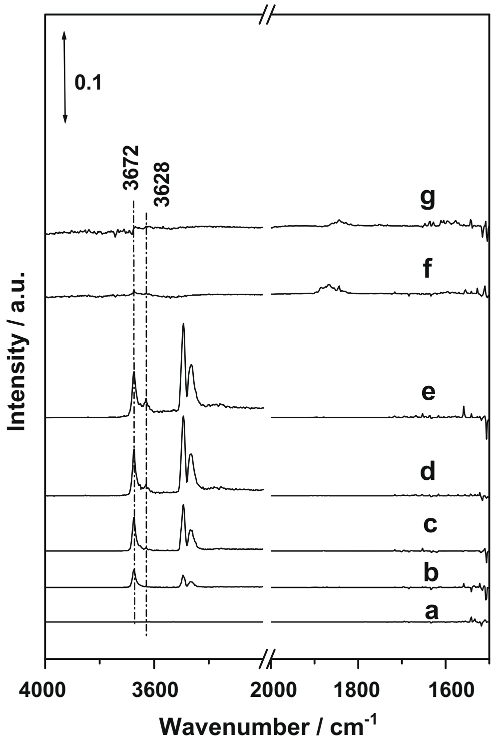

Fig. 7. In situ DRIFT spectra of N_2O decomposition at 523 K on Fe/ZSM-5 at certain time intervals: (a) 0 min, (b) 3 min, (c) 5 min, (d) 10 min, (e) 15 min, and then followed by NO regeneration at (f) 623 K and (g) 723 K.

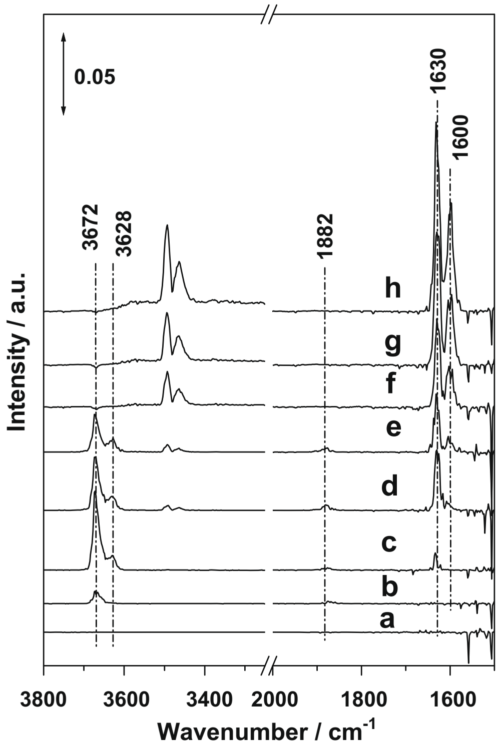

Fig. 8. In situ DRIFT spectra of N_2O decomposition on Fe/ZSM-5 in the presence of 1 vol.% NO at 633 K at certain time intervals: (a) 0 min, (b) 2 min, (c) 3 min, (d) 4 min, (e) 5 min, (f) 10 min, (g) 15 min, (h) 30 min.

the intensities of these two bands firstly reach their maximum, and then decrease with the evolution of the reaction time. After 10 min, these two bands completely disappeared. This result shows that the presence of NO removes the hydroxyl groups bound to the Fe species during N_2O direct decomposition. Additionally, a band at 1630 cm^{-1} was tentatively assigned to NO_2 adsorbed on the Fe species. With the evolution of the reaction time, a band at 1600 cm^{-1} was also observed, which is due to the gas-phase/adsorbed NO_2 [7,23].

4. Discussion

4.1. Regeneration of the active sites for N_2O decomposition with NO treatment

It was reported that trace amount of water vapor can lead to the deactivation of the catalysts during N_2O decomposition since water vapor can result in the hydroxylation of the active Fe sites [36–38]. Similar results were also obtained in this work. In situ Raman spectroscopic studies combined with transient response results show that the band at 743 cm^{-1} is directly associated with the deactivation of the catalysts. According to the Raman assignments of the bi-nuclear iron models [39], the band at 743 cm^{-1} is tentatively assigned to the Fe–O–Fe asymmetric stretching mode of the bi-nuclear Fe sites, which generally present in the Fe/ZSM-5 catalysts [12,30,31,40–43]. It is the first time to obtain the structural information of the inactive Fe sites under reaction condition by in situ Raman spectroscopy. According to the transient response results, the deactivated bi-nuclear Fe sites should be the bi-nuclear Fe^{3+} sites since it derived from the oxidation of the active Fe^{2+} sites by N_2O decomposition (Fig. 2), i.e., the bi-nuclear Fe^{2+} sites are active sites for the N_2O decomposition in the presence of NO. It was proposed that the active sites are the isolated Fe sites [6] by DFT calculation or the oligo-nuclear Fe sites [8] by transient response method for the NO-assisted N_2O decomposition. By combining both IR and Raman to explore the symmetric and asymmetric vibrations of Fe species in ZSM-5, we have obtained more detailed real information on the active sites, that is, dehydroxylated bi-nuclear Fe^{2+} sites is responsible for the decomposition of N_2O.

The in situ IR spectroscopic results further showed that the bands at 3628 and 3672 cm^{-1}, assigned to the hydroxyl groups bound to the Fe species, disappeared upon NO treatment, indicating that the regeneration of catalyst is through the removal of the hydroxyl groups bound to the inactive Fe sites. It has been proposed that NO reacted with the adsorbed oxygen species to form gas-phase NO_2 and then regenerate the active sites [8]. Heyden et al. proposed that NO can react with $Z^-[Fe(OH)_2]^+$ to form active $Z^-[Fe(OH)]^+$ sites and HNO_2 species based on theoretical calculation method [6]. However, by combining IR with Raman spectral results, it seems more reasonable that NO treatment can remove the hydroxyl groups bound to the hydroxylated bi-nuclear Fe^{3+} sites to form the bi-nuclear Fe^{2+} sites by releasing molecular O_2 and H_2O.

It is very interesting that NO treatment can regenerate the deactivated Fe sites at low temperature. It appears that NO is an analogous "catalyst" since it can reduce the hydroxylated Fe^{3+} sites into the dehydroxylated Fe^{2+} sites without any consumption during the regeneration processes of the active sites. Peréz-Ramírez et al. have proposed that NO could scavenge the surface oxygen atoms to form NO_2, which further reacts with a second deposited oxygen atom to reproduce NO accompanied by the O_2 release [8]. On the basis of this view, the amount of NO should be equal to that of released O_2 during NO treatment of the deactivated catalyst. However, pulse response experiment shows that the amount of released O_2 is much larger than that of NO in the first pulse (Fig. 4A), which is inconsistent with the proposal that adsorbed NO_2 reacts with a second oxygen atom to form O_2. It is most likely that regeneration process of the active site is a radical reaction, i.e., NO or oxygen species act as radicals. Interestingly, it was reported that NO can play a regulatory role in the redox cycles between the heme Fe^{3+} and Fe^{2+} species in nitric oxide reductase and relevant model complexes [44]. And we believe that similar mechanism may apply to explain the regulatory role of NO in the transformations of the iron species in Fe/ZSM-5 during N_2O decomposition.

4.2. The promotional effect of NO on the activity of N_2O decomposition

In this study, steady-state N_2O decomposition results show that the addition of NO significantly increases the activity of N_2O decomposition. The apparent activation energy varies from 140 kJ/mol in the presence of NO to 184 kJ/mol in the absence of NO. Transient response experiments show that the desorption of O_2 and N_2 is almost simultaneous during N_2O decomposition in the presence of NO at 633 K, while O_2 is always delayed relative to N_2 during N_2O direct decomposition in the absence of NO at 693 K (Fig. 5).

The reason why addition of NO can promote desorption of O_2 has been extensively discussed in the literature [45–47]. Peréz-Ramírez et al. reported that the presence of NO can regenerate the active sites and accelerate the recombination of oxygen from N_2O. In addition, NO has been proposed to play an important role in the transportation and storage of surface oxygen atoms [8]. In this work, the adsorbed NO_2 species was observed by in situ IR spectroscopy during the decomposition of N_2O in the presence of NO. It was suggested that the adsorbed NO_2 reacts with another adjacent NO_2 to form NO and O_2 since the two adsorbed NO_2 are in intimate distances. This assumption was also manifested by the transient response results that the presence of NO can accelerate desorption of O_2 during N_2O decomposition (Fig. 5B). It is also possible that an adsorbed NO_2 reacts with a gas-phase N_2O to release O_2. Bulushev et al. reported that the adsorbed NO_2 species facilitates the recombination and desorption of surface oxygen atoms [46,47]. Hence, a possible explanation for the promotional effect of NO is that NO facilitates the migration, recombination, and desorption of O_2 during N_2O decomposition.

4.3. Active sites and reaction mechanism of N_2O decomposition

In our previous work, observation of Raman band at 867 cm^{-1} demonstrated that the α-sites, where oxygen is bridged to a bi-nuclear Fe^{3+} sites in the form of peroxide (α-oxygen), are actually the bi-nuclear Fe^{2+} sites [30]. In this work, a new Raman band at 743 cm^{-1} was observed, which is assigned to the hydroxylated bi-nuclear Fe^{3+} sites. In situ Raman and transient response study, all showed that NO treatment could decrease the amount of hydroxylated bi-nuclear Fe^{3+} sites by the formation of dehydroxylated bi-nuclear Fe^{2+} sites, accompanied by O_2 release. It has been reported that the dehydroxylated bi-nuclear Fe^{2+} sites show higher activity on N_2O decomposition than the hydroxylated bi-nuclear Fe sites based on density functional theory [42,43]. Hence, the posi-

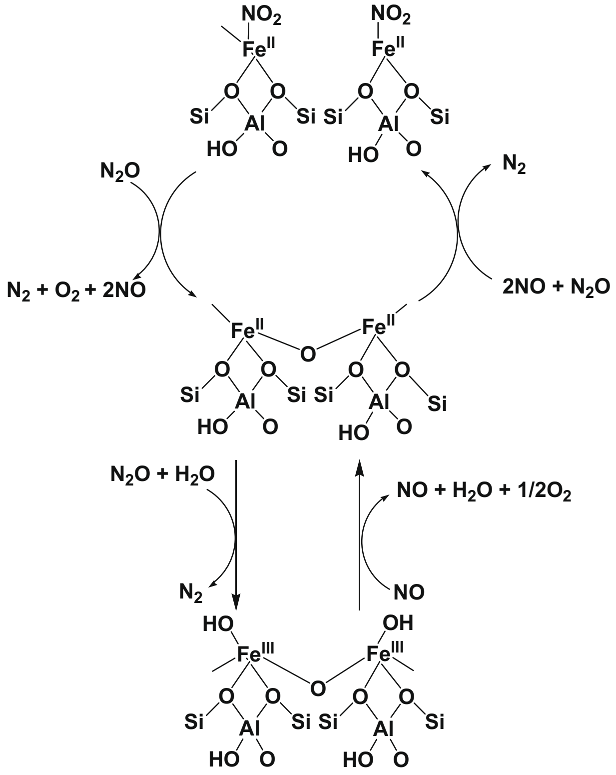

Fig. 9. Schematic description of the promotional effect of NO on direct N_2O decomposition.

tive role of NO in N_2O decomposition can be explained by one of the facts that NO can convert the hydroxylated bi-nuclear Fe sites into the active dehydroxylated bi-nuclear Fe sites.

To simply explain the role of NO in N_2O decomposition, schematic description of catalytic cycles is shown in Fig. 9. On the basis of the results from in situ spectroscopy and transient response method study, for the first time, bi-nuclear Fe sites are proposed to be the active sites for the NO-assisted N_2O decomposition. Moreover, the role of water in the structural transformation between the dehydroxylated and the hydroxylated bi-nuclear Fe sites was also elucidated. We think that the NO_2 species adsorbed on bi-nuclear Fe sites could be an intermediate species in N_2O decomposition in the presence of NO. The two adjacent NO_2 adsorbed on the bi-nuclear Fe sites could react with each other to release O_2, or adsorbed NO_2 species could react with N_2O to release O_2.

It has been shown that the structure of the Fe species in Fe/ZSM-5 is strongly dependent on the synthesis method, zeolite precursor, amount of Fe loading, and pretreatment condition [12,20,21,23,48]. The Fe/ZSM-5 samples studied in this work also contain isolated Fe ions, bi- and oligo-nuclear Fe sites as reported in our previous work. The percentage of the bi-nuclear Fe sites in all Fe sites is about 28% based on the transient response method [30]. Therefore, we cannot completely exclude the contributions from the isolated Fe ion sites simply based on no direct observation of its Raman band in visible Raman spectroscopy. However, the in situ Raman spectroscopic studies do provide direct evidences that the bi-nuclear Fe sites truly participate in the NO-assisted N_2O decomposition.

5. Conclusions

The presence of NO could increase the activity and decrease the apparent activation energy of N_2O decomposition on Fe/ZSM-5. Trace amount of water vapor results in the hydroxylation of the active Fe sites during N_2O decomposition, while NO treatment can regenerate the deactivated catalyst by releasing O_2 at low temperatures.

For the first time, we found that the in situ Raman spectral and transient step results show that a Raman band at 743 cm^{-1}, ascribed to the dehydroxylated bi-nuclear Fe sites, is directly related with the deactivation and regeneration of the active sites for the NO-assisted N_2O decomposition. In situ IR spectroscopic study further demonstrates that the NO treatment of the deactivated Fe/ZSM-5 catalyst could remove the hydroxyl groups bound to the deactivated Fe sites. Transient response results show that the desorption rates of N_2 and O_2 are almost synchronous during N_2O decomposition in the presence of NO, while the desorption rate of O_2 is always slower than that of N_2 during N_2O decomposition in the absence of NO. The promotional effect of NO on N_2O decomposition as follows: (1) NO can catalyze the transformation of the hydroxylated bi-nuclear Fe^{3+} sites into the dehydroxylated bi-nuclear Fe^{2+} sites, which are the active sites for the N_2O decomposition and (2) NO can also promote desorption of O_2 during N_2O decomposition.

Acknowledgments

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