研究简报

N_2O 活化的 Fe/ZSM-5 表面活性氧的表征

温 广*,[1] 张 朋[2]

([1]石油大学(华东)研究生院,北二路 271 号,东营 257061)

([2]联合环境能源公司,Thorn 227 号,纽约,14127,美国)

关键词:活性氧;Fe/ZSM-5 催化剂;N_2O 处理;程序升温还原;$[Fe\text{-}O\text{-}Fe]^{2+}$二元体

中图分类号:X506 **文献标识码**:A **文章编号**:1001-4861(2005)10-1535-06

Characterization of Active Surface Oxygen in N_2O-activated Fe/ZSM-5

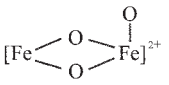
WEN Guang*,[1] ZHANG Peng[2]

([1]*Graduate School of University of Petroleum*, 271 *BeiEr Road, Dongying* 257061)

([2]*United Environment & Energy, LLC.*, 227 *Thorn Ave., Building B, Orchard Park, NY* 14127, *USA*)

Abstract: Temperature-programmed reduction (H_2-TPR) was employed to quantitatively characterize the active oxygen species generated from a high Fe-loading Fe/ZSM-5 catalyst exposed to N_2O at 250 ℃. $[Fe\text{-}O\text{-}Fe]^{2+}$ dimer was determined as the active iron complex for N_2O decomposition to produce the active oxygen. Reduction of Fe^{3+} to Fe^{2+} by H_2 in the dimer and removal of OH^- groups from Fe^{2+} dimer by heating Fe/ZSM-5 to 700 ℃ were the prerequisites for the formation of this active Fe complex. A linear correlation with a slope of 1.0 between the amount of $[Fe\text{-}O\text{-}Fe]^{2+}$ and that of active oxygen species was observed. Maximum amount of active oxygen species can be generated by reducing Fe/ZSM-5 catalyst with H_2 at the temperatures over 500 ℃ and then heating the resulting product in Ar to 700 ℃, followed by N_2O exposure at 250 ℃.

The ratio of the total number of oxygen atoms (O_{de}) deposited by interaction of $[Fe\text{-}O\text{-}Fe]^{2+}$ with N_2O to the amount of $[Fe\text{-}O\text{-}Fe]^{2+}$ was 2. However, not all the deposited oxygen atoms were active oxygen (O_a); the ratio of O_a and O_{de} was 0.5. The iron dimer complex composing active oxygen is a five-atom ion $[Fe_2O_3]^{2+}$; the most probable structure is as follows:



Key words: active oxygen; Fe/ZSM-5; N_2O treatment; temperature-programmed reduction; $[Fe\text{-}O\text{-}Fe]^{2+}$ dimmer

0 Introduction

Recently, considerable attention has been given to Fe/ZSM-5 catalyst due to its promising performance in hydrocarbon oxidation[1], N_2O decomposition[2], and reduction of NO[3]. Of the most interesting are the surface oxygen generation and its role in selective oxidation of hydrocarbons. Panov et al.[1] showed that Fe/ZSM-5 with a low iron loading catalyzed the oxidation of benzene with nitrous oxide (N_2O) to phenol in one step. They observed that these Fe/ZSM-5 catalysts pretreated at high temperature were able to abstract

收稿日期:2005-03-06。收修改稿日期:2005-06-10。

*通讯联系人。E-mail:dyslofwg@sohu.com

第一作者:温 广,男,37 岁,硕士,工程师;研究方向:工程管理。

an oxygen atom from an impinging N_2O molecule at 250 ℃, without releasing O_2 to the gas phase. These authors called this special form of adsorbed oxygen as "a-oxygen". The nature of this active oxygen has been subject to much debate. Yoshizawa et al.[4] assumed that an $[FeO]^+$ adduct was formed and then reduced, in a catalytic cycle, to Fe^+. Yokovlve et al.[5] reported that the interaction of $[Fe\text{-}O\text{-}Fe]^{2+}$ ion with N_2O transformed $[Fe\text{-}O\text{-}Fe]^{2+}$ into an $[Fe\text{-}O\text{-}Fe\text{-}O]^{2+}$ ion with a terminal $Fe^{4+}\text{-}O^-$ bond based on Density Functional Theory (DFT) analysis. With a very low Fe loading in ZSM-5 (0.35%), Panov et al.[1,6] did the quantitative calculation of the amount of different state ions based on M?ssbauer data. They claimed that the active iron composing a-sites was the binuclear complex, which was able to decompose nitrous oxide. The formation of a-oxygen was accompanied by the oxidation of Fe^{2+} to Fe^{3+} ions. However, in their studies, the concentration of Fe was very low. From a statistical point of view, the possibility is low to form binuclear oxocations at low Fe contents.

More recently, it has been found that Fe/ZSM-5 with an Fe/Al atomic ratio of unity (with Si/Al=23, Fe: 4wt%) can be prepared by subliming $FeCl_3$ vapor onto H/ZSM-5[7]. After exchange of Cl^- by OH^- groups and the following calcination, a major portion of the Fe is present in such catalysts as an oxygen-bridged binuclear iron ion $[(OH)\text{-}Fe\text{-}O\text{-}Fe\text{-}(OH)]^{2+}$, as shown by CO-TPR, H_2-TPR, and ESR data. With a large amount of this binuclear iron complex, it is relatively easy to characterize the formation of active oxygen and the corresponding change of iron structure.

In this work, temperature-programmed reduction (TPR) technique was used to quantitatively characterize Fe/ZSM-5 prepared by sublimation method and pretreated under different conditions. The prerequisites for the formation of the maximum amount of active oxygen were investigated and the structure of the iron complex composing active sites was determined.

1 Experimental

1.1 Sample preparation

H-ZSM-5 was obtained by three-fold ion exchange of Na-ZSM-5 (Si/Al=23) with a diluted NH_4NO_3 solution (0.5 mol·L^{-1}) at ambient temperature, followed by calcination of the NH_4^+ form of the zeolite in a high purity O_2 flow (300 mL·min^{-1}) at 550 ℃ for 3 hours. Sublimation of $FeCl_3$ in an Ar flow at 320 ℃ was used by directing the vapor onto the heated H-ZSM-5 (**1**). In a glove bag under N_2, 10.0 g of the calcined H-ZSM-5 was loaded into one side of a U-shaped reactor, and 2.0 g $FeCl_3$ was loaded into the other side of the same reactor. A porous frit kept the zeolite separated from the $FeCl_3$. Chemical vapor deposition was carried out in an Ar (200 mL·min^{-1}) while the temperature of the reactor was kept at 320 ℃.

$$\text{H-ZSM-5} + FeCl_3 \rightarrow Cl_2Fe\text{-ZSM-5} + HCl \qquad (\mathbf{1})$$

$$Cl_2Fe\text{-ZSM-5} + 2H_2O \rightarrow (OH)_2Fe\text{-ZSM-5} + 2HCl \qquad (\mathbf{2})$$

The sample was then removed and washed with doubly deionized (DDI) water. Hydrolysis occurred during washing (**2**). The slurry was vacuum filtered; the solid was dried at 120 ℃ in air and calcined in O_2 at 550 ℃. This sample will be called Fe/ZSM-5. Elemental analysis via inductively coupled plasma spectroscopy (ICP) gave the following compositions in atomic ratios relative to Al:

Fe/ZSM-5: Na/Al=0 Si/Al=23 Fe/Al=1.01

Fe/ZSM-5 has a Fe/Al ratio about unity, which corresponds to 4.0wt% Fe for the dry catalyst.

1.2 Temperature-programmed reduction (TPR)

H_2-TPR experiments were performed with a H_2/Ar (5%) flow of 40 mL·min^{-1} from 25 to 800 ℃ with a ramp of 8 ℃·min^{-1}. The samples (100 mg) were pretreated under different conditions (for details, see "Results and Discussion" section). The H_2 consumption was determined by a TCD detector, with H2O being trapped in a cooled trap. CuO was used as a standard to calibrate the consumption of H_2.

1.3 N_2O treatment

Treatment of 100 mg Fe/ZSM-5 with N_2O was performed at 250 ℃. After pretreatments and Ar purge at 250 ℃, N_2O in 30 mL·min^{-1} was passed through the catalyst for 20 min. Subsequently, the sample was cooled down to 25 ℃ and purged with Ar for 1 h.

1.4 Temperature-programmed desorption (TPD)

H_2O adsorption was carried out at room temperature by leaving 100 mg Fe/ZSM-5 in air overnight. After Ar purge at room temperature and the background level of H_2O was stable, the sample was heated to 750 ℃ at a ramp of 8 ℃·min^{-1} in flowing Ar (40

mL·min^{-1}) and the desorbed species were monitored on-line by a quadruple mass spectrometer (Balzers Oministar, Quadrupole).

2 Results and discussion

Fig.1 gives the TPR profiles of Fe/ZSM-5 after a variety of pretreatments. Profile A corresponds to Fe/ZSM-5 after calcination in O_2 at 550 ℃ for 30 min. The broad peak centered at 410 ℃ (a′) corresponds to the reduction of the bridging oxygen in $[(HO)Fe\text{-}O\text{-}Fe(OH)]^{2+}$ to $[(HO)Fe\text{-}\square\text{-}Fe(OH)]^{2+}$ [7].

$$[(HO)Fe\text{-}O\text{-}Fe(OH)]^{2+} + H_2 \rightarrow [(HO)Fe\text{-}\square\text{-}Fe(OH)]^{2+} + H_2O \quad (3)$$

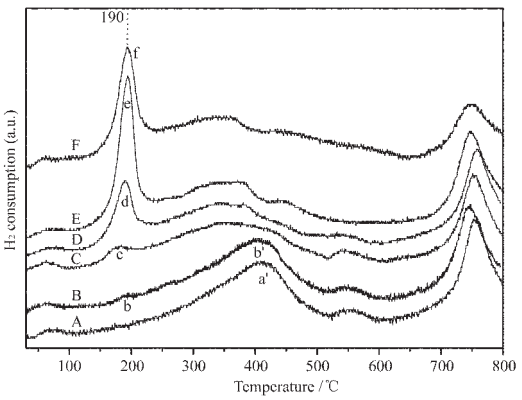


Fig.1 H_2-TPR profiles of Fe/ZSM-5 after pretreatments
A: calcination in O_2 at 550 ℃; B: calcination in O_2 at 550 ℃, followed by exposure to N_2O at 250 ℃; C, D, E, and F: calcination in O_2 at 550 ℃, followed by H_2 reduction at 400 (C), 500 (D), 600 (E) and 700 ℃ (F) for 5 min, respectively, and then exposure to N_2O at 250 ℃.

The small peak at 550 ℃ was assigned to the reduction of a small amount of iron oxide to Fe^0, and the sharp peak located at 750 ℃ was related to the further reduction of Fe^{2+} in the dimers to Fe^0. The small peak near 60 ℃ was an artifact caused by desorption of Ar. After calcination in O_2 of Fe/ZSM-5 at 550 ℃, the sample was cooled to 250 ℃. N_2O treatment was performed after Ar purge, and then H_2-TPR was recorded (profile B). No significant changes caused by N_2O treatment were observed except a very small shoulder near 190 ℃. Profile C, D, E, and F were obtained after the pretreatments as shown in Fig. 1 caption. There was a broad peak between 230 and 530 ℃ in these profiles. No significant changes were observed for the peak located at 750 ℃. However, it is worthwhile to note that a sharp spike at 190 ℃ appeared. High exothermicity of this reduction event was apparent from a marked deviation of the temperature from the programmed value. Clearly, the chemical signature of this Fe-oxygen complex was different from that of the oxide and bridging oxygen species. This peak corresponded to the reduction of active oxygen species, which was also observed in Fe/Beta by Mauvezin et al.[8]. Reduction temperature had a significant effect on the formation of this active oxygen. 400 ℃ pre-reduction of Fe/ZSM-5 only led to generation of a small amount of this oxygen. With the increase of pre-reduction temperature, the amount of this oxygen increased markedly. Pre-reduction at 600 ℃ resulted in the largest amount. Further increasing the reduction temperature to 700 ℃ led to a decrease in the active oxygen amount due to the reduction of Fe^{2+} to Fe^0. The amount of the active oxygen in Fe/ZSM-5 counted by integrating the H_2-TPR spikes at 190 ℃ and the amount of the bridging oxygen in $[(HO)Fe\text{-}O\text{-}Fe(OH)]^{2+}$ complex are listed in Table 1. The reduction of Fe/ZSM-5 at 500 and 600 ℃ both lead to the total reduction of Fe^{3+} in the complexes to Fe^{2+}. However, the amount of active oxygen produced in profile E almost doubles that in profile D. This means that the extent of the reduction of the Fe ions in the dimer is not the only factor to affect the formation of this active oxygen.

Table 1 Amount of H_2 consumption for the peaks in Fig.1 and 2

Peak	H_2 consumption / mmol
a′	0.032 0
b′	0.032 8
b	0.001 0
c	0.003 8
d	0.009 6
e	0.019 8
f	0.014 6
g	0.030 8
g′	0.029 6
h	0.030 4
h′	0.030 1

To identify other factors which may affect the generation of active oxygen, the H_2-TPR profiles after the following pretreatments (Fig.2) were recorded. Calcination in O_2 at 550 ℃ for 30 minutes, followed by H_2 reduction at 600 (G) or 500 (H), and then heating

the sample in Ar to 700 ℃ at a ramp of 8 ℃·min^{-1}, followed by N_2O treatment at 250 ℃. For comparison, the profiles Fig.1A and Fig.1E are also included in Fig.2. It is interesting to note that the amount of active oxygen produced in profile G is much larger than that in profile E (see Table 1). However, the only difference for the sample pretreatment in profile G and E was the heating of the sample in Ar to 700 ℃. This means that sample heating in Ar to higher temperature also has significant effect on the generation of active oxygen.

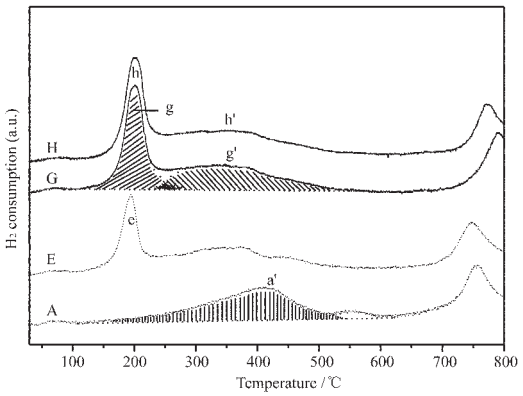


Fig.2 H_2-TPR profiles of Fe/ZSM-5
A and E are the same as Fig.1 A and 1 E; G and H: calcination in O_2 at 550 ℃, followed by H_2 reduction at 600 ℃ (G) and 500 ℃ (H), then heating in Ar to 700 ℃, followed by exposure to N_2O at 250 ℃.

After calcination in O_2 at 550 ℃, the majority of Fe in Fe/ZSM-5 were present as binuclear oxygen-bridged ions $[(HO)Fe\text{-}O\text{-}Fe(OH)]^{2+}$ and $[Fe\langle^{O}_{O}\rangle Fe]^{2+}$ (which was formed from the dehydration of $[(OH)Fe\text{-}O\text{-}Fe(OH)]^{2+}$)[5]. Exposure of this sample to N_2O at 250 ℃ only generated a very small amount of active oxygen (Fig.1B), indicating that both $[(HO)Fe\text{-}O\text{-}Fe(OH)]^{2+}$ and $[Fe\text{-}O_2\text{-}Fe]^{2+}$ are not the active iron species to interact with N_2O to generate active oxygen. Reduction at 500 or 600 ℃ converted all the Fe^{3+} in the dimers to Fe^{2+}. However, the amount of active oxygen formed was significantly different. This difference can be eliminated by heating the samples in Ar to 700 ℃ after reduction at 500 or 600 ℃, as seen in Fig.2G and 2H. This means that the heating in Ar is a very important step. Reduction at 500 and 600 ℃ led to the same amount of Fe^{2+} dimer species in two different states $[(HO)Fe\text{-}\square\text{-}Fe(OH))^{2+}$ and $[Fe\text{-}O\text{-}Fe]^{2+}$.

$$[(HO)Fe\text{-}\square\text{-}Fe(OH))^{2+} \rightarrow [Fe\text{-}O\text{-}Fe]^{2+} + H_2O \quad (4)$$

Reduction at 600 ℃ led to more $[Fe\text{-}O\text{-}Fe]^{2+}$ in the sample as compared with reduction at 500 ℃ because of dehydration. After reduction at 500 or 600 ℃ and subsequently heating the sample in Ar to 700 ℃, all the $[(HO)Fe\text{-}\square\text{-}Fe(OH)]^{2+}$ complexes were transformed to $[Fe\text{-}O\text{-}Fe]^{2+}$ by removing the OH^- groups, as shown in Fig.3. At this stage, the maximum amount of active oxygen was obtained. This shows that $[Fe\text{-}O\text{-}Fe]^{2+}$ rather than $[(HO)Fe\text{-}\square\text{-}Fe(OH)]^{2+}$ is the active iron species which interacts with N_2O to form active oxygen.

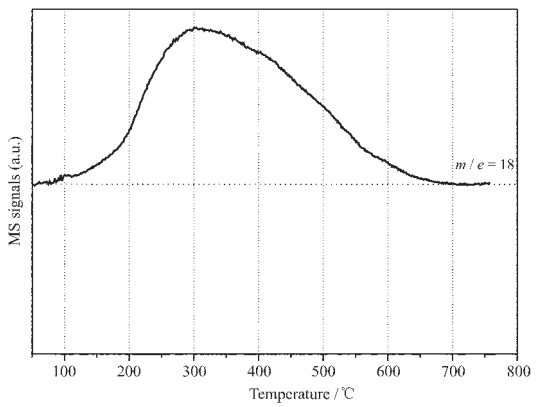


Fig.3 TPD of H_2O from Fe/ZSM-5

TPD of H_2O from Fe/ZSM-5 (Fig.3) shows that no H_2O can be detected after 690 ℃. This means that all the OH^- groups can be removed by heating the sample in Ar to 700 ℃. This confirms that after reduction of the sample at 500 ℃ and followed by heating it in Ar to 700 ℃, only $[Fe\text{-}O\text{-}Fe]^{2+}$ dimmers are present. For the samples in Fig.2G and 2H, all the iron ions in dimers are present as $[Fe\text{-}O\text{-}Fe]^{2+}$ before N_2O treatment.

To quantitatively calculate how many $[Fe\text{-}O\text{-}Fe]^{2+}$ dimmers are present in the sample after different pretreatments, TPR were further performed and recorded after the following pretreatments of Fe/ZSM-5, respectively: (1) heating in Ar to 700 ℃ at a ramp of 8 ℃·min^{-1} (auto thermal reduction); (2) H_2 reduction from 25 to 500 ℃, and then heating in Ar to 700 ℃ at a ramp of 8 ℃·min^{-1}; (3) the same as (2) except that the reduction temperature was from 25 to 300 ℃. The peaks at 410 ℃ in the H_2-TPR profiles correspond to the reduction of $[Fe\text{-}O_2\text{-}Fe]^{2+}$ left after the above pretreatments, from which the amount of Fe^{2+} dimers $[Fe\text{-}O\text{-}Fe]^{2+}$ can be calculated. The peaks at 190 ℃ corre-

spond to the amount of active oxygen after the above pretreatments. To correlate the amount of $[Fe\text{-}O\text{-}Fe]^{2+}$ with that of active oxygen, Fig.4 gives the amount of active oxygen atoms as a function of the amount of $[Fe\text{-}O\text{-}Fe]^{2+}$. A linear correlation between the amount of $[Fe\text{-}O\text{-}Fe]^{2+}$ and that of active oxygen is observed. This leaves no doubt that $[Fe\text{-}O\text{-}Fe]^{2+}$ is the active iron species for N_2O decomposition to form active oxygen.

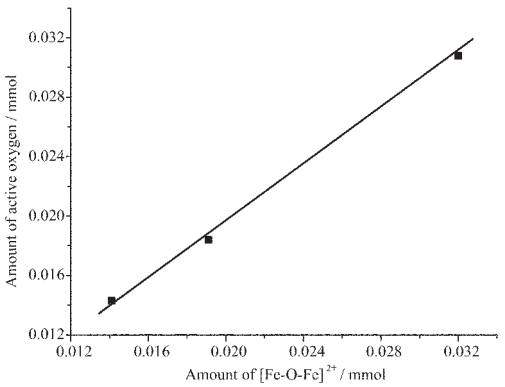
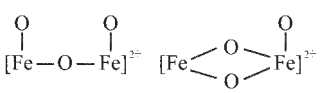


Fig.4　Amount of active oxygen atoms as a function of $[Fe\text{-}O\text{-}Fe]^{2+}$

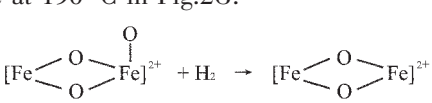
The above results show that reduction of Fe^{3+} in the dimers to Fe^{2+} and heating the sample at high temperature to remove the OH^- groups from Fe^{2+} complex are the prerequisites for the formation of active iron species $[Fe\text{-}O\text{-}Fe]^{2+}$ in a state of high coordinative unsaturation. After these two processes are fulfilled completely, all the iron dimers will be present as $[Fe\text{-}O\text{-}Fe]^{2+}$ and a maximum amount of active oxygen will be generated by the interaction of this iron complex with N_2O.

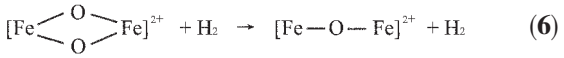
After determining the active iron complex as $[Fe\text{-}O\text{-}Fe]^{2+}$ and the conditions to produce this complex, next question needed to be answered is how this complex interacts with N_2O to generate the active oxygen. As said in the "Introduction", the structure of iron complex composing active oxygen remains an open question, mainly focusing on $[Fe\text{-}O\text{-}Fe\text{-}O]^{2+}$[5], and more recently on $[O\text{-}Fe\text{-}OH\text{-}Fe\text{-}O]^{+}$[6]. In Fig.4, the slope of the line is 1, indicating that the ratio of the amount of active oxygen and that of $[Fe\text{-}O\text{-}Fe]^{2+}$ is 1, *i. e.*, O_a:Fe_{di}=0.5. O_a represents the number of active oxygen atoms and Fe_{di} represents the number of Fe^{2+} in $[Fe\text{-}O\text{-}Fe]^{2+}$. It is very interesting to note that in Fig.2G, except peak g, there is another broad peak g′ between 230 and 530 ℃. The oxygen relates to the second peak g′ in Fig.2G can only come from the deposited oxygen by N_2O decomposition because the reduction of $[Fe\text{-}O\text{-}Fe]^{2+}$ occurs at the temperature of 700 ℃ or higher. The peak g′ is similar to the reduction peak of $[Fe\text{-}O_2\text{-}Fe]^{2+}$. The number of the oxygen atoms counted by integrating the second peak g′ is equal, within experimental error, to that of active oxygen atoms counted by integrating the sharp spike g. Therefore, the ratio of the number of oxygen atoms deposited by interaction of $[Fe\text{-}O\text{-}Fe]^{2}$+ with N_2O to that of iron atoms in the dimers is 1 i. e., O_{de}:Fe_{di}=1. O_{de} represents the number of deposited oxygen atoms. Among these oxygen atoms, one half is active oxygen related to sharp H_2-TPR spike at 190 ℃; another half is not active oxygen, just like the bridging oxygen in $[(HO)Fe\text{-}O\text{-}Fe(OH)]^{2+}$ or in $[Fe\text{-}O_2\text{-}Fe]^{2+}$ complex. Based on Mössbauer measurement, more recently, Panov et al.[6] also reported that each binuclear complex consisted of two a-sites, showing that O_{de}:Fe_{di}=1. However, they claimed that all these deposited oxygen atoms were active oxygen. This is probably due to the very low Fe content in the Fe/ZSM-5 employed. It is difficult to discriminate these two oxygen species when the amount of deposited oxygen is very low.

Based on above results, two oxygen species (active oxygen and regular oxygen) with ratio of 1 to 1 are formed upon the interaction of $[Fe\text{-}O\text{-}Fe]^{2+}$ with N_2O at 250 ℃. The ratio of total number of deposited oxygen atoms to that of $[Fe\text{-}O\text{-}Fe]^{2+}$ is 2. Because all the oxygen atoms deposited were related to Fe^{2+} dimers, the structure of the iron dimer complex composing active oxygen should be five-atom ion $[Fe_2O_3]^{2+}$, not $[Fe_2O_2]^{2+}$. Two candidate models can be considered for this dimer species $[Fe_2O_3]^{2+}$:



The former is similar to the model proposed by Panov et al.[6], by which no discrimination is made between active oxygen and regular oxygen. The latter is the most probable model for the product of interaction of $[Fe\text{-}O\text{-}Fe]^{2+}$ with N_2O. Upon H_2-TPR, the removal of the terminal O from this complex corresponds to the spike at 190 ℃ in Fig.2G:





(6)

Further reduction of [Fe-O_2-Fe] corresponds to the broad peak between 230 and 530 ℃.

3 Conclusions

Fe/ZSM-5 prepared by sublimation is a suitable catalyst to be used for generating active oxygen by the interaction with N_2O. The active oxygen can be characterized by H_2-TPR due to the high concentration of Fe dimer complex. The unusual TPR spike at 190 ℃ is characteristic of the active oxygen species. $[Fe\text{-}O\text{-}Fe]^{2+}$ dimer is the active iron complex for N_2O decomposition to produce active oxygen. Reduction of Fe^{3+} in the dimer to Fe^{2+} and heating at high temperature to remove the OH^- groups from Fe^{2+} dimer are the prerequisites for the formation of this active Fe complex. A linear correlation with slope of 1 exists between the amount of $[Fe\text{-}O\text{-}Fe]^{2+}$ and that of active oxygen species. Maximum amount of active oxygen species can be generated by reducing Fe/ZSM-5 catalyst with H_2 at the temperatures over 500 ℃ and then heating the sample in Ar to 700 ℃, followed by N_2O exposure at 250 ℃.

Ratio of the total number of oxygen atoms deposited by interaction of $[Fe\text{-}O\text{-}Fe]^{2+}$ with N_2O (O_{de}) to that of $[Fe\text{-}O\text{-}Fe]^{2+}$ is 2. Not all the deposited oxygen atoms are active oxygen (O_a); the ratio of O_a and O_{de} is 0.5. The iron dimer complex composing active oxygen is five-atom ion $[Fe_2O_3]^{2+}$.

References:

[1] Panov G I, Uriarte A K, Rodkin M A, et al. *Catal. Today*, **1998**,**41**:365~385

[2] Kapteijn F, Rodriguez-Mirasol J, Moulijn J A. *Appl. Catal. B*, **1996**,**9**:25~64

[3] Feng X, Hall W K. *J. Catal.*, **1997**,**166**:368~376

[4] Yoshizawa K, Yumura T, Shiota Y, et al. *Bull. Echem. Soc. Japan*, **2000**,**73**:29~36

[5] Yakovlev A L, Zhidomirov G M, van Santen R A. *J. Phys. Chem. B*, **2001**,**105**:12297~12302

[6] Dubkov K A, Ovanesyan N S, Shteinman A A, et al. *J. Catal.*, **2002**,**207**:341~352

[7] Chen H Y, Sachtler W M H. *Catal. Today*, **1998**,**42**:73~83

[8] Mauvezin M, Delahay G, Coq B, et al. *J. Phys. Chem. B*, **2001**,**105**:928~935