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Preparation and pretreatment temperature influence on iron species distribution and N_2O decomposition in Fe–ZSM-5

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Fe–ZSM-5 catalysts are prepared by $FeCl_3$ sublimation between 320 and 850 °C. The catalysts are characterised by XRD, H_2–TPR, NH_3–TPD, NO adsorption by DRIFTs, and catalytic activity is evaluated for N_2O decomposition. The influence of high temperature (850 °C) and pretreatment environment (air, He, He + H_2O and H_2) on the nature of iron species in Fe–ZSM-5 is further investigated by DRIFTs. High temperature $FeCl_3$ sublimation results in decreased FeO_x formation, easily reducible and narrow distribution of iron species in close proximity to alumina in Fe–ZSM-5. High temperature $FeCl_3$ sublimation or pretreatment results in isolated hydroxylated iron species, –$Fe(OH)_2$, which are not significant in Fe–ZSM-5 prepared by 320 °C $FeCl_3$ sublimation followed by calcination below 600 °C. Fe–ZSM-5 prepared by high temperature $FeCl_3$ sublimation show high N_2O decomposition activity and the improved performance can be correlated to –$Fe(OH)_2$ species in close proximity to alumina.

KEY WORDS: Fe–ZSM-5; sublimation; high temperature pretreatment; isolated iron species; hydroxylated iron species; –$Fe(OH)_2$; N_2O decomposition; DRIFTs.

1. Introduction

Iron–zeolite catalysts are very active among others for selective catalytic reduction (SCR) of NO with NH_3 and hydrocarbons (HC), N_2O decomposition/reduction and HC oxidations [1,2]. Fe–ZSM-5 catalysts are extensively investigated for exhaust gas cleaning applications due to its superior activity, selectivity and stability in the presence of H_2O and SO_2 in the feed streams, which are typically present in exhaust gases [3–7]. The present investigation is to study the influence of Fe–ZSM-5 preparation and pretreatment parameters on iron species distribution and its influence on N_2O, a green house gas, conversion to N_2. Iron can be introduced into ZSM-5 during the zeolite synthesis (isomorphous substitution) or post-synthesis methods (for example aqueous ion-exchange and $FeCl_3$ sublimation). Activation of isomorphously substituted Fe–ZSM-5 is usually carried out at high temperatures in order to migrate the iron species from framework coordinatively saturated sites towards extraframework coordinately unsaturated sites [8–11]. Various iron species have been observed and/or proposed as a result of high temperature activation procedure, and have been correlated to the observed improvement in N_2O decomposition and hydrocarbon selective oxidation activity. Iron oxide clusters are proposed as active sites for N_2O decomposition and isolated iron species are proposed as responsible for N_2O reduction with CO [10]. On the ccontrary both the isolated iron species and isolated and hydroxylated iron species ($Z^{-}[Fe(OH)_2]^{+}$) are suggested as the starting precursor for N_2O decomposition and hydrocarbon oxidation by experimental and theoretical studies [11–15].

Sublimation of $FeCl_3$ into H–ZSM-5 is an extensively studied post-synthesis Fe–ZSM-5 catalyst preparation method. Fe–ZSM-5 prepared by sublimation leads to >100% iron ion-exchange and such catalysts are found to be very active in NO reduction with NH_3 and HC, and N_2O decomposition. Isomorphously substituted Fe–ZSM-5 catalyst probably lead to well defined but low iron content zeolites; on the other hand, a broad iron species distribution in high iron containing zeolites, prepared by post synthesis methods, are reported [16–19]. Activation of Fe–ZSM-5 prepared by post-synthesis method is usually carried out by thermal treatment below 600 °C. As iron is directly introduced at extra-framework locations by post-synthesis method, high temperature thermal and hydrothermal treatment can be expected to dealuminate the zeolite and also detach iron from ion-exchanged positions. High temperature thermal and hydrothermal catalyst activation is found to have a positive influence, especially in N_2O decomposition and selective hydrocarbon oxidation activity, even in post-treatment prepared Fe–zeolite catalysts [20–23]. From spectroscopic characterization it is proposed that high temperature activation leads to the redispersion of iron oxide clusters to zeolitic ion-exchanged sites and, therefore, the N_2O decomposition activity is increased [21–23]. Some of the other suggested active iron species, on high temperature activated catalysts for N_2O

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decomposition and selective HC oxidation, are small iron oxide clusters, –Fe–O–Al– like species, and isolated Fe^{2+} species [20–27]

The formation of different iron species is very sensitive to all the catalyst preparation parameters, and even a small change in catalyst preparation/pretreatment procedure leads to changes in the structure of active iron species and its relative distribution. Because of the different Fe-zeolite catalyst preparation and pretreatment methods reported in literature, a variety of active iron species are identified and are proposed as responsible for observed activity in various catalysed reactions. Recently, $Z^{-}[FeOH)_2]^{+}$ and –Fe–O–Al– like species that are observed/proposed in Fe–ZSM-5 due to high temperature activation are shown to be the active sites for N_2O activation/decomposition [11,26]. It has been identified that $FeCl_3$ sublimation at high temperature leads to narrow distribution of iron species in the resulting Fe–ZSM-5 catalyst with the formation of $Z^{-}[Fe(OH)_2]^{+}$ like species with consequent increase in SCR activity [28]. This paper shows the changes in iron species distribution by changing Fe–ZSM-5 catalyst preparation/activation procedure and these changes will be related to the activity in N_2O decomposition.

2. Experimental

2.1. Catalyst preparation

Na–ZSM-5 (Si/Al = 11, TOSOH), crystallite size ~2 μm, is converted to H-ZSM-5, by aqueous NH_4^{+} exchange followed by calcination at 600 °C for 5 h. Fe–ZSM-5 is prepared by modifying the sublimation method developed in Sachtler's group [1]. The set-up described in reference [29] is used for $FeCl_3$ sublimation. In the modified sublimation method, anhydrous $FeCl_3$ (99.99%, Aldrich) is dropped over activated H-ZSM-5 at different sublimation temperatures (320–850 °C). The thus obtained $FeCl_2$-ZSM-5 materials are washed with deionised water until free of chloride ions ($AgNO_3$ test), followed by drying at 100 °C overnight, and subsequently calcined at 600 °C for 5 h in static air. The physico-chemical properties of some catalysts are listed in table 1. The catalysts are assigned as Fe–ZSM-5-*x*(*y*), where '*x*' is $FeCl_3$ sublimation temperature and '*y*' in the parenthesis is iron ion exchange percentage. The influence of high temperature pretreatment and environment on iron species distribution are studied over Fe–ZSM-5-320(69) and Fe–ZSM-5-320(80) catalysts. The conditions of high temperature pretreatment conditions are summarised in table 2.

2.2. Characterisation

The materials are characterized by XRD (Philips X-ray diffractometer, PW 1840) with Ni-filtered Cu*Kα* radiation ($\lambda = 0.1541$ nm). H_2–TPR is carried out in a Micromeritics pulse chemisorb (2900) TPD–TPR instrument. 20 mg of fresh and used samples are activated at 600 °C for 1 h in air flow and cooled to room temperature. TPR is carried out in 5 vol% H_2 in Ar with a heating rate of 10 °C/min till 900 °C, and maintained for prolonged times at 900 °C.

^{27}Al MAS NMR experiments are performed at 9.4 T on a Varian VXR-400 S spectrometer operating at 104 MHz with pulse width of 1 ms and 1600 scans are collected. The chemical shifts are reported with respect to $Al(NO_3)_3$ as external standard.

Nicolet Magna IR 860 spectrometer equipped with liquid nitrogen cooled MCT detector is used for Diffuse Reflectance Infrared Fourier Transform spectroscopic study (DRIFTs). A spectratech DRIFT high temperature cell, equipped with CaF_2 windows, is filled with the powdered catalyst. The catalyst samples are activated *in situ* at 450 °C for 1 h in 10 vol% O_2 or He or in 10 vol% H_2, and cooled to 50 °C. The catalysts are flushed at 50 °C in He and the background spectra of the activated zeolites are collected. About 5 vol% NO in He with a flow rate of 20 mL/min is used for adsorption study at 50 °C. Sixty-four scans are collected with 4 cm^{-1} spectral resolution.

2.3. N_2O decomposition

Fe–ZSM-5 catalysts (50 mg) are activated at 500 °C for 1 h in He before N_2O decomposition study. 4500 ppm N_2O in He (66 mL/min) is used for decomposition study between 200 and 550 °C with a resulting space velocity of 40,000 L/l/h. The concentration of N_2O, N_2, and O_2 are monitored with a gas chromatograph. The N_2O conversions are calculated from the

Table 1

Preparation conditions and ion-exchange percentage of Fe–ZSM-5 [29]

H-ZSM-5-600 pre-treatment in He before $FeCl_3$ sublimation, °C/h	$FeCl_3$ sublimation temperature, °C/h	Iron ion-exchange, %	Catalyst
850/1	–	–	H–ZSM-5-850
600/1	320/3	69	Fe–ZSM-5-320(69)
600/1	320/3	80	Fe–ZSM-5-320(80)
700/1	700/1	51	Fe–ZSM-5-700
850/30	850/1	28	Fe–ZSM-5-850

H–ZSM-5-600 is obtained by calcining NH_4–ZSM-5 at 600 °C in air for 5 h.
All the catalysts are calcined at 600 °C in static air for 5 h.

Table 2
High temperature pre-treatment conditions

Sample	High temperature treatment atmosphere/ temperature,[a] °C/time, h	Catalyst
Fe–ZSM-5-320(69)	He/850/1	HT–He1
Fe–ZSM-5-320(69)	He/850/3	HT–He3
Fe–ZSM-5-320(69)	Air/850/1[b]	HT–Air
Fe–ZSM-5-320(69)	2% H_2O in He/850/1[c]	HT–H_2O
Fe–ZSM-5-320(69)[d]	H_2/450/1	HT–H_2
Fe–ZSM-5-320(80)	He/850/1	HT–He2

[a] 100 mL/min He flow.
[b] static air.
[c] 100 mL/min He passed through the water saturator at room temperature. After high temperature pretreatment the catalysts are cooled in the same flow before exposing to air at room temperature.
[d] Not exposed to high temperature, the treatments are done in DRIFT cell.

measurements after at least 45 min of time on stream at each reaction temperature.

3. Results and discussion

3.1. XRD

With increasing sublimation temperature the amount of iron loading in the final Fe–ZSM-5 catalysts decreased (table 1). The low ion-exchange percentages are due to very short residence time of gas phase $FeCl_3$ through the activated zeolite bed. XRD patterns of H–ZSM-5 and Fe–ZSM-5-850, prepared by sublimation of $FeCl_3$ at 850 °C are shown in figure 1. Significant changes are not observed in Fe–ZSM-5-850 XRD pattern compared with parent H–ZSM-5-600. Apparently, zeolite structure did not collapse due to high concentration of gas phase HCl, which is produced during the sublimation ion-exchange procedure at high temperatures. No XRD detectable FeO_x phases are identified from Fe–ZSM-5 catalysts mentioned in table 1 [29].

3.2. DRIFT spectra of hydroxyl groups

Figure 2 shows DRIFT spectra in hydroxyl group region of H-ZSM-5-600 and Fe–ZSM-5 catalysts. The three prominent bands, observed for H-ZSM-5-600, around 3600, 3650, and 3737 cm^{-1} can be correlated to bridging hydroxyls ($\equiv$AlO(H)Si$\equiv$), hydroxyls associated with extraframework alumina (referred as extra-framework Al) and silanol groups ($\equiv$Si–OH) [30]. The intensity of 3600 cm^{-1} band decrease in all Fe–ZSM-5 catalysts compared with H–ZSM-5-600, due to replacement of most of the bridging hydroxyl groups by iron species. Significant zeolite dealumination is observed in Fe–ZSM-5-700 and Fe–ZSM-5-850 due to severe catalyst preparation conditions (table 1). The

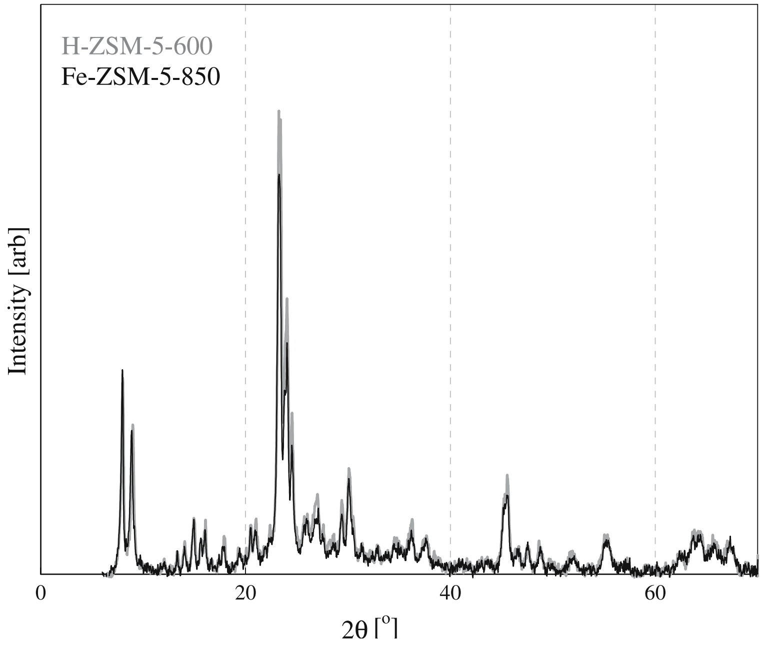

Figure 1. XRD patterns of H-ZSM-5-600 and Fe–ZSM-5-850.

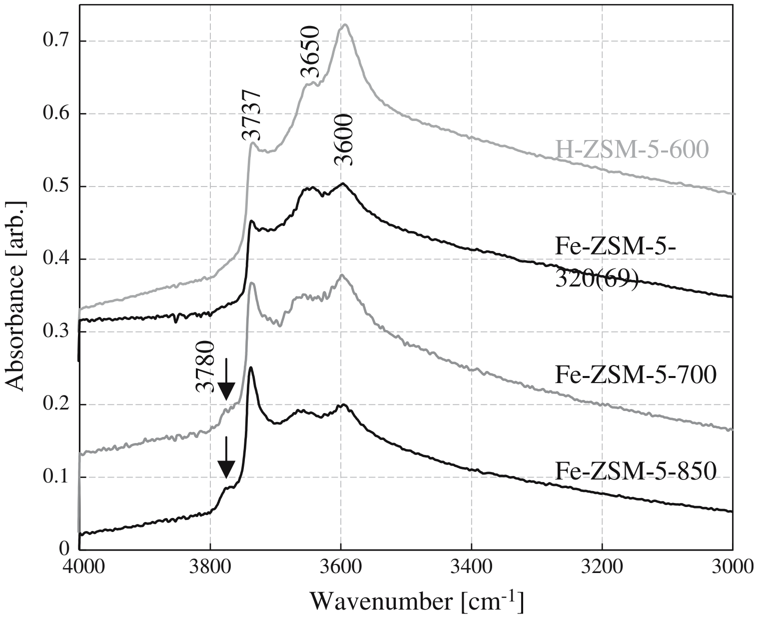

Figure 2. DRIFT spectra of zeolite hydroxyl groups with KBr back ground. The catalysts are pretreated in He for 1 h at 450 °C and the spectra is recorded at the same temperature.

dealumination in Fe–ZSM-5-850 is envisaged from the increase in relative intensity of terminal hydroxyls, silanol (3737 cm^{-1}) and –Al–OH, (3780 cm^{-1}), compared with H–ZSM-5-600 or Fe–ZSM-5-320(69). With increase in $FeCl_3$ sublimation temperature the relative intensity of the above bands is found to increase. This suggests an increase in dealumination with increase in sublimation temperature. However, the low intensity 3650 cm^{-1} bands indicate that extraframework Al is probably in aggregated form.

3.3. ^{27}Al MAS NMR

Figure 3 shows ^{27}Al MAS NMR spectra of selected materials. The resonance band at 54 and 0 ppm in H–ZSM-5-600 corresponds to tetrahedrally (framework) and octahedrally (extraframework) coordinated alumina, respectively [18]. On pretreatment at 850 °C, H–ZSM-5-850, the extent of extraframework Al increases along with appearance of a band at 25 ppm corresponding to pentacoordinated Al [23]. The above changes are due to high temperature pretreatment leading to extensive zeolite dealumination. Due to paramagnetic nature of iron the intensity of the Al resonance bands decreases when iron species are present in close proximity to alumina species [18]. In Fe–ZSM-5-850, the intensity at 54 ppm decreases relative to both H–ZSM-5 zeolites. This confirms that iron is bound at ion-exchange positions. Extraframework Al in Fe–ZSM-5-850 is also evident by the band at 0 ppm. This is in agreement with IR characterisation (figure 2). Iron species are also interacting with pentacoordinated and extraframework alumina as evident from the significant decrease in the intensity of the bands at 25 and 0 ppm, respectively. The decrease in the intensity of the extraframework Al bands suggests the possible presence of –Fe–O–Al– like compounds as proposed by Hensen *et al.* [23]. From ^{27}Al MAS NMR different possible active species present in Fe–ZSM-5-850 are iron species bound at ion-exchanged positions, extraframework alumina, and iron species interacting with extraframework alumina (–Fe–O–Al–).

3.4. H_2–TPR

The normalised H_2–TPR profiles of Fe–ZSM-5 catalysts are shown in figure 4. H_2 consumption around 410 °C over Fe–ZSM-5-320(80) corresponds to the reduction of framework Fe^{3+}, and a shoulder around 540 °C and a broad peak above 750 °C can be attributed to the reduction of iron oxide (FeO_x) particles [29,31]. FeO_x particles are absent in Fe–ZSM-5-320(69), Fe–ZSM-5-700, and Fe–ZSM-5-850 catalysts. This can be attributed due to modified catalyst preparation and low iron exchange percentage, especially for the high temperature $FeCl_3$ sublimed catalysts. For these catalysts most of the iron species can be expected to present at ion-exchanged positions. The Fe^{3+} species are reduced at relatively low temperatures in Fe–ZSM-5-700 and Fe–ZSM-5-850 compared to Fe–ZSM-5-320. This suggests the different nature of some of the exchange-iron species in the former catalysts [28].

3.5. DRIFT spectra of NO adsorption

All the above techniques indirectly show the association or interaction of iron species with different zeolitic sites, but they do not characterise the nature of iron species in Fe–ZSM-5. NO forms various iron nitrosyls that are sensitive to the iron species coordination or location in the zeolite channels [32,33]. Therefore, the

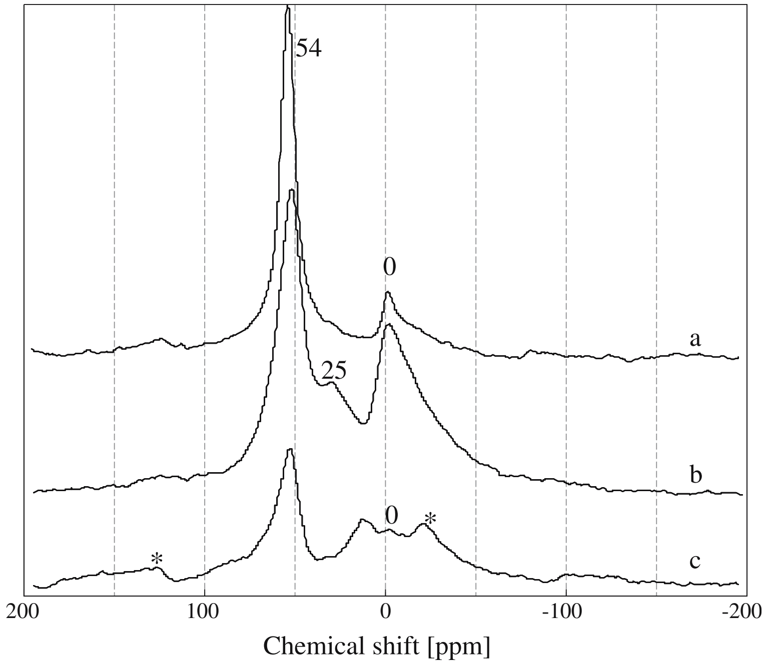

Figure 3. ^{27}Al MAS NMR spectra of (a) parent H–ZSM-5-600, (b) H–ZSM-5-850, and (c) Fe–ZSM-5-850. * – spinning side bands.

nature of iron species in zeolite can be effectively probed by characterising the NO stretching vibrations by IR [6,7,29,33–41]. NO adsorption studies over auto-reduced Fe–ZSM-5 catalysts are presented in Ref. [29]. It is found that significant auto-reduction does not take place below 500 °C. This is also as noted in Ref. [22]. Furthermore, characterisation of oxidised and reduced catalysts gives important information on the nature and concentration of iron species. To gain more insight into the nature of iron species NO adsorption is studied over oxidised and H_2 reduced catalysts (figures 5–8). Different NO adsorption sites on the catalyst are saturated quickly due to high concentration of NO (5 vol%) in He, and the dynamics of band evolution and disappearance will be mentioned if necessary. In general, the IR bands, observed during NO adsorption studied over oxidised and reduced Fe–ZSM-5 catalysts, can be divided into five groups.

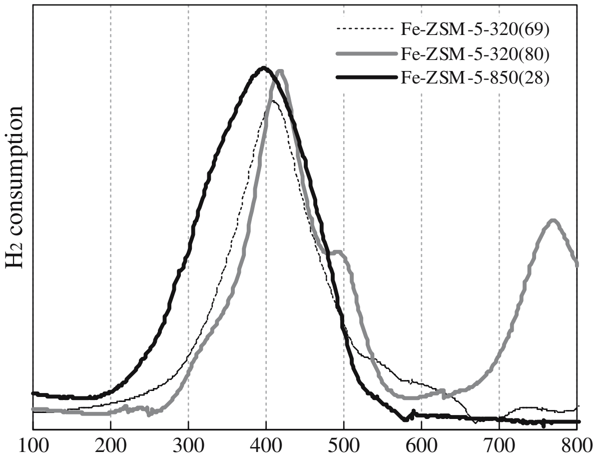

Figure 4. H_2–TPR profiles of selected Fe–ZSM-5 catalysts.

Group 1 IR bands: Positive IR bands around 2132 cm^{-1} (figure 5) are due to stretching vibrations of $NO^+/NO_2{}^+$ adsorbed over hydroxyl groups in the zeolite [6,38,42]. The negative IR bands at 3606 and a very broad band around 3650 cm^{-1}, accompanying the positive bands, are due to hydroxyl stretching of bridging and extraframework Al. 2132 cm^{-1} band is prominent over oxidised Fe–ZSM-5 catalysts (figure 5) and small over reduced catalysts (figure 6). This indicates that NO^+ is arising from Fe^{3+} species [42]. High temperature $FeCl_3$ sublimed catalysts have shown relatively low intensity bands at 3606 cm^{-1}. Desorption spectra (figure 5) show that, as soon as NO + He flow is switched to He, the negative 3606 cm^{-1} band disappears quickly with a consequent decrease in intensity at 2132 cm^{-1}.

Group 2 IR bands: The negative bands at 3677 and 3630 cm^{-1} (figures 5, 7) are due to NO^+ adsorbed on hydroxyl groups of iron species. Chen *et al.* [5] have reported that the hydroxyl group stretching over binuclear iron species in Fe–ZSM-5 prepared by sublimation method at 3665 cm^{-1}. Hydroxylated iron species are also observed by Mauvezin *et al.* [31] and Kameoka *et al.* [43] in Fe–BEA and by Wood *et al.* [11] in Fe/AlZSM-5. Wood *et al.* [11] have attributed the observed IR bands at 3680 and 3628 cm^{-1} to symmetric and asymmetric stretching vibrations of isolated iron species having two hydroxl groups (–$Fe(OH)_2$). In oxidised Fe–ZSM-5 catalysts (figures 5, 7), a broad negative IR

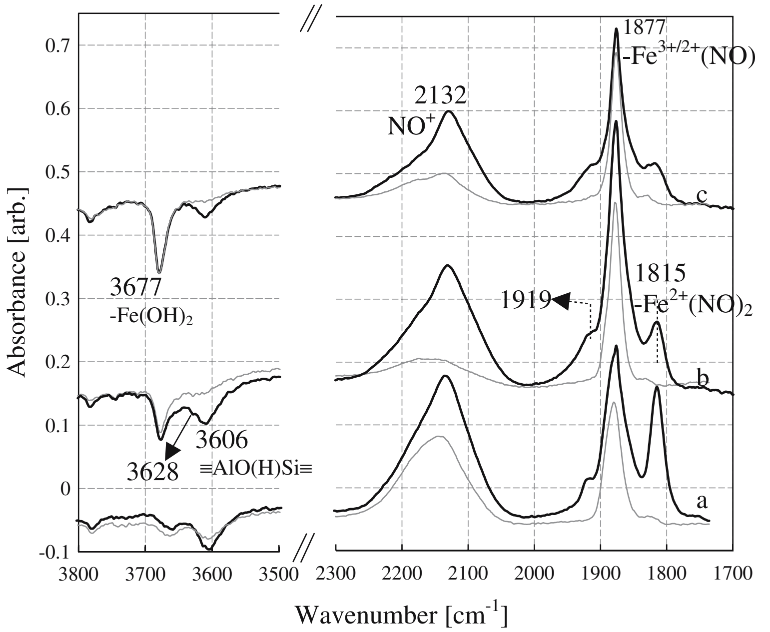

Figure 5. DRIFT spectra during NO adsorption/desorption over (a) Fe–ZSM-5-320(80), (b) Fe–ZSM-5-700, and (c) Fe–ZSM-5-850. Solid lines-during adsorption and broken lines-during desorption in He. Catalysts are oxidised at 450 °C in 10 vol% O_2, before NO adsorption (5 vol% NO in He) at 50 °C. Desorption is carried out in He.

band at 3630 cm^{-1} of varying intensity is clearly evident. Therefore, in agreement with Wood *et al.* [11] the iron species responsible for 3677 cm^{-1} IR band can be correlated to –Fe(OH)$_2$. On desorption, unlike the 3606 cm^{-1} band, the intensity of 3677 cm^{-1} band does not change significantly (figure 5) indicating very strong bonding of NO^+ to hydroxyl groups of iron species. Hydroxylated iron species are only observed over oxidised Fe–ZSM-5 catalysts (Fe^{3+} oxidation state). The 3677 cm^{-1} band intensity decreases due to dehyroxylation in He (not shown) or reduction to Fe^{2+} (figure 6) in agreement with previous reports [31,43]. Further experiments confirmed that the positive bands corresponding to NO^+ (adsorbed on iron hydroxyl groups) stretching vibrations also appears at 2132 cm^{-1} [44].

Group 3 IR bands: The IR bands around 1877 cm^{-1} are correlated NO stretching vibrations of monomitrosyl iron species, $Fe^{3+/2+}$(NO) (figures 5–8). On reduction

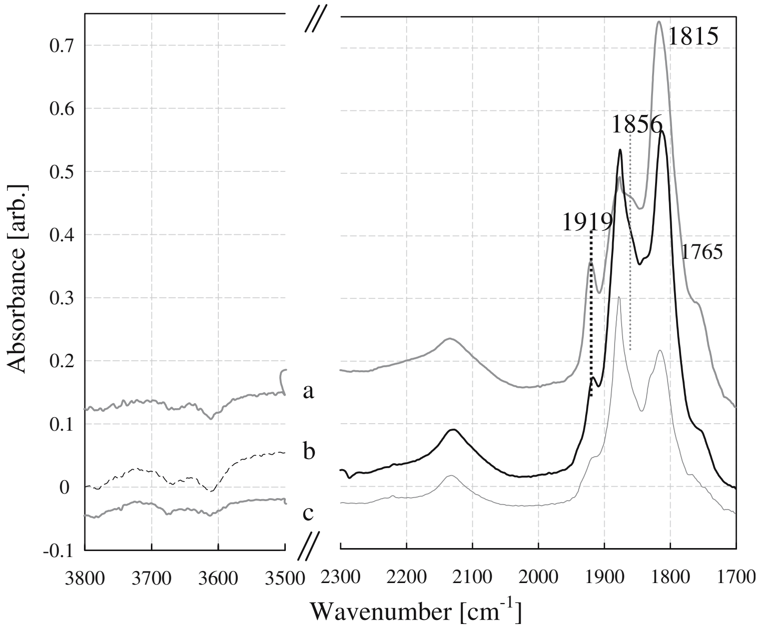

Figure 6. DRIFT spectra during NO adsorption over (a) Fe–ZSM-5-320(80), (b) Fe–ZSM-5-700, and (c) Fe–ZSM-5-850. Catalysts are reduced at 450 °C in H_2 before NO adsorption.

the 1877 cm^{-1} band intensity does not change significantly compared with oxidised catalyst. This in agreement with the above iron mononitrosyl assignment and previous observations [41]. The 1877 cm^{-1} band is not observed when iron species are expected to be present as FeO_x particles, for example as in iron silicalite after steam extraction of iron to extraframework and over iron oxide on SiO_2 [33,35,37,45–47]. Therefore, in Fe–ZSM-5 catalysts, the contribution of FeO_x to mononitrosyl band at 1877 cm^{-1} will be negligible. On the other hand high intensity 1877 cm^{-1} band is always observed when the iron is present in zeolite containing framework alumina and also M^{3+} ions other than Al^{3+} [6,7,29,33,34,38,39,41,48]. Mul *et al.* [38] have speculated that 1877 cm^{-1} band is arising due to NO bound to FeAlOx like nano particles due to steam extraction of iron to extraframework. The iron mononitrosyl species are observed even in catalysts that are not severely treated, for example Fe–ZSM-5-320(80) (figures 5, 6). Furthermore, H_2–TPR, DRIFT spectra of zeolite hydroxyl groups and ^{27}Al NAM NMR (figures 2–4) of Fe–ZSM-5 catalysts clearly show that Fe^{3+} is bound to the framework ion-exchange sites. Therefore, the major contribution to the 1877 cm^{-1} IR band arises from iron species in close proximity to framework Al at ion-exchanged positions. The contribution of FeAlOx like species to 1877 cm^{-1} band is, therefore, expected to be relatively small.

Group 4 IR bands: Bands at 1815 and 1919 cm^{-1} are correlated to symmetric and asymmetric NO stretches of iron dinitrosyl species ($Fe^{2+}(NO)_2$) and the shoulder at 1765 cm^{-1} is due to the mononitrosyl of the same iron species (figures 5–8) [41]. The iron dinitrosyl bands are observed over iron species present at zeolite ion-exchanged positions as well as in FeO_x containing samples [6,7,29,33–41,46]. Due to high coordinative unsaturation of iron species (present in easily accessible straight channels) it is proposed to form di-, and even polynitrosyls [37,45]. Dinitrosyls are only formed with iron in reduced state (Fe^{2+}) as evident from very weak and high intensity bands over oxidised (figure 5) and reduced (figure 6) Fe–ZSM-5 catalysts, respectively.

Group 5 IR bands: IR bands around 1834 and 1856 cm^{-1} are observed over highly reduced Fe–ZSM-5 catalysts (figures 6, 8) which are assigned to iron mononitrosyls [38]. Group 5 bands in Fe–ZSM-5 catalysts are not well resolved and appear as a shoulder over the reduced catalysts due to overlap of different bands. The relative intensity of 1856 cm^{-1} band is high in Fe–ZSM-5-320(80) catalysts which contain FeO_x particles (figure 6). H_2-TPR shows that at high temperatures (around 540 °C) the FeO_x species can be reduced and the 1856 cm^{-1} band is due to such reduced particles. This is further supported by the fact that such IR bands are observed over iron silicalite, which mainly consist of FeO_x particles [6,7,29,33–41,45,46]. No correlations are found between group 3, group 4, and group 5 iron nitrosyl bands and, therefore, these are considered as three different iron species.

3.5.1. *Influence of $FeCl_3$ sublimation temperature on the nature of iron species*

The catalyst preparation temperature has significant influence on the nature and distribution of different iron species as evident from the relative intensity of NO and hydroxyl group IR vibrations over oxidised and reduced Fe–ZSM-5 catalysts. A gradual decrease in 3606 cm^{-1} band intensity with increase in $FeCl_3$ sublimation temperature is observed in oxidised Fe–ZSM-5-700 and Fe–ZSM-5-850 catalysts (figure 5). This is due to more efficient replacement of bridging hydroxyl groups by Fe^{3+} as well as to the increased zeolite dealumination with increasing $FeCl_3$ sublimation temperature. These observations are in agreement with DRIFT spectra of hydroxyl groups, H_2–TPR and ^{27}Al MAS NMR (figures 2–4) results. In Fe–ZSM-5-320 the concentration of $–Fe(OH)_2$ species is low as evident from the weak intensity around 3677 cm^{-1}(figures 5, 7). Majority of iron species in Fe–ZSM-5-320 can be, therefore, considered to be present in dehydroxylated from. The above observation indicates the possible presence of polynuclear iron species at ion-exchanged positions or due to FeO_x particles on which the number of hydroxyl groups are expected to be sub stoichiometric. With increase in sublimation temperature $–Fe(OH)_2$ concentration increases as evident from relatively high intensity 3677 cm^{-1} band (figure 5). A maximum relative concentration of $–Fe(OH)_2$ species is observed over Fe–ZSM-5-850 having low ion-exchange percentage (figure 5 and table 1) and low ion-exchange percentage catalysts mainly contains isolated iron species [7]. In isomorphously substituted Fe/AlZSM-5 having low iron content, the hydroxylated iron species are formed due to the high temperature iron extraction to the extraframework and is proposed to be present as isolated sites [11]. Hydroxylated iron species are observed in Fe–ZSM-5 and Fe–BEA catalysts which are not exposed to high temperatures [5,31,43]. The hydroxylated iron species observed in different catalysts indicate that its formation depends on other factors such as structure and pretreatment conditions. In the next section it will be further elucidated that high temperature treatment seems to be critical in the formation $–Fe(OH)_2$ like species.

The relative intensity of IR bands over oxidised/reduced catalysts (figures 5, 6) indicates that Fe–ZSM-5-320 mainly contains iron species that are capable of forming dinitrosyls. The low intensity of negative IR bands at 3677 cm^{-1} over Fe–ZSM-5-320 further suggests that the majority of the species are polynuclear (dehydroxylated) iron species, mainly present in straight channels of zeolite [7]. With increase in $FeCl_3$ sublimation temperature to 700 and 850 °C, the relative concentration of the iron species in close proximity to Al increases as evident from the intensity of 1877 cm^{-1}

band, (figures 5, 6). The iron species in close proximity to framework Al are most likely encountered at the sterically hindered locations of zeolite, where the framework oxygen coordination can effectively compensate the charge of iron species [7,49]. High temperatures will favour the migration of exchanged $-FeCl_2$ to sterically hindered and stable zeolitic locations [29,49]. It can be argued that the $-Fe(OH)_2$ species form mononitrosyl complexes in close proximity to Al species (1877 cm^{-1} IR band). If $-Fe(OH)_2$ is present as dinitrosyl forming iron species, the relative intensity of 1815 cm^{-1} band in reduced Fe–ZSM-5-850 should have higher intensity than that is observed (figure 6). However, comparison of the relative intensities of oxidised and reduced catalysts (figures 5, 6), no linear correlation is found between 3677 and 1877 cm^{-1} bands. This indicates that 1877 cm^{-1} band is formed due to a variety of iron species, hydrated and dehydrated, but in close proximity to Al.

To summarise, Fe–ZSM-5-320 catalysts contain a broad distribution of iron species, which are mainly present as dehydroxylated polynuclear iron species, that are capable in forming dinitrosyls. Increasing the sublimation temperature increases the concentration of hydroxylated iron species ($-Fe(OH)_2$) and iron species present in close proximity to alumina in Fe–ZSM-5-700 and Fe–ZSM-5-850 catalysts. Both can be considered as isolated species, as its relative concentration increases with a decrease in ion-exchange percentage. Besides this, Fe–ZSM-5-700 and Fe–ZSM-5-850 catalysts contain extraframework alumina and possibly –Fe–O–Al– like species as evident from DRIFTs and ^{27}Al MAS NMR characterisation. From H_2–TPR (figure 4) and DRIFTs (figure 2) the easily reducible iron species can be correlated to $-Fe(OH)_2$.

3.5.2. Influence of pretreatment temperature and environment

The nature of iron species and its distribution is investigated by exposing Fe–ZSM-5-320(69) and Fe–ZSM-5-320(80) catalysts to high temperatures and various environments (table 2). The catalysts are pretreated at 850 °C in different environments and cooled to room temperature in the same environment followed by exposure to air. Before DRIFT study the above catalysts are either oxidised in 10 vol% O_2 or reduced in H_2 *in situ* in the DRIFT cell, at 450 °C for 1 h. Figures 7 and 8 show DRIFT spectra of NO adsorbed over oxidised and reduced Fe–ZSM-5-320(69) and Fe–ZSM-5-320(80) catalysts, respectively, pretreated at high temperatures. The DRIFT spectra of NO adsorption over parent Fe–ZSM-5-320(69) catalyst is also shown for comparison (reference spectra for Fe–ZSM-5-320(80) can be found in figure 5).

In general, high temperature pretreatment leads to significant decrease of bridging hydroxyl groups as evident from the decrease in intensity of negative 3606 and positive 2132 cm^{-1} bands (figure 7). High temperature pretreatment increases the concentration of hydroxylated iron species ($-Fe(OH)_2$, 3677 and 3630 cm^{-1} IR band). The relative intensities of different bands indicate that the concentration of iron species in close proximity to Al (IR band at 1877 cm^{-1}) increases on high temperature treatment compared to parent catalyst (fig-

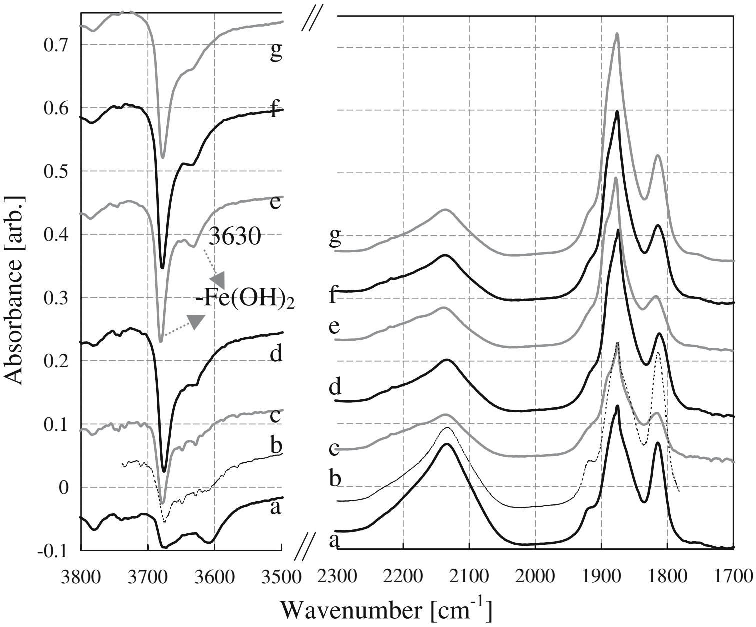

Figure 7. DRIFT spectra during NO adsorption over (a) Fe–ZSM-5-320(69) and (b) HT–H_2 and after treating Fe–ZSM-5-320(69) at 850 °C (table 2) in (c) HT–Air, (d) HT–He1, (e) HT–H_2O, (f) HT–He3, and (g) HT-He2. Catalysts are calcined in 10 vol% O_2 at 450 °C *in situ* in the DRIFT cell. Attenuated (*2) hydroxyl group range spectra are shown.

ures 7, 8). The concentration of iron species that can form dinitrosyls in all the oxidised and reduced catalysts decreases significantly (figure 8, band at 1815 cm^{-1}).

The high temperature treatment environment (He, air, $He + H_2O$ or H_2) has a significant influence on the extent of different irons species formed. The increase in relative concentration of hydroxylated iron species (3677 cm^{-1} band, figure 7) is more on inert gas treated catalysts (HT–He, table 2) compared to air or H_2 pretreated catalysts (HT–Air and HT–H_2). The presence of H_2O during pretreatment has a similar influence as that of He on –$Fe(OH)_2$ formation. With increase in high temperature exposure time from 1 to 3 h, only slightly increases the concentration of –$Fe(OH)_2$ species. High temperature air treated catalysts (HT–Air) lead to the formation of FeO_x particles as indicated by IR band around 1856 cm^{-1} (figure 8). H_2 reduction at 450 °C followed by oxidation in O_2 (not exposed to high temperature) does not significantly increase –$Fe(OH)_2$ species (figure 7, spectra b). From different spectra in figure 7 it can be concluded that high temperature is very critical compared to other synthesis and pretreatment parameters.

High temperature exposure is suggested to redisperse FeO_x species to bridging hydroxyl groups (exchange positions) [22,23]. In Fe–ZSM-5-320(69) most of the iron is already present at ion-exchange positions as evident from H_2–TPR (figure 4) and DRIFTs (figure 2). Furthermore, if the redispersion of FeO_x is extensive on high temperature treatment, as suggested by the complete disappearance of bridging hydroxyl groups in Fe–ZSM-5-320(69) and especially in Fe–ZSM-5-320(80) having FeO_x phases (figure 7), the total intensity of IR bands due to iron nitrosyl species is expected to significantly increase. This is, however, not the case (1815 and 1877 cm^{-1}, figure 8). Therefore, the disappearance of bridging hydroxyl groups cannot be explained entirely based on the migration of FeO_x particles to framework ion-exchange positions. In fact the detachment of iron from the framework ion-exchange positions to form bigger FeO_x particles and dealumination explains the significant decrease in the intensity of IR nitrosyl bands at 1815 cm^{-1} and bridging hydroxyl groups at 3606 cm^{-1}, respectively. The above reasoning is in agreement with the study of high temperature influence on iron species distribution by Hensen *et al.* [23].

Based on DRIFTs characterisation of HT treated Fe–ZSM-5-320 catalysts, the tentative steps that can be involved in the transformation of polynuclear iron species to –$Fe(OH)_2$, is explained by Scheme 1. High temperature treatment in the first step leads to dehydroxylation and auto-reduction of polynuclear iron species in Fe–ZSM-5-320, for simplicity binuclear iron species is depicted. This is followed by detachment of part of the iron species from ion-exchange positions (forming FeO_x) and subsequently alumina from framework (forming extraframework Al), which will result in isolated iron species. The detachment of Al from framework ensures that FeO_x will not migrate back to form polynuclear species. At the same time the iron species formed can either migrate to more stable positions or form larger iron oxide particles. The isolated and reduced $[FeO]^+$ like species upon cooling and exposure to air form hydroxylated iron species (–$Fe(OH)_2$). A similar mechanism is proposed by Pirngruber *et al.* [22].

From the DRIFT studies on $FeCl_3$ sublimed at different temperatures and high temperature treated Fe–ZSM-5 catalysts the main changes are the results of

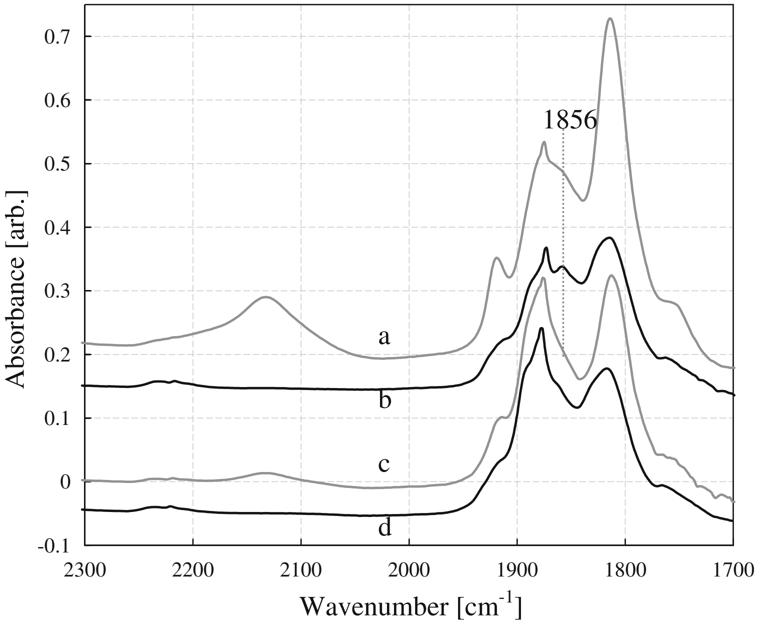

Figure 8. DRIFT spectra during NO adsorption over (a) Fe–ZSM-5-320(69) and after treating Fe–ZSM-5-320(69) at 850 °C in (b) HT–Air, (c) HT–He1, and (d) HT–H_2O. The catalysts are reduced in H_2 at 450 °C before NO adsorption.

increased temperature. They influence (i) the nature of iron species, i.e., increases the concentration of –$Fe(OH)_2$ (increased band intensity at 3677 and 3630 cm^{-1}), increase (ii) iron species in close proximity to Al (increased relative intensity of 1877 cm^{-1} band), and leads (iii) to dealumination (decreased 3606 cm^{-1} negative band) and also possibly forms larger FeO_x particles (increase in intensity around 1856 cm^{-1}, figure 8). These results are in agreement with DRIFTs, H_2–TPR, and ^{27}Al MAS NMR characterisation techniques (figures 2–4). Comparison of relative band intensities of figure 6 with figure 8 indicates relatively high concentration of FeO_x particles (decreased the total iron nitrosyl band area) in the high temperature treated catalysts.

3.6. N_2O decomposition activity

The sublimed catalysts are chosen for studying N_2O decomposition as they have insignificant amount of FeO_x phases. Figure 9 shows N_2O decompostion in He over Fe–ZSM-5 catalysts prepared by varying $FeCl_3$ sublimation temperatures. The catalysts are activated in He at 500 °C for 1 h before N_2O decomposition. Fe–ZSM-5-320(80) and Fe–ZSM-5-320(69), prepared by 320 °C $FeCl_3$ sublimation, have shown similar N_2O conversions, despite FeO_x phase in the former catalyst. High temperature $FeCl_3$ sublimed catalysts, Fe–ZSM-5-700 and Fe–ZSM-5-850 show significantly higher N_2O conversions despite their low iron ion-exchange percentage (table 1). From several studies it is proposed that different iron species have different intrinsic activity and only a fraction of these iron species are active for N_2O decomposition [9–11,15]. In Fe–ZSM-5, prepared or pretreated at high temperatures, this fraction of the intrinsically active iron species should increase to explain the observed improvement in N_2O decomposition activity despite the lower ion-exchange percentage. N_2O decomposition reaction mechanism with hydroxylated iron species as starting precursors over high temperature treated Fe/AlZSM-5 catalyst is proposed as one of the routes [11,13]. Dehydroxylation of –$Fe(OH)_2$ to form –FeO like species is suggested to be crucial in activating N_2O. In high temperature treated catalysts, for example in Fe–ZSM-5-850, apart from iron at ion-exchange positions in close proximity to Al, isolated –$Fe(OH)_2$, also extraframework Al and –Fe–O–Al– like species increase as evident from different characterisation techniques. Recent study on iron containing zeolites of different topology show that, despite relatively lower concentration of –$Fe(OH)_2$, compared to Fe–ZSM-5-850, the presence of extraframework alumina further increases N_2O decomposition activity [44]. Though the active species have not been identified, Sun *et al.* [20] have shown that the combination of high temperature and extraframework Al increased N_2O decomposition activity. Among the catalysts studied, Fe–ZSM-5-850 has increased amounts of both –$Fe(OH)_2$ and extraframework Al species, both of which are involved in N_2O decomposition. Assuming only a fraction of –$Fe(OH)_2$ species leads to active species responsible for N_2O decomposition, an increase in –$Fe(OH)_2$ concentration will increase N_2O decomposition activity. This is in good agreement with the correlation of 3677 cm^{-1} band intensity with N_2O decomposition activity (turn over frequency, figure 9(b)).

4. Conclusions

High temperature (850 °C) $FeCl_3$ sublimation results in decreased FeO_x particles in Fe–ZSM-5, easily reducible and narrow distribution of iron species in the resulting Fe–ZSM-5. DRIFTs study shows that high temperature catalyst preparation or pretreatment leads to isolated and hydroxylated iron species (–$Fe(OH)_2$) which are not significant in Fe–ZSM-5 prepared by 320 °C $FeCl_3$ sublimation followed by 600 °C calcina-

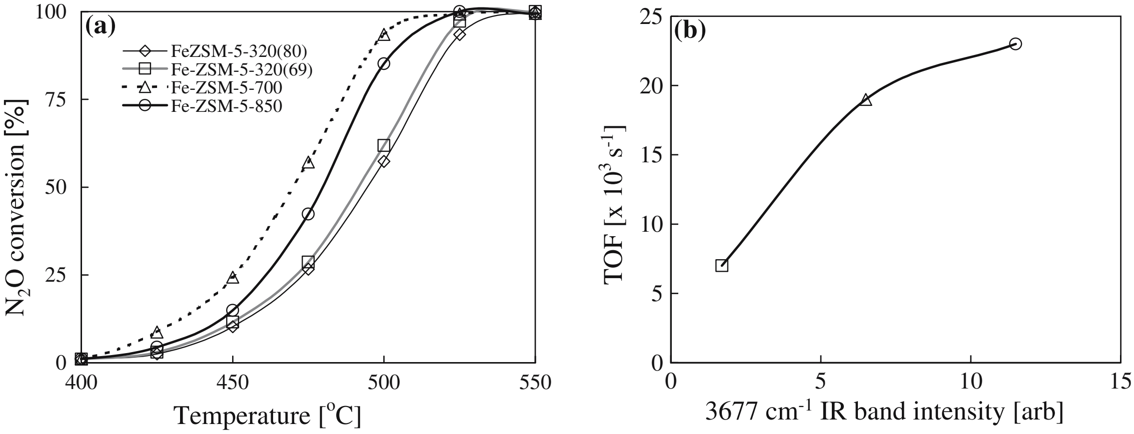

Figure 9. (a) N_2O conversion over Fe–ZSM-5 catalysts and (b) correlation of –$Fe(OH)_2$ peak area with TOF (turn over frequency). Reaction conditions: 4500 ppm N_2O in He flow, GHSV = 40 000 L/l/h.

tion. The catalyst containing extraframework Al and $-Fe(OH)_2$, possibly in close proximity to Al, shows high activity in N_2O decomposition.

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References

[1] H.Y. Chen and W.M.H. Sachtler, Catal. Today 42 (1998) 73.
[2] V.N. Parmon, G.I. Panov, A. Uriarte and A.S. Noskov, Catal. Today 100 (2005) 115.
[3] G. Carja, G. Delahay, C. Signorile and B. Coq, Chem. Commun. (2004) 1404.
[4] J. Perez-Ramirez, F. Kapteijn, G. Mul and J.A. Moulijn, Appl. Catal. B 35 (2002) 227.
[5] H.Y. Chen, T. Voskoboinikov and W.M.H. Sachtler, J. Catal. 186 (1999) 91.
[6] R. Joyner and M. Stockenhuber, J. Phys. Chem. B 103 (1999) 5963.
[7] L.J. Lobree, I.C. Hwang, J.A. Reimer and A.T. Bell, J. Catal. 186 (1999) 242.
[8] G. Berlier, G. Ricchiardi, S. Bordiga and A. Zecchina, J. Catal. 229 (2005) 127.
[9] D.A. Bulushev, L. Kiwi-Minsker and A. Renken, J. Catal. 222 (2004) 389.
[10] J. Perez-Ramirez, J. Catal. 227 (2004) 512.
[11] B.R. Wood, J.A. Reimer, A.T. Bell, M.T. Janicke and K.C. Ott, J. Catal. 225 (2004) 300.
[12] A. Heyden, B. Peters, A.T. Bell and F.J. Keil, J. Phys. Chem. B 109 (2005) 1857.
[13] A. Heyden, A.T. Bell and F.J. Keil, J. Catal. 233 (2005) 26.
[14] J.F. Jia, K.S. Pillai and W.M.H. Sachtler, J. Catal. 221 (2004) 119.
[15] B.R. Wood, J.A. Reimer, A.T. Bell, M.T. Janicke and K.C. Ott, J. Catal. 224 (2004) 148.
[16] P. Marturano, L. Drozdova, G.D. Pirngruber, A. Kogelbauer and R. Prins, Phys. Chem. Chem. Phys. 3 (2001) 5585.
[17] M.S. Kumar, M. Schwidder, W. Grunert and A. Bruckner, J. Catal. 227 (2004) 384.
[18] P. Marturano, L. Drozdova, A. Kogelbauer and R. Prins, J. Catal. 192 (2000) 236.
[19] A.A. Battiston, J.H. Bitter, F.M.F. de Groot, A.R. Overweg, O. Stephan, J.A. van Bokhoven, P.J. Kooyman, C. van der Spek, G. Vanko and D.C. Koningsberger, J. Catal. 213 (2003) 251.
[20] K.Q. Sun, H.D. Zhang, H. Xia, Y.X. Lian, Y. Li, Z.C. Feng, P.L. Ying and C. Li, Chem. Commun. (2004) 2480.
[21] Q. Zhu, R.M. van Teeffelen, R.A. van Santen and E.J.M. Hensen, J. Catal. 221 (2004) 575.
[22] G.D. Pirngruber, P.K. Roy and N. Weiher, J. Phys. Chem. B 108 (2004) 13746.
[23] E.J.M. Hensen, Q. Zhu, M.M.R.M. Hendrix, A.R. Overweg, P.J. Kooyman, M.V. Sychev and R.A. van Santen, J. Catal. 221 (2004) 560.
[24] P.K. Roy and G.D. Pirngruber, J. Catal. 227 (2004) 164.
[25] A. Waclaw, K. Nowinska, W. Schwieger and A. Zielinska, Catal. Today 90 (2004) 21.
[26] E.J.M. Hensen, Q. Zhu, R.A.J Janssen, P.C.M.M. Magusin, P.J. Kooyman and R.A. van Santen, J. Catal. 233 (2005) 123.
[27] E.J.M. Hensen, Q. Zhu and R.A. van Santen, J. Catal. 233 (2005) 136.
[28] K. Krishna and M. Makkee, Catal. Today (2005) accepted for publication.
[29] K. Krishna, G.B.F. Seijger, C.M. van den Bleek, M. Makkee, G. Mul and H.P.A. Calis, Catal. Lett. 86 (2003) 121.
[30] E. Loeffler, U. Lohse, C. Peuker, G. Oehlmann, L.M. Kustov, V.L. Zholobenko and V.B. Kazansky, Zeolites 10 (1990) 266.
[31] M. Mauvezin, G. Delahay, B. Coq, S. Kieger, J.C. Jumas and J. Olivier-Fourcade, J. Phys. Chem. B 105 (2001) 928.
[32] J.A. McCleverty, Chem. Rev. 104 (2004) 403.
[33] K.I. Hadjiivanov, Cat. Rev. Sci. Eng. 42 (2000) 71.
[34] L.M. Aparicio, W.K. Hall, S.M. Fang, M.A. Ulla, W.S. Millman and J.A. Dumesic, J. Catal. 108 (1987) 233.
[35] G. Berlier, G. Spoto, S. Bordiga, G. Ricchiardi, P. Fisicaro, A. Zecchina, I. Rossetti, E. Selli, L. Forni, E. Giamello and C. Lamberti, J. Catal. 208 (2002) 64.
[36] G. Berlier, A. Zecchina, G. Spoto, G. Ricchiardi, S. Bordiga and C. Lamberti, J. Catal. 215 (2003) 264.
[37] G. Berlier, G. Ricchiardi, S. Bordiga and A. Zecchina, J. Catal. 229 (2005) 127.
[38] G. Mul, J. Perez-Ramirez, F. Kapteijn and J.A. Moulijn, Catal. Lett. 80 (2002) 129.
[39] G. Mul, M.W. Zandbergen, F. Kapteijn, J.A. Moulijn and J. Perez-Ramirez, Catal. Lett. 93 (2004) 113.
[40] M.T. Nechita, G. Berlier, G. Ricchiardi, S. Bordiga and A. Zecchina, Catal. Lett. 103 (2005) 33.
[41] K.i. Segawa, Y. Chen, J.E. Kubsh, W.N. Delgass, J.A. Dumesic and W.K. Hall, J. Catal. 76 (1982) 112.
[42] K. Hadjiivanov, Catal. Lett. 68 (2000) 157.
[43] S. Kameoka, T. Nobukawa, S. Tanaka, S. Ito, K. Tomishige and K. Kunimori, Phys. Chem. Chem. Phys. 5 (2003) 3328.
[44] K. Krishna and M. Makkee, unpublished results.
[45] G. Berlier, F. Bonino, A. Zecchina, S. Bordiga and C. Lamberti, Chem. Phys. Chem. 4 (2003) 1073.
[46] A.M. Ferretti, C. Oliva, L. Forni, G. Berlier, A. Zecchina and C. Lamberti, J. Catal. 208 (2002) 83.
[47] S. Yuen, Y. Chen, J.E. Kubsh, J.A. Dumesic, N. Topsoe and H. Topsoe, J. Phys. Chem. 86 (1982) 3022.
[48] G. Mul, J. Perez-Ramirez, F. Kapteijn and J.A. Moulijn, Catal. Lett. 77 (2001) 7.
[49] Z. Sobalik, J. Dedecek, D. Kaucky, B. Wichterlova, L. Drozdova and R. Prins, J. Catal. 194 (2000) 330.