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Preparation of Fe-ZSM-5 with enhanced activity and stability for SCR of NO_x

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Abstract

Fe-ZSM-5 catalysts are prepared by 320 and 700 °C $FeCl_3$ sublimation into H-ZSM-5 and are characterised by XRD, H_2-TPR, NH_3-TPD, ^{27}Al MAS NMR, and NO adsorption by DRIFT. Selective catalytic reduction of NO with NH_3 and i-C_4H_{10} and NO oxidation to NO_2 have been studied. Fe-ZSM-5 prepared by 700 °C $FeCl_3$ sublimation is more active compared with Fe-ZSM-5 prepared by 320 °C $FeCl_3$ sublimation. NO adsorption study by DRIFT shows that $FeCl_3$ sublimation temperature effects the relative distribution of different iron species in Fe-ZSM-5. High temperature $FeCl_3$ sublimation leads to isolated and hydroxylated iron species (–$Fe(OH)_2$) attached to the ion-exchange positions of ZSM-5. Isolated iron species are intrinsically more active in SCR of NO with NH_3 and i-C_4H_{10}, and NO oxidation to NO_2. All Fe-ZSM-5 catalysts deactivate under simulated exhaust gases at 600 °C. Deactivation is due to extensive detachment of iron species from the ion-exchange positions followed by dealumination of zeolite.

Keywords: Selective catalytic reduction (SCR); NO_x; Fe-ZSM-5 catalysts

1. Introduction

Among the different pollutants, NO_x ($NO + NO_2$), N_2O, CO_2, and particulate matter (soot) contribute to majority of problems starting from local pollution causing health effects to global warming. Selective catalytic reduction (SCR) of NO_x with NH_3 or urea is widely used technology for cleaning exhaust gases of stationary sources [1]. Zeolite based catalysts are found to efficiently convert NO_x to N_2 using NH_3 or hydrocarbon (HC) as a reductant and are considered as suitable materials for exhaust-gas cleaning for mobile applications [2]. Among the zeolite-based catalysts, Fe-ZSM-5 is one of the most studied and very active catalytic system for SCR of NO_x with NH_3 and HC [3–7]. Besides SCR, Fe-ZSM-5 is also extensively investigated in N_2O decomposition and selective HC oxidations [8–10]. Fe-ZSM-5 catalysts prepared by $FeCl_3$ sublimation into H-ZSM-5, developed by Sachtler's group [3], is found to have high catalytic activities in SCR of NO_x with NH_3 and HCs [5]. $FeCl_3$ sublimation is also very effective method for high levels of iron ion exchange into zeolite. The over-exchange Fe-ZSM-5 catalysts prepared by $FeCl_3$ sublimation are reported to be very stable even in the presence of H_2O [3].

A variety of Fe species formed/deposited inside the zeolite pore network are proposed as active centers to explain the observed high activities on Fe-zeolite catalysts in SCR, N_2O decomposition, and selective HC oxidations. Different starting materials, catalyst preparation methodologies, and characterisation techniques have led to the proposal of a large number of active species structure in Fe-ZSM-5. Among others the active sites postulated for catalysing different reactions are $[HO–Fe–O–Fe–HO]^{2+}$, α-oxygen, Fe_4O_4, isolated Fe^{3+}, isolated Fe^{2+}, –Fe–O–Al– clusters, and –$Fe(OH)_2$ [5,9–15]. A systematic study of Fe-ZSM-5 preparation from $FeCl_3$ sublimation by Marturano et al. [16] and by Battiston et al. [11] has shown that every step during catalyst preparation influences the active species or active species distribution in Fe-ZSM-5. An over-exchange Fe-ZSM-5 may contain many of such active sites to different extents [17]. The intrinsic activity of different iron species in Fe-ZSM-5 is expected to be different due to their structure, location, electronic and steric environment around the active sites.

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Based on DRIFT studies of NO adsorbed Fe-ZSM-5 it is suggested that $FeCl_3$ sublimation temperature influences the population and the nature of the iron species in zeolite pore network [18]. In the DRIFT studies all iron species, due to the catalyst pretreatment used, have not been fully elucidated [18–20]. In the present investigation further characterisation of iron species in Fe-ZSM-5 catalysts prepared by 320 and 700 °C $FeCl_3$ sublimation and its activity in various SCR reactions, stability, and causes for deactivation are presented. A correlation of the NO_x conversion to the observed active species in Fe-ZSM-5 will be made.

2. Experimental

2.1. Fe-ZSM-5 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 [3]. The set-up described in Ref. [18] 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 or 700 °C). All $FeCl_2$-ZSM-5 samples 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 air. The physico-chemical properties of some catalysts are listed in Table 1.

2.2. Catalytic activity

Fe-ZSM-5 catalysts (0.1 g) are screened for SCR of NO_x with NH_3 between 300 and 550 °C. SCR of NO_x is carried out with synthetic exhaust-gas mixture contained 1000 ppm NO, 1000 ppm NH_3, 10 vol% O_2, 9 vol% H_2O, and balance N_2. High space velocities (GHSV) of 750,000 h^{-1} have been applied. The catalyst ageing is studied at 600 °C for 100 h time on stream with exhaust gas containing 9 vol% H_2O at a GHSV of 1,400,000 h^{-1}. During ageing after every 15 h of time on stream (TOS) at 600 °C the NO_x conversion at low temperatures are measured. SCR of NO with *iso*-butane (i-C_4H_{10}) is carried out with feed gas containing 1000 ppm NO, 1000 ppm i-C_4H_{10}, 10 vol% O_2, and N_2 as balance at a GHSV of 50,000 h^{-1}. NO oxidation to NO_2 is studied under similar conditions, in the absence of i-C_4H_{10}. NO_x and N_2O are monitored with a chemiluminescence detector and gas chromatography, respectively. The formation of N_2O over the catalysts is negligible under all reaction conditions.

Table 1
Preparation conditions and IE percentage of Fe-ZSM-5 [2]

Catalyst	$FeCl_3$ sublimation temperature (°C)	IE (%)
Fe-ZSM-5-320	350	69
Fe-ZSM-5-700	700	51

2.3. Characterisation

NH_3-TPD and H_2-TPR are carried out in a Micromeritrics pulse chemisorb (2900) TPD-TPR instrument. For NH_3-TPD 20 mg of fresh and aged samples are activated at 600 °C for 1 h in He and cooled to 200 °C. NH_3 is adsorbed at 200 °C for 0.5 h and flushed with He for 0.5 h to remove any physically adsorbed NH_3. Desorption is carried at a heating rate of 10 °C min^{-1} till 600 °C. For H_2-TPR 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^{-1} till 900 °C and maintained for prolonged times at 900 °C.

Nicolet Magna IR 860 spectrometer equipped with liquid nitrogen cooled MCT detector is used for diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) study. A spectratech DRIFT high temperature cell, equipped with CaF_2 windows, is filled with the powdered catalyst. The catalyst samples are activated at 450 °C for 1 h in 10 vol% O_2 or He or 10 vol% H_2, and cooled to 50 °C. The activated zeolite IR spectra are recorded and used as background for collecting NO adsorption spectra at 50 °C. Sixty four scans are collected with 4 cm^{-1} spectral resolution.

^{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. The chemical shifts are reported with respect to $Al(NO_3)_3$ as external standard. Around 1600 scans are collected (similar but not identical for all samples).

The materials are also characterised by XRD (Philips X-ray diffractometer, PW 1840) with Ni-filtered Cu Kα radiation (λ = 1.541 Å).

3. Results and discussion

3.1. Characterisation

3.1.1. H_2-TPR

Fig. 1 shows H_2-TPR profiles of Fe-ZSM-5 catalysts. The Fe^{3+} species in Fe-ZSM-5-700, prepared by 700 °C $FeCl_3$ sublimation, are reduced at relatively low temperatures compared with Fe-ZSM-5-320, prepared by 320 °C $FeCl_3$ sublimation. The reduction of Fe^{3+} to Fe^{2+} at zeolite ion-

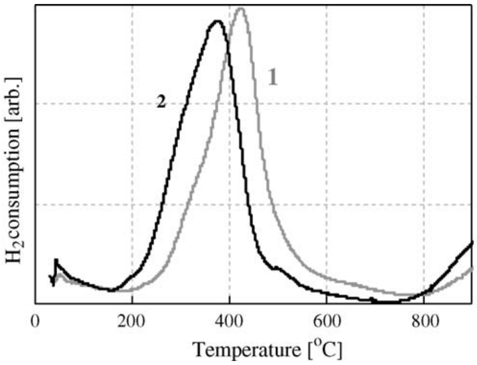

Fig. 1. H_2-TPR profiles of Fe-ZSM-5-320 (1) and Fe-ZSM-5-700 (2) catalysts prepared by 320 and 700 °C $FeCl_3$ sublimation, respectively.

exchange positions is observed around 390 and 410 °C for 700 and 320 °C $FeCl_3$ sublimed catalysts, respectively. If extensive FeO_x phases have been present, than they generally show reduction peaks around 540 °C. Above 800 °C FeO_x nanoparticles/Fe^{2+} at ion-exchange positions can be reduced [18,21]. Both the Fe-ZSM-5 catalysts did not show H_2 consumption due to significant amount of FeO_x species. This is further supported by XRD spectra (not shown) in which the presence of FeO_x phases in Fe-ZSM-5 have not been observed. The absence of FeO_x phases is due to the low Fe^{3+} exchange levels and to some extent to the modified Fe-ZSM-5 preparation method. The facile reduction of Fe^{3+} species in Fe-ZSM-5-700 compared with Fe-ZSM-5-320 suggests the different nature of some of the iron species in the former catalyst.

3.1.2. ^{27}Al MAS NMR

High temperature (700 °C) $FeCl_3$ sublimation generates aggressive condition (high concentration of gas-phase HCl), and apart from ion exchange, H-ZSM-5 is expected to dealuminate leading to additional extra-framework alumina. $FeCl_3$ or FeO_x can also react with extra-framework alumina during high temperature catalyst preparation to form –Al–O–Fe– like species as suggested by Hensen et al. [22,23]. To analyse for the presence of any such species ^{27}Al MAS NMR spectra of H-ZSM-5 and Fe-ZSM-5 catalysts are recorded (Fig. 2). The resonance band at 54 and 0 ppm in H-ZSM-5 corresponds to tetrahedrally (framework) and octahedrally (extra-framework) coordinated alumina, respectively [16]. The relative intensities indicate that small amounts of extra-framework alumina are already present in starting H-ZSM-5. The intensity of the NMR resonance bands in Fe-ZSM-5 is expected to decrease compared with H-ZSM-5 as shown in Fig. 2. When iron species is present in close proximity to alumina species, for example at ion-exchange positions, the magnetic field generated by unpaired electrons of iron species will perturb the resonance of Al nuclei leading to a decreased intensity [16]. The high intensity spinning side bands around 135 and −20 ppm, due to dipolar interaction between electron spin of iron species and Al nuclei support that Fe^{3+} is at framework ion-exchange positions. The extra-framework alumina at 0 ppm is clearly evident in Fe-ZSM-5-700. This suggests that iron species are not extensively interacting with extra-framework alumina. In Fe-ZSM-5-320 the extra-framework alumina is not very clear due to the broad spinning side band. Marturano et al. [16] have shown that extra-framework alumina does not strongly interact with iron in Fe-ZSM-5 prepared by 320 °C $FeCl_3$ sublimation, as observed in our Fe-ZSM-5 NMR spectra. From ^{27}Al MAS NMR it can be concluded that iron species is present at ion-exchange positions or as FeO_x. The presence of extensive FeO_x phases can, however, be ruled out from H_2-TPR (which did not show H_2 consumption around 540 or 800 °C) and XRD prompting us to suggest that most of the active species are present at the ion-exchange positions in Fe-ZSM-5 catalysts.

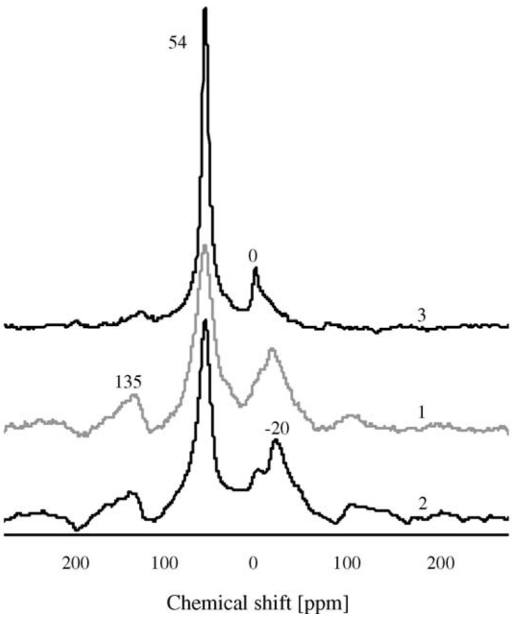

Fig. 2. ^{27}Al MAS NMR of Fe-ZSM-5-320 (1), Fe-ZSM-5-700 (2), and parent H-ZSM-5 (3).

3.1.3. NO adsorption by DRIFT

Different zeolitic and iron species present in Fe-ZSM-5 catalysts are probed by NO adsorption in DRIFT [12,19,24–26]. Fig. 3a and b shows the DRIFT spectra of NO adsorbed Fe-ZSM-5. Fe-ZSM-5 catalysts are either in situ calcined (10 vol% O_2) or reduced (10 vol% H_2) at 450 °C before NO adsorption study. The dynamics of the band evolution is not presented here,

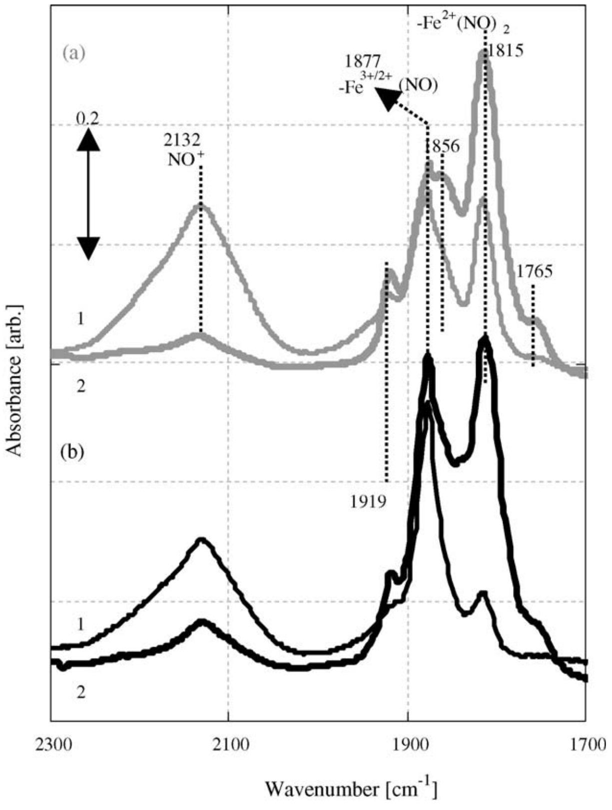

Fig. 3. IR spectra of NO adsorption over (a) Fe-ZSM-5-320 and (b) Fe-ZSM-5-700, oxidised (1) and reduced (2) catalysts.

however, it should be mentioned that all the bands saturated quickly due to high NO (5 vol%) concentration used for the adsorption. IR bands at 1815 and 1919 cm^{-1} are due to symmetric and assymmertic NO stretches of iron dinitrosyl ($Fe^{2+}(NO)_2$) species, respectively, and the shoulder at 1765 cm^{-1} is due to the mononitrosyl of the iron dinitrosyl species [25,27]. The iron species present in ZSM-5 straight channels, which are also easily accessible, are proposed as responsible for the band at 1815 cm^{-1} [25–27]. The appereance of 1815 cm^{-1} band in all Fe-ZSM-5 catalyst shows that some iron species are present in 2+ oxidation state, even in oxidised catalyst. Comparison of 1815 cm^{-1} band relative intensity over oxidised Fe-ZSM-5-320 and Fe-ZSM-5-700 indicates that high temperature sublimation mainly leads to Fe^{3+} species in easily accessible locations in the former catalyst. On He treatment at 450 °C (not shown) 1815 cm^{-1} band intensity is not influenced significantly and, therefore, autoreduction of Fe^{3+} to Fe^{2+} is very limited in both Fe-ZSM-5 catalysts. In the previous report Fe-ZSM-5-320 catalyst pretreated in He, has shown high intensity 1815 cm^{-1} band. This has to be related to HC impurities during pretreatment [18]. The intensity of 1815 cm^{-1} band increases by several folds on H_2 reduction in both Fe-ZSM-5 catalysts. Comparing the relative intensity of 1815 cm^{-1} band it can be postulated that most of the iron species in Fe-ZSM-5-320 are present in straight channels (iron species that can form dinitrosyls) [27,25,26].

IR band around 1856 cm^{-1} is only visible on prolonged reduction at 450 °C, and more of such iron species are present in Fe-ZSM-5-320. Different authors correlated this band to different species as discussed by Mul et al. [19]. These iron species are proposed to be present at the intersections of ZSM-5 pore network [18,19,25]. We believe since these species appear after prolonged reduction, their participation in the redox reactions is limited.

IR band at 1877 cm^{-1} in oxidised Fe-ZSM-5 is assigned to NO stretchings of mononitrosyl iron species ($Fe^{3+}(NO)$) at ion-exchange positions. 1877 cm^{-1} band is often corrrelated to isolated iron species (observed in low iron-exchange Fe-ZSM-5) and to iron species located at sterically hindered zeolitic locations [18,25,27]. During the $FeCl_3$ sublimation, high temperatures drives the iron species to occupy most stable configuration and locations in a ZSM-5 pore network. The most stable locations in a zeolite are sterically hindered locations (γ sites) and the iron species present here will be stabilised by close co-ordination shell of framework oxygens [28]. Significant amount of isolated Fe^{3+} species are present in both Fe-ZSM-5 catalysts and its concentration is much higher in Fe-ZSM-5-700. The intensity of 1877 cm^{-1} band only slightly increases on reduction. This suggests that Fe^{3+} or Fe^{2+}, at these sterically hindered positions, will only form mononitrosyls and this is in agreement with open literature [27,26].

IR band around 2132 cm^{-1} is assigned to NO_2^+ and/or NO^+ over bridging hydroxyl groups [25,26]. The intensity is in accordance with the ion-exchange percentage of Fe-ZSM-5, in which significant amount of bridging hydroxyl groups are still available for NO^+ adsorption. On reduced Fe-ZSM-5, the amount of NO^+ adsorption on Brønsted sites decreases as indicated by decreased intensity at 2132 cm^{-1}. This suggests that NO^+ is originated from Fe^{3+} sites [26]. If NO^+ is interacting with Brønsted protons, it should lead to the corresponding negative bands and indeed negative bands are observed in hydroxyl stretching region, 3500–3800 cm^{-1} (Fig. 4). Depending on $FeCl_3$ sublimation temperature two to three prominent bands are observed in 3500–3800 cm^{-1} region. The negative band at 3606 cm^{-1} is a result of NO^+ adsorption on bridging hydroxyl groups and 3663 cm^{-1} band can be correlated to NO^+ adsorption over extra-framework alumina. Chen et al. [4] in their study correlated the negative band around 3663 cm^{-1} to hydrocarbon interaction with hydroxyls associated with binuclear iron species, $[–(OH)Fe–O–Fe(OH)–]^{2+}$. On Fe-ZSM-5-700, prepared by 700 °C $FeCl_3$ sublimation, apart from 3666 cm^{-1} band a new band at 3677 and a shoulder at 3628 cm^{-1} are observed. IR band at 3677 cm^{-1} is arising due to NO^+ adsorbed on the hydroxyl groups of iron species. Such species have been observed by Wood et al. [10] in Fe/Al-ZSM-5, by Mauvezin et al. [21] and Kameoka et al. [29] in Fe-BEA. Duplication of Fe-ZSM-5 catalyst preparation by 320 °C $FeCl_3$ sublimation never lead to hydroxyl groups associated with iron species with such high intensity. On the other hand such iron species is consistently observed by $FeCl_3$ sublimation in to H-ZSM-5 above 700 °C.

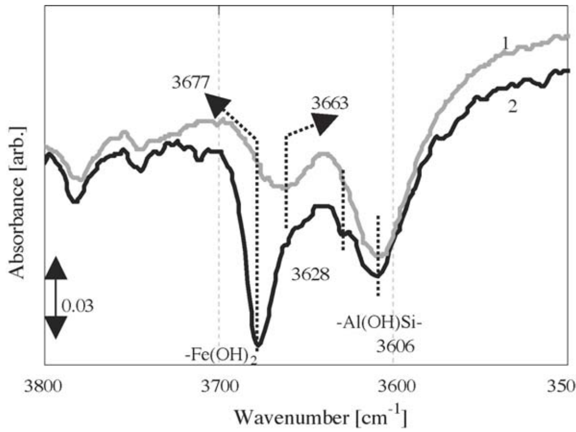

Fig. 4. IR spectra of NO adsorption in hydroxyl stretching region. Fe-ZSM-5-320 (1) and Fe-ZSM-5-700 (2) oxidised catalysts.

Keeping in mind the aggressive Fe-ZSM-5-700 catalyst preparation conditions, the iron species, having hydroxyl groups, are either at ion-exchange positions or associated with extra-framework alumina ($–Al–O–Fe(OH)_x$ like species). ^{27}Al MAS NMR (Fig. 2) shows the presence of extra-framework alumina in Fe-ZSM-5-700, and therefore, iron species is not in close proximity to extra-framework alumina. This rules out extensive $–Al–O–Fe(OH)_x$ like species formation. The hydroxylated iron species, therefore, should be present at zeolite ion-exchange positions. Wood et al. [10] have suggested such a species to be $–Fe(OH)_2$, based on intensity ratios between 3673 cm^{-1} (assymmetric) and 3628 cm^{-1} (symmetric) stretching vibrations. During NO adsorption study by DRIFT, due to high NO concentration used, the dynamics of the bands at 3677 and 3628 cm^{-1} could not be followed. The Fe/Al-ZSM-5 catalyst preparation by Wood et al. [10] and in the present investigation (Fe-ZSM-5-700) involve high temperature treatment and it is reasonable to assign 3677 and 3628 cm^{-1} bands to –Fe(OH)$_2$. This iron species is suggested as isolated active sites associated with framework alumina. Further experiments have revealed that high temperature sublimation is necessary to create –Fe(OH)$_2$ and with increase in $FeCl_3$ sublimation temperature the concentration of –Fe(OH)$_2$ increase [30]. Upon reduction –Fe(OH)$_2$ bands disappeared due to dehydroxylation, similar observation made by Kameoka et al. [29]. H_2-TPR shows that iron species in Fe-ZSM-5-700 can be reduced at relatively low temperature, and if –Fe(OH)$_2$ like species are reduced it should lead to –Fe(OH) like species. Further experiments are needed to confirm such iron species.

Comparison of the IR spectra in 1700–4000 cm^{-1} region shows that Fe-ZSM-5-700 has relatively more isolated iron species that form monomintosyls, whereas Fe-ZSM-5-320 has iron species that form dinitrosyls. From DRIFT and ^{27}Al MAS NMR it can be concluded that isolated –Fe(OH)$_2$ are present in Fe-ZSM-5-700 and these are associated with framework alumina. The –Fe(OH)$_2$ seems to form only mononitrosyl complex on NO adsorption (1877 cm^{-1} IR band). If –Fe(OH)$_2$ is present in the straight channels of ZSM-5 the relative intensity of 1815 cm^{-1} band is expected to be much higher than what is observed in reduced Fe-ZSM-5-700. The –Fe(OH)$_2$ species are only formed on high temperature $FeCl_3$ sublimation. The catalysts containing such species are also reported to be active for N_2O decomposition and HC oxidation [10,21,29].

3.2. Catalytic activity

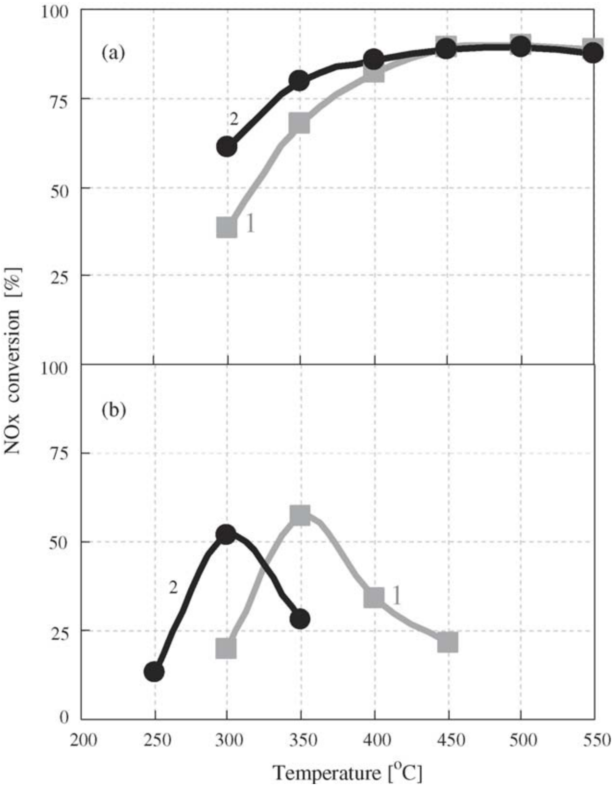

Fig. 5. SCR of NO_x with (a) NH_3 and (b) i-C_4H_{10} over Fe-ZSM-5-320 (1) and Fe-ZSM-5-700 (2) catalysts. *Reaction conditions*: $NO_x = NH_3 = 1000$ ppm, $O_2 = 10$ vol%, $H_2O = 9$ vol% balance N_2, GHSV = 750,000 h^{-1} and (b) SCR with i-C_4H_{10}. *Reaction conditions*: $NO_x = i$-$C_4H_{10} = 1000$ ppm, $O_2 = 10$ vol% balance N_2, GHSV = 50,000 h^{-1}.

Fig. 5a shows SCR of NO_x with NH_3. The NO_x reduction with NH_3 over various Fe-ZSM-5 catalysts prepared by $FeCl_3$ sublimed at different temperatures are discussed in an earlier paper [18]. Fe-ZSM-5-320 and Fe-ZSM-5-700 are in general very active and selective in NO_x reduction with NH_3 even under very high space velocities and in the presence of 9 vol% H_2O. Though the ion-exchange percentage in Fe-ZSM-5-700 is less than Fe-ZSM-5-320, the former catalyst is more active in SCR of NO with NH_3. The turn-over-frequency (number of NO molecules converted per iron site per second) at 300 °C, over Fe-ZSM-5-700 is 19, a factor of 2 higher than that observed over Fe-ZSM-5-320. Fig. 5b shows SCR of NO with i-C_4H_{10}. Fe-ZSM-5-320 has shown maximum NO_x conversion of around 55% at 350 °C. Over Fe-ZSM-5-700 the maximum NO_x conversion is 50%. This is however observed at 300 °C. The decrease of NO_x conversion above 300 °C is due to direct oxidation of HC to CO_x, which decreases the concentration of the reductant necessary for SCR. Fe-ZSM-5 shows an order of magnitude low activity using HC as a reductant, even in the absence of H_2O compared with NH_3 as a reductant. NO_2 is a more powerful reactant, and NO oxidation to NO_2 over various SCR catalysts is considered as a primary step [26]. NO oxidation to NO_2 over Fe-ZSM-5 catalysts is shown in Fig. 6. Fe-ZSM-5-700 shows very high conversion approaching thermodynamic equilibrium limits around 300 °C. Fe-ZSM-5-320 catalyst has a lower conversion of NO to NO_2 compared with Fe-ZSM-5-700. The NO_x conversion during SCR with NH_3 and i-C_4H_{10} is in agreement with NO conversion to NO_2 trends over the respective catalysts.

The Fe-ZSM-5 catalysts prepared by 320 °C $FeCl_3$ sublimation and aqueous ion exchange (not shown), consistently show low conversions in various reactions involved in SCR, compared with Fe-ZSM-5 catalyst prepared by 700 °C $FeCl_3$ sublimation. The low activity observed over Fe-ZSM-5-320 or ion-exchange Fe-ZSM-5 catalysts cannot be correlated to the presence of FeO_x phases. It is shown by XRD and H_2-TPR that FeO_x phases are almost absent in Fe-ZSM-5-320. In

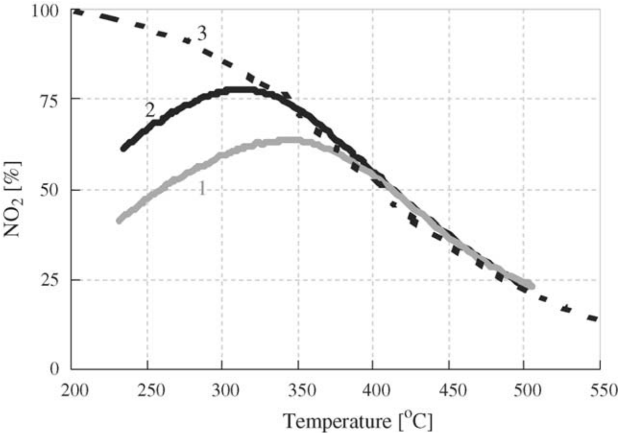

Fig. 6. NO conversion to NO_2 over Fe-ZSM-5-320 (1), Fe-ZSM-5-700 (2), and thermodynamic equilibrium (3). *Reaction conditions*: $NO_x = 1000$ ppm, $O_2 = 10$ vol% balance N_2, GHSV = 50,000 h^{-1}.

Fe-ZSM-5-320 relatively high concentration of iron species are present in the easily accessible straight channels (iron species that can form –$Fe^{2+}(NO)_2$) compared with the isolated species (that can form –$Fe^{3+/2+}(NO)$). Though all iron species are active in various SCR reactions studied, the intrinsic activity of iron species present in easily accessible straight channels seems to be low. High temperature $FeCl_3$ sublimation leads to high concentration of isolated species in Fe-ZSM-5-700 relative to iron species present in straight channels or compared with Fe-ZSM-5-320. These isolated iron species in Fe-ZSM-5-700 are also found to be associated with hydroxyl groups (–$Fe(OH)_2$), which are absent in Fe-ZSM-5-320. From ^{27}Al MAS NMR, the extensive interaction of iron species with extra-framework alumina, at present stage, can be ruled out, and the isolated –$Fe(OH)_2$ species are present at ion-exchange positions of ZSM-5. The improved activity over Fe-ZSM-5-700 has to be related to intrinsically high activity of the isolated iron species (–$Fe(OH)_2$) at ion-exchange positions.

3.3. Stability of Fe-ZSM-5 catalysts

The catalyst deactivation is one of the major problems in using zeolite-based materials in real exhaust-gas applications. Fe-ZSM-5 is shown to be resistant to dealumination and, therefore, very stable. However, ageing of Fe-ZSM-5 is generally performed below 500 °C and the conversions are generally >80% where the catalyst deactivation is hardly observed [3]. In the present investigation the SCR activity at 600 °C for 100 h TOS is studied over Fe-ZSM-5-320 and Fe-ZSM-5-700 catalysts (Fig. 7a). During the SCR of NO_x with NH_3 at 600 °C, catalysts are subjected to simulated exhaust gases containing 10 vol% H_2O at high space velocities. After every 15 h of TOS at 600 °C, the NO_x conversion at low reaction temperatures is measured (only the activities after selected time intervals are shown in Fig. 7b). The NO_x conversion decreases over both the Fe-ZSM-5 catalysts with increase of TOS at 600 °C (Fig. 7a). The deactivation is rather fast during the initial 25 h TOS followed by a gradual decrease in NO_x conversion. Stable NO_x conversion is not reached over both the Fe-ZSM-5 catalysts during 100 h of TOS. The initial NO_x conversion over both the Fe-ZSM-5 catalysts in the temperature range 450–600 °C is around 80% (Fig. 7b) and the low temperature activity further decreases with increasing ageing time at 600 °C. From Fig. 7 it should be noted that Fe-ZSM-5-700 prepared by high temperature $FeCl_3$ sublimation is more active and seems to be relatively more stable than that of Fe-ZSM-5-320. This is in agreement with our previous study [18]. Irrespective of Fe-ZSM-5 preparation method, catalysts deactivate under simulated exhaust gases containing H_2O. Lee and Rhee [31] have reported that NO_x reduction with i-C_4H_{10} also decreases due to ageing under similar conditions.

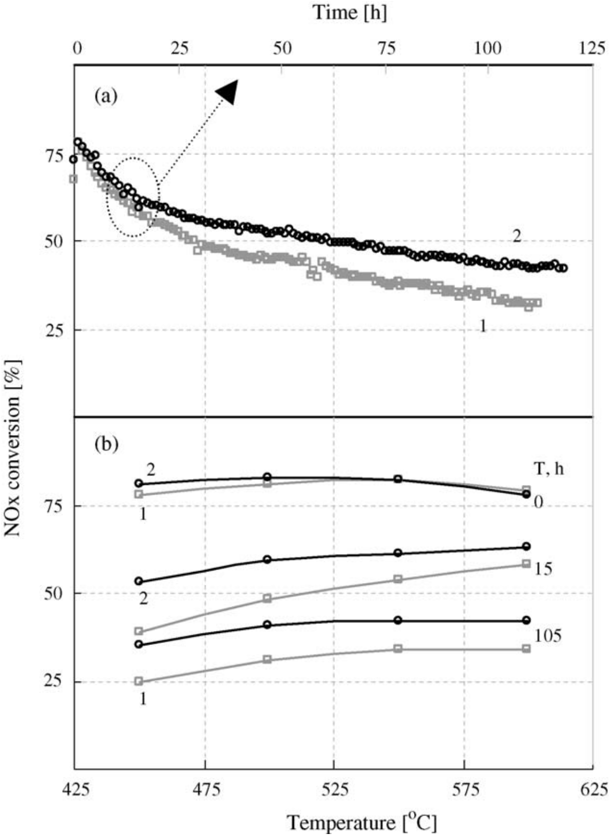

Fig. 7. SCR of NO_x with NH_3 (a) TOS at 600 °C and (b) NO_x conversion below 600 °C, after maintaining '*T*' hours at 600 °C. Fe-ZSM-5-320 (1) and Fe-ZSM-5-700 (2). *Reaction conditions*: $NO_x = NH_3 = 1000$ ppm, $O_2 = H_2O = 9$ vol% balance N_2, GHSV = 1,400,000 h^{-1}.

3.4. Characterisation of aged Fe-ZSM-5 catalysts

The 600 °C aged catalysts are characterised by various techniques and compared with the fresh catalysts. Fig. 8 shows H_2-TPR profiles of fresh and aged Fe-ZSM-5-700. The iron species that are easily reducible in fresh Fe-ZSM-5-700 are completely lost and the reduction of Fe^{3+} in aged catalysts seems to be more difficult as evident from shift in H_2-TPR profile to >420 °C. H_2 consumption above 600 °C is relatively more in aged catalyst indicating the presence of FeO_x phases. The broad H_2 consumption peak above 900 °C is due to slow reduction of Fe^{2+} attached to zeolite framework to Fe^0 or reduction of FeO_x nano-particles [18,21]. The intensity of the

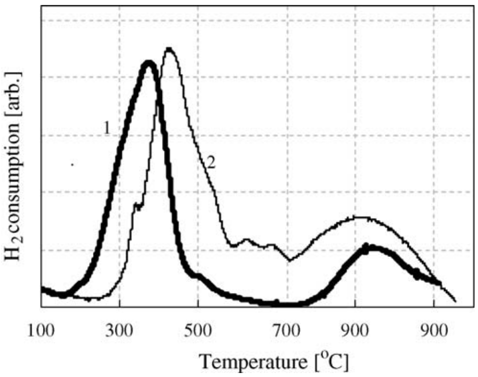

Fig. 8. H_2-TPR profiles of Fe-ZSM-5-700, fresh (1) and aged (2) (>100 h at 600 °C) catalyst.

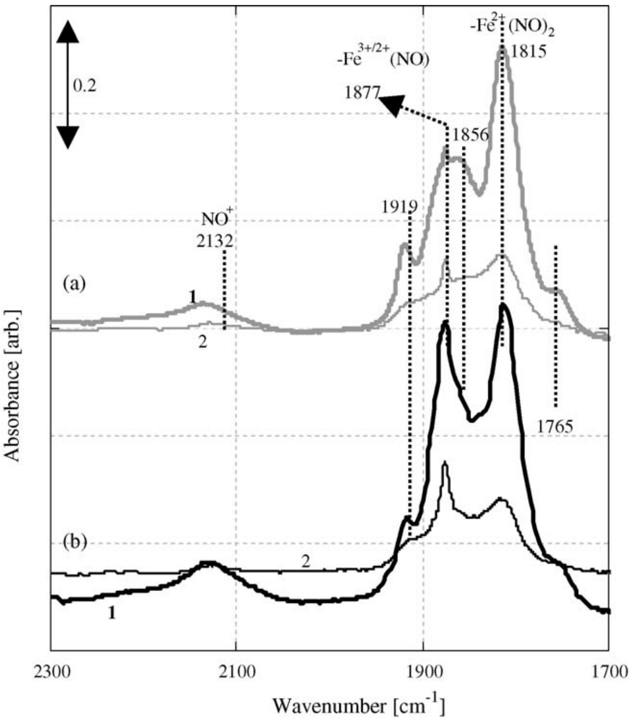

Fig. 9. IR spectra of NO adsorption over reduced (a) Fe-ZSM-5-320 and (b) Fe-ZSM-5-700, fresh (1) and aged (2) (>100 h at 600 °C) catalysts.

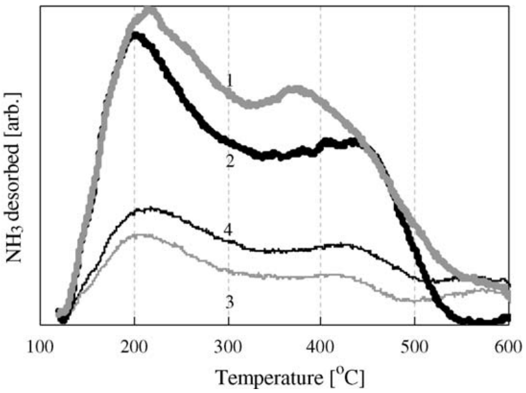

Fig. 10. NH_3-TPD over Fe-ZSM-5-320 (1 and 3) and Fe-ZSM-5-700 (2 and 4). Thick lines—fresh and thin lines—aged (>100 h at 600 °C) catalysts.

high temperature peak increases on ageing and shifts to low temperature indicating increased amount of FeO_x particles in Fe-ZSM-5-700.

Fig. 9 shows DRIFT spectra of NO adsorbed at 50 °C over fresh and aged Fe-ZSM-5 catalysts (before NO adsorption catalysts are reduced in H_2 at 450 °C). Reduction treatment leads to the detection of all possible iron species (as Fe^{3+} ions present in straight channels will not form nitrosyls). The intensity of IR bands arising from nitrosyls of iron attached at the framework ion-exchange positions (1815, 1856, and 1877 cm^{-1}), drastically decreased in both aged Fe-ZSM-5 catalysts compared with the fresh catalysts, respectively. In aged catalysts significant amount of Fe^{3+} can be reduced around 450 °C (Fig. 8), however majority of the Fe^{2+} do not seem to form nitrosyls. Therefore, the decrease in IR band intensity is correlated to the formation of FeO_x particles that only weakly adsorbs NO [26]. The intensity of 1877 cm^{-1} band (isolated iron species) in aged Fe-ZSM-5-700, compared to aged Fe-ZSM-5-320 and iron species in straight channels (1815 cm^{-1}) of respective catalysts, indicates that the isolated iron species are relatively more stable. From DRIFT it is concluded that in both aged Fe-ZSM-5 catalysts Fe^{3+} is extensively detached from the zeolite framework leading to FeO_x formation. The isolated iron species, in Fe-ZSM-5-700, are relatively more stable and most active species in SCR of NO_x.

Fig. 10 shows NH_3-TPD over fresh and aged Fe-ZSM-5 catalysts. All catalysts show two NH_3 desorption peaks. The peak around 200 °C is due to desorption of weakly bound NH_3 followed by desorption around 400 °C due to strongly bound NH_3. The strongly bound NH_3 is arising from Fe-ZSM-5 unoccupied Brønsted hydroxyl groups (bridging hydroxyls) and strong Lewis iron sites. The significant decrease in NH_3 desorption in the aged catalysts implies that Fe^{3+} is detached from ZSM-5 ion-exchange positions followed by extensive dealumination of zeolite. This is in agreement with H_2-TPR and DRIFT.

Irrespective of catalyst preparation method, all Fe-ZSM-5 catalysts deactivate when aged at 600 °C for prolonged times. From characterisation it is shown that the catalyst deactivation is due to the detachment of Fe^{3+} form the ion-exchange positions leading to the formation of FeO_x. The detachment of Fe^{3+} further leads to extensive zeolite dealumination. Fe-ZSM-5 catalysts aged at 700 °C have lower rates of deactivation but similar deactivation mechanism is applicable [18,31]. Even at low temperature the deactivation occurs but the rate of deactivation will be much smaller. Fe-ZSM-5 catalysts are very active in SCR of NO_x with NH_3 and HCs, the stability of these materials in the presence of H_2O will be an impeding problem for their real applications.

4. Conclusions

Fe-ZSM-5 catalysts prepared by 700 °C $FeCl_3$ sublimation are more active in SCR of NO with NH_3, with i-C_4H_{10}, and NO conversion to NO_2 compared with Fe-ZSM-5 prepared by 320 °C $FeCl_3$ sublimation. The nature and population iron species at different zeolite locations can be influenced by changing $FeCl_3$ sublimation temperature. High temperature $FeCl_3$ sublimation results in isolated iron species having hydroxyl groups (–$Fe(OH)_2$) at framework ion-exchange positions as confirmed by ^{27}Al MAS NMR and NO adsorption by DRIFT. Such isolated iron species are found to be intrinsically more active in various reactions involved in SCR. Irrespective of Fe-ZSM-5 preparation method all catalysts severely deactivate when they are aged in simulated exhaust gases at 600 °C. The deactivation is due to extensive detachment of Fe from the framework followed by dealumination.

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