Catalysis Letters Vol. 91, Nos. 1–2, November 2003 (© 2003)

Fourier transform IR study of NO + CH_4 + O_2 coadsorption on In-ZSM-5 DeNO_x catalyst

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Received 9 June 2003; accepted 7 August 2003

Reactivity of the NO and NO_2 adspecies in the coadsorption of NO with CH_4 and O_2, and the effect of Si/Al ratio of In-ZSM-5 were studied by FTIR *in situ*. The relation between the adsorbed species and catalytic activity in the SCR of NO_x to N_2 was also investigated. The adsorption of NO over this catalyst was performed at room temperature with pure NO followed by purging with vacuum. When NO was introduced to the samples, three peaks were observed by FTIR: 1622 and 1575 cm^{-1}, which can be assigned to adsorbed (ONO)- over InO^+ site and NO_2 over InO^+ site, respectively, and at 1680 cm^{-1} corresponding to NO_3^--H. Coadsorption of nitrogen monoxide, methane and oxygen at room temperature of the samples with Si/Al ratio of 17(a), 27(b) and 50(c), allowed us to determine that sample (b) has large amount of NO_2–InO^+ adsorbed species, which are the most important intermediates in the SCR of NO_x. The bands at 1575 and 1680 cm^{-1} are more intense in samples (a) and (c). When the coadsorption of the mixture was performed at 400 °C, we can see that the adsorbed species are larger in sample (b). Taking into account the catalytic performance of the catalysts and the PAC results obtained by us earlier, this last indium specie, only present in the sample with Si/Al = 27, should be associated with the catalytic active specie for the SCR of NO_x.

KEY WORDS: NO_x and methane adsorption; FTIR; intermediate species.

1. Introduction

The nitrogen oxides are undesired air pollutants since they are highly toxic and are one of the main reasons for the appearance of smog and acid rain [1]. That is why the NO_x removal from different waste gases is a central problem in modern industry. One of the most widely applied techniques for deNO_x-ing is the selective catalytic reduction (SCR) [2–6]. The reducing agent utilized in the actual commercial processes, when the gas source is stationary, is ammonia and the most used catalysts are V_2O_5-WO_3-TiO_2 or V_2O_5-MoO_3-TiO_2 [2–7]. However, the potential use of SCR for the purification of diesel exhaust gases has suggested the search for effective catalysts for the reduction of NO_x by hydrocarbons. Recently, successful SCR deNO_x by different hydrocarbons has been reported on some copper, cobalt, nickel, rhodium, indium and gallium exchanged zeolites [8–10].

The three-way catalyst, which contains supported noble metals, transforms NO_x to N_2 by nonselective reduction with hydrocarbon residues, carbon monoxide and hydrogen. However, for diesel engines or gasoline engines operating under lean burn conditions, such catalysts cannot be applied because of the predominant direct oxidation of the reductants and a fast catalyst deactivation. There has been much effort to develop alternative catalysts for the SCR of NO_x with hydrocarbons in the presence of excess oxygen. In particular, zeolites modified with various redox components (transition and/or precious metals) have been investigated [11]. In the case of exhaust gases from diesel engines on ship and gas or diesel engines used for electricity generation, ammonia is employed for the selective reduction of NO_x on V, WO_x/TiO_2 and copper zeolite catalysts [12]. A substitution of ammonia by methane or light alkanes could become a promising alternative, in particular, with natural gas–fuelled engines. However, an SCR deNO_x with methane requires catalysts activating the relatively inert methane molecule more selective than zeolites promoted with transition metal ions, being suitable for SCR by alkenes or higher alkanes. Gallium or indium supported on zeolites was discovered to be better suitable for CH_4-SCR than copper or iron, which favors the direct oxidation of CH_4 to CO_2 [13–15]. Ogura and colleagues [16] have reported that indium ion exchanged into H-ZSM-5 showed high catalytic activity for the CH_4-SCR, and the reduction of NO with CH_4 on the catalysts seems to proceed in two stages: firstly NO is oxidized to NO_2 and then NO_2 reacts with CH_4 into N_2. It has also been indicated [17] that NO oxidation on the acidic site of the zeolite is strongly retarded by water vapor. On the other hand, InO^+ site, which is ion exchanged in the zeolites [18], moderately catalyzed NO_2-CH_4 reaction even in the wet conditions. However, it has not been clear whether the adsorbed NO_2 on InO^+ sites is

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1011-372X/03/1100–0019/0

involved in the reaction mechanism for NO reduction with CH_4.

A series of indium-loaded ZSM5 catalysts with Si/Al ratios of 17, 27 and 50 was studied in a previous work [19]. The catalytic activity for the SCR of NO followed the $27 > 17 = 50$ order. Reaction results of NO_x conversion to N_2 and CH_4 conversion among the samples studied showed that indium exchanged on NH_4-ZSM5 with $Si/Al = 27$ is the most active catalyst in both cases (80 mol% conversion of NO_x to N_2 and 100 mol% conversion of CH_4 at 550 °C). This fact is related to the special features of this sample compared with the other In-exchanged ZSM5 zeolites with different Si/Al ratios (17 and 50). TPAD (temperature-programmed ammonium desorption) of In-exchanged samples indicated that indium ions were incorporated as counterions blocking preferentially the stronger Brönsted acid sites, the remaining protons having weak or medium acidic strength [19]. The concentration of these sites depends on the Si/Al ratios of the samples. Indium mainly interacts with the stronger sites, especially in the case of $Si/Al = 27$. The exchanged indium species generated new and strong acceptor electron sites, as indicated by the FTIR results. The time differential observation of the perturbed angular correlation (PAC) of γ-rays emitted from radioactive ^{111}In allows us to characterize different indium species by means of hyperfine interactions. This technique, by means of the determination of the gradient of local electric field in the site of a probe atom, can give information on the characteristics (coordination, symmetry, distortion, etc.) of the different surroundings from the probe, its concentrations and modifications by *in situ* analysis conditions (temperature, atmosphere, pressure, etc.). Often, a probe of PAC is introduced as an impurity, but in the present case the information from PAC turns out to be more reliable since the probe does not constitute an impurity considering that ^{111}In is a component of the catalyst. Thus, the nature of the indium species was determined by the PAC technique using ^{111}In as a probe [19]. We found three different hyperfine interactions associated with two different indium sites. Two of them have the same parameters of ^{111}In in In_2O_3 oxide [20] and constitute the 72, 58 and 49% of all the indium sites in the zeolites with Si/Al ratio of 17, 27 and 50 respectively. A third minority interaction has a distributed electric field gradient (EFG). The EFG is a second-range tensor, and, hence, it also contains information about the symmetry of the environment of the ^{111}In-probe atoms. These results from the charge-density distribution reflect the nature of the chemical bonds. Since the electric field gradient depends mainly on the local environment of the probe, this minority interaction can be attributed to indium species with a short-range order. The indium species different from In_2O_3 present in samples with $Si/Al = 17$ and 50 are similar and both are different from that with $Si/Al = 27$ [19].

In this study, the reactivity of the NO_x adspecies towards CH_4 on In-ZSM-5 with Si/Al ratios of 17, 27 and 50 will be studied with a pressure swing adsorption method and *in situ* infrared spectroscopy from the viewpoint of NO_x chemisorption under the reaction conditions. To obtain information on the reasons for the high SCR activity of In-ZSM-5 with Si/Al ratio of 27, we investigated NO adsorption and $NO + O_2 + CH_4$ coadsorption on these zeolites.

2. Experimental

2.1. Sample preparation

Three ZSM5 zeolites with $Si/Al = 17$, 27 and 50 were obtained by hydrothermal synthesis using tetrapropyl ammonium hydroxide (TPA) as the template [21]. The ammonium form of the catalyst was prepared by ion exchange with 1-M ammonium chloride at 80 °C for 40 h. In-H-ZSM-5 samples were prepared using NH_4-ZSM5 zeolites by ion exchange with $InCl_3$ followed by 10 h calcinations in air at 500 °C. In all samples, the quantity of indium introduced was two times the number of aluminium atoms in the zeolite. The indium remaining in the zeolite after the ion exchange was estimated from the intensity of ^{111}In-radioactive probes in the samples. We found the following values: 2.5, 1.5 and 1.6 wt% of indium for $Si/Al = 17$, 27 and 50, respectively. However, the relevant values of indium concentration should be considered from indium species different from In_2O_3 determined in a previous work [19].

2.2. FTIR studies

Infrared measurements were performed on a JASCO 5300 FTIR spectrometer. For structure characterization, the samples were mixed with KBr and pressed, forming a wafer. The IR spectra of the catalyst in the region of 1400–400 cm^{-1} (not shown in this paper) indicates that all the samples have good crystallinity, taking into account the ratio of the intensity at 550/450 cm^{-1}, characteristic of MFI phase. For the In-containing zeolites, the spectra do not show any alteration from the mother samples, indicating that the indium species are not in framework positions. $NO/CH_4/O_2$ adsorption experiments with In-H-ZSM5 samples were carried out using a thermostatized cell with CaF_2 windows connected to a vacuum line, with a self-supported wafer.

2.3. Catalytic experiments

Steady state kinetic experiments were performed using a single-pass, diameter of 5 mm and 300 mm long, flow reactor made of fused silica operating at atmospheric pressure, catalyst sample load was 0.5 g. The reacting mixture was obtained by mixing four gas lines independently controlled with mass flow controllers, in order to obtain 1000 ppm of NO, 1000 ppm of CH_4 and 10% of oxygen, the balance in helium. The temperature ranged between 300 and 650 °C [19].

3. Results and discussion

3.1. *Adsorption of nitrogen monoxide*

Introduction of NO (760 torr) to the calcined In-ZSM-5 samples and subsequent evacuation (10^{-1} torr) is shown in figure 1. From FTIR spectrum of In-ZSM-5 at room temperature, the bands at 2000 and 1882 cm^{-1} are due to the zeolite overtone bands. The 1633 cm^{-1} band is likely due to the adsorbed H_2O (See figure 1(a, b and c)). NO was adsorbed on these catalysts at room temperature for 30 min followed by vacuum desorption. When NO was introduced to the samples, two strong peaks were observed at 1846 cm^{-1} (this band is close to the vibration frequency of gas-phase NO at 1880 cm^{-1}) and has been assigned to mononitrosyl species and other at cm^{-1} not assigned. After the NO-treated sample was desorbed, these bands (1750 and 1846 cm^{-1}) disappeared and three small peaks were observed. A 1622 cm^{-1} band can be assigned to adsorbed (ONO)-over InO^+ site and a 1575 cm^{-1} band to NO_2 over InO^+ site [16]. Other authors attribute the 1575 cm^{-1} band to NO_3^- [22]. The third band at 1680 cm^{-1} is probably due to the adsorbed nitrate species adsorbed on protonic sites. This suggests that NO molecules are weakly adsorbed and some of them were oxidized to NO_2 and nitrate species by the residual O_2 species that are weakly adsorbed on the catalyst. Moreover, figure 1 shows a shoulder at 1740 cm^{-1} due to N_2O_4, according to J. Szanyi *et al.* [23]. As can be seen, this band is very low, considering that it is attributed to N_2O_4 adsorbed onto Na/Me-MFI and not on H-Me-MFI [24].

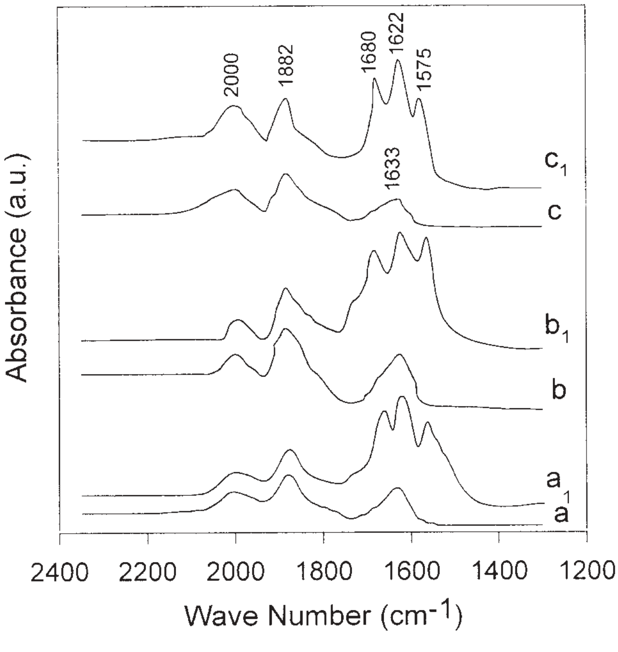

Figure 1. FTIR spectra of NO adsorbed (760 torr equilibrium pressure at 25 °C, after vacuum activation at 500 °C) on In-ZSM-5 (a: Si/Al = 17, b: Si/Al = 27, c: Si/Al = 50, calcinated samples, a_1, b_1 and c_1: NO chemisorbed).

Figure 2 shows the relative absorbance (referred to the 1882 cm^{-1} In-ZSM-5 overtone) versus desorption temperature. NO was adsorbed (760 torr) during 30 min and evacuated (10^{-1} torr) during 10 min. After the samples were heated, all the bands either decreased sharply or disappeared at 400 °C. The intensity of the band at 1680 cm^{-1} assigned above to NO_3^-–H^+, is much higher for the sample (a), (figure 2(a)) than the other samples. This is due to the biggest quantity of strong and medium Brönsted sites present in this sample. The NO_2–InO^+ or (ONO)–InO^+ adspecies (1575 and 1622 cm^{-1} bands respectively) is present in much higher extent in sample (a) than (b) and (c), figure 2(a), (b) and (c), according to the quantity of active sites of indium present in the different samples [19]. According to our experimental results, the NO_2 and NO_3^- adspecies showed a diminution when methane was introduced with NO. The bands assigned to these adspecies are even present at the reaction temperature, indicating that NO_2 and NO_3^- adspecies might play an important role in the SCR of NO_x over In-containing zeolite, in agreement with M. Ogura *et al.* [16].

3.2. *Coadsorption of nitrogen monoxide, methane and oxygen*

The coadsorption of NO, CH_4 and O_2 (10 torr of NO, 50 torr of CH_4, 10 torr of O_2 equilibrium pressure for 30 min, followed by a 15-min evacuation) in helium balance at ambient temperature on In-ZSM-5 gives rise to the appearance of three bands with maxima at 1680 cm^{-1} assigned above to NO_3^-–H^+, 1622 cm^{-1} assigned to NO_2–InO^+ or (ONO)–InO^+ and 1575 cm^{-1} assigned to NO_2–InO^+. Another band appears at 1635 cm^{-1} attributed to N_2O (this band is close to the vibration frequency of gas-phase N_2O). The spectra are shown in figure 3. The comparison between the intensities of the peaks for the different species adsorbed in the three samples at room temperature is illustrated in the figure 4(a). The band at 1622 cm^{-1} has a stronger intensity in sample (b). This specie is one of the most important intermediates in the CH_4-SCR process. The 1575 and 1680 cm^{-1} bands are more intense in samples (a) and (c) than in sample (b). Heating the samples in vacuum (10^{-1} torr) at 300 °C for 15 min (figure 5) indicated the disappearance of the band at 1680 cm^{-1}; the 1622-cm^{-1} band scarcely decreased at 300 °C and the 1575-cm^{-1} band decreased linearly for all the samples. At 300 °C, an appreciable

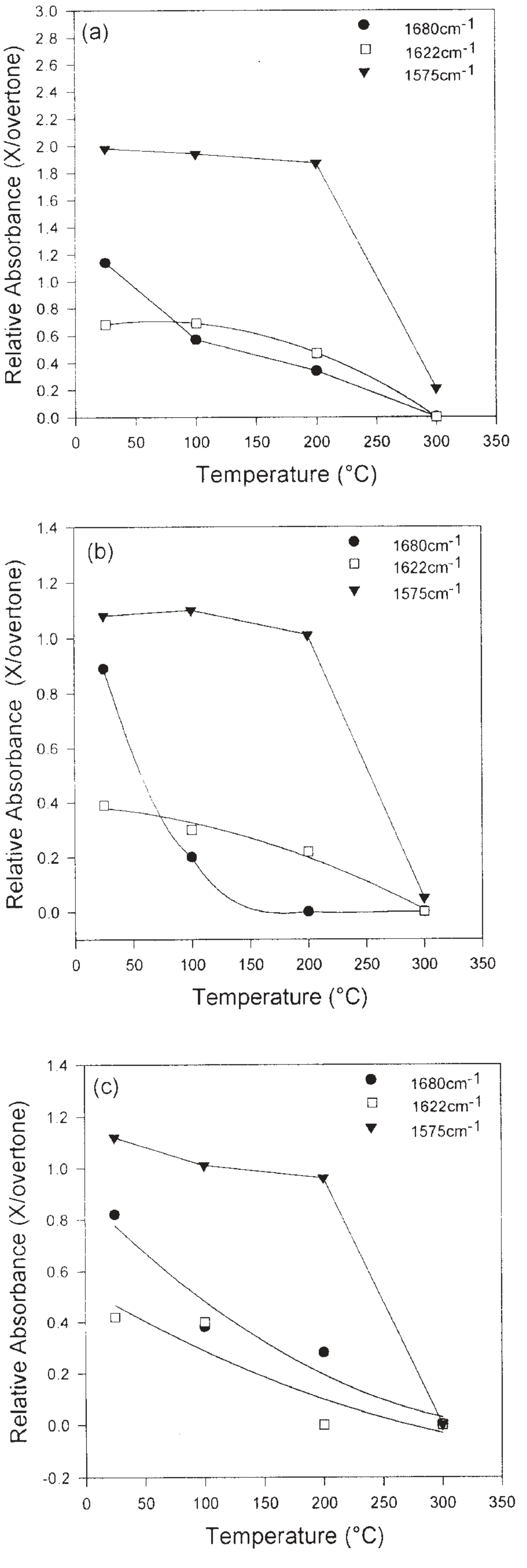

Figure 2. Relative absorbance of NO (760 torr) versus temperature for the three absorption bands. Catalyst: In-ZSM-5. (a) Si/Al = 17, (b) Si/Al = 27 and (c) Si/Al = 50.

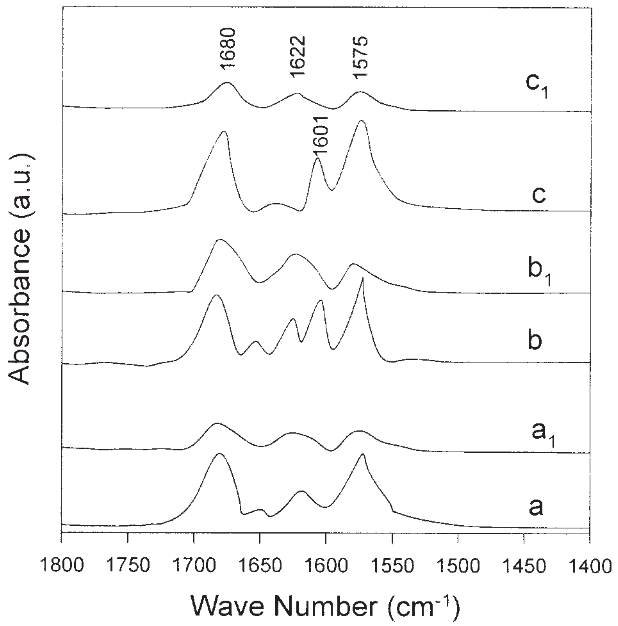

Figure 3. FTIR spectra of NO + CH_4 + O_2 adsorbed on In-ZSM-5, after vacuum activation at 500 °C. (a: Si/Al = 17, b: Si/Al = 27, c: Si/Al = 50, adsorbed at 25 °C and a_1, b_1 and c_1: adsorbed at 400 °C).

amount of this specie remained adsorbed. All the bands disappeared completely at 500 °C.

3.3. *Coadsorption of nitrogen monoxide, methane and oxygen at 400 °C*

The results of the coadsorption of NO, CH_4 and O_2 (10 torr of NO, 50 torr of CH_4, 10 torr of O_2 equilibrium pressure for 30 min, followed by a 15-min evacuation) in helium balance at 400 °C on In-ZSM-5 are shown in figure 4(b). We can observe that the higher intensity bands are present in sample (b) except the 1575 cm^{-1} band, so sample (b) has a higher amount of intermediate adspecies for SCR reaction. According to data of relative absorbance from the spectra at room temperature and at 400 °C (figure 4(a) and (b)), we can observe low-intensity bands for the spectrum at 400 °C in samples (a) and (c). In the case of sample (b), the intensities of the bands (1680 and 1622 cm^{-1}) are the same for both temperatures, except for the 1575 cm^{-1} band that is slightly lower at 400 °C. The catalytic activity for the NO reduction of In-loaded ZSM-5 catalyst with Si/Al ratios of 17, 27 and 50 (samples (a), (b) and (c) respectively) was previously studied by Anunziata *et al.* [19]. Among the samples studied, it can be seen that indium exchanged on NH_4-ZSM5 with Si/Al = 27 is the most active catalyst in NO_x conversion to N_2 and CH_4 conversion to CO_2. This fact is related to the special features of this sample compared with the other In-exchanged ZSM-5 zeolites with different Si/Al ratios (17 and 50). For sample (b), the active sites are

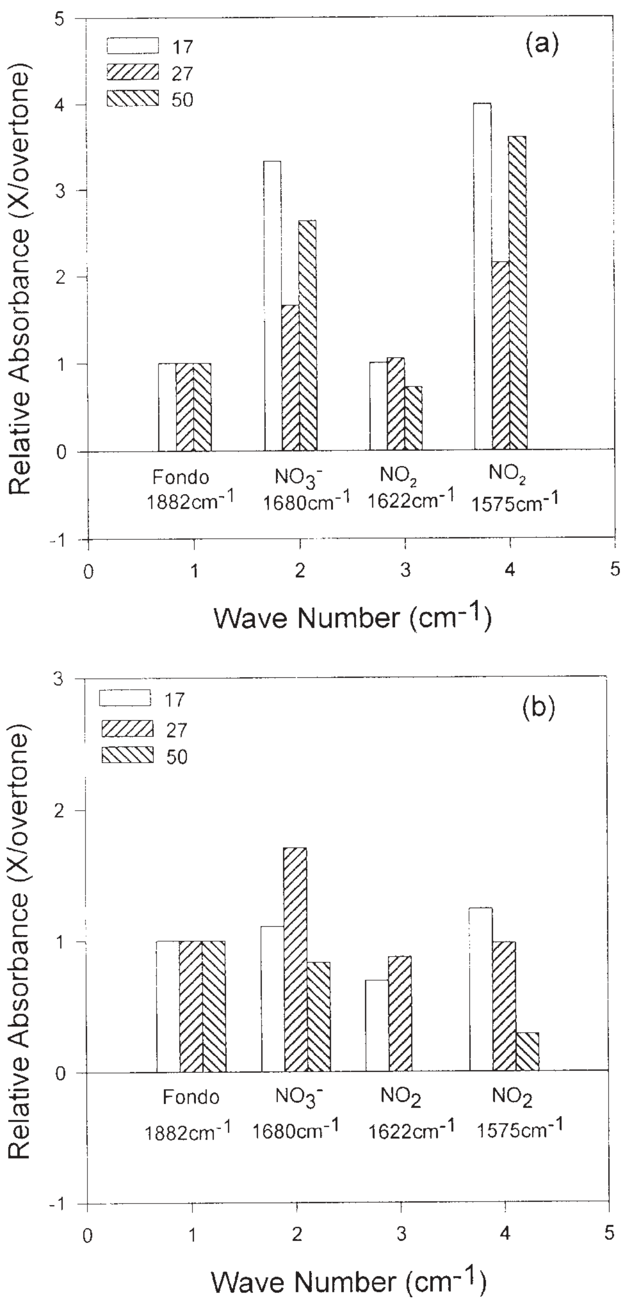

Figure 4. Coadsorption of $NO + CH_4 + O_2$ on In-ZSM-5: (a) $T = 25\,°C$, (b) $T = 400\,°C$.

capable of forming species with higher thermal stability; therefore, chemisorbed NO_x begin to reduce to N_2 at lower temperature. The conversion was 80 mol% at 500 °C for this sample in comparison with 30 mol% for the other samples at the same temperature.

Perturbed angular correlation experiments' (PAC) [19] results indicate, at least, the presence of three different hyperfine interaction associates with two different indium sites. Two of them have the same parameters of ^{111}In in In_2O_3 oxide [24] and constitute the 72, 58 and 49% of all the indium sites in the zeolites with Si/Al ratio of 17, 27 and 50 respectively. Slight differences with the pure In_2O_3 should be associated with the small dimensions of the crystallites present in the catalysts. A third minority interaction has a distributed EFG. Since the electric field gradient depends mainly on the local environment of the probe, this minority interaction can be attributed to the indium

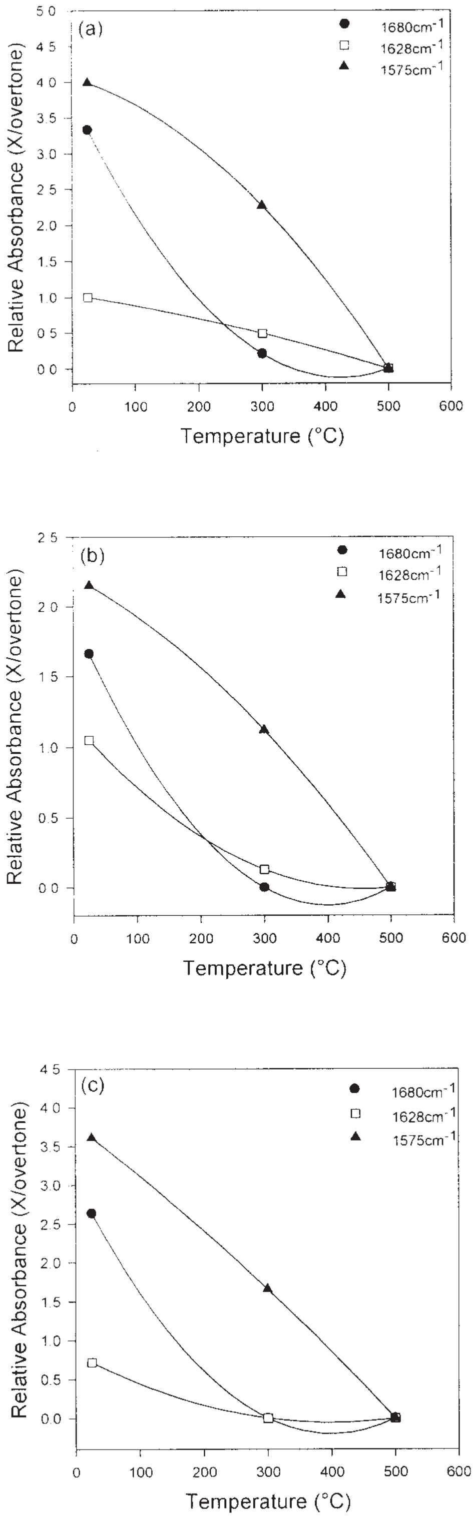

Figure 5. Relative absorbance of $NO + CH_4 + O_2$, versus temperature for the three absorption bands. Catalyst: In-ZSM-5: (a) Si/Al = 17, (b) Si/Al = 27 and (c) Si/Al = 50.

species with a short-range order. The indium species different form In_2O_3 present in samples with $Si/Al = 17$ and 50 are similar and both are different from that with $Si/Al = 27$. Taking into account the catalytic performance of the catalysts, this last indium specie, only present in the sample with $Si/Al = 27$, should be associated with the catalytic active specie for the SCR of NO_x.

According to temperature-programmed ammonium desorption (TPAD) and FTIR studies, indium is distributed inside zeolite channels, interacting with Brönsted acid sites. Indium ions, introduced in ZSM5 zeolites by ammonium exchange decrease the concentration of the strongest Brönsted sites by blocking negatively charged tetrahedral AlO_4 groups, producing new and stronger acceptor electron sites (Lewis sites). From the catalysts studied, the material with the highest activity for the SCR of NO with CH_4 is the In-H-ZSM5 with Si/Al ratio of 27, and coincidently this sample presents the highest Lewis-to-Brönsted-sites ratio.

On the other hand, In-H-ZSM5 with $Si/Al = 27$ shows the formation of a new, strong electron-donor-acceptor adduct (EDA) of Pyridine–Lewis sites at $1452\,cm^{-1}$, probably due to an In-unoccupied molecular orbital interaction with the probe molecule. This adduct is also observed in the other samples but to a much lower extent. This result strongly suggests that these EDA sites play a fundamental role in the selective reduction of NO_x in presence of CH_4 and O_2.

4. Conclusions

The results obtained in this work provide further evidence to support the conclusion that the activation of methane is initiated by NO_2 and NO_3^- chemisorbed species on InO^+ sites of the In-ZSM-5 zeolite. The remaining fraction of indium species (other than In_2O_3) may be associated with very highly dispersed phases. The indium local environment inhomogeneities are the lowest for $Si/Al = 27$ (the sample with the higher catalytic activity). Finally, it is concluded that In-active species for the SCR of NO with CH_4 are present, in major quantity in sample (b), in the form of very highly dispersed phases containing strong Lewis sites formed during the ionic exchange process.

Acknowledgments

Oscar A. Anunziata, Liliana B. Pierella and Andrea R. Beltramone are grateful to CONICET of Argentina for financial support of their research. The research was also partially supported by Agencia Córdoba Ciencia grant, PID/2001–2005.

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