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Catalysis Today 54 (1999) 553–558

CATALYSIS TODAY

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# In-containing H-ZSM5 zeolites with various Si/Al ratios for the NO SCR in the presence of $CH_4$ and $O_2$. PAC, TPAD and FTIR studies

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## Abstract

A series of In-loaded ZSM5 catalysts with Si/Al ratios of 17, 27 and 50 was studied. The catalytic activity for the NO reduction followed the $27 > 17 = 50$ order. The acid properties were investigated by FTIR of pyridine as probe molecule desorbed in vacuum at different temperatures and by Temperature-Programmed Ammonium Desorption (TPAD) of $NH_4$–In–ZSM5. The nature of the In-species was determined by the Perturbed Angular Correlation (PAC) technique using $^{111}$In as a probe. The contribution of indium to the acidity nature of the samples seems to be important taking into account that the number of Brönsted acid sites was reduced after the In exchange. In the same way new and strong electron-donor acceptor sites were generated. The PAC results indicate that there exists an important fraction of the indium present in the active sample coordinated as in the $In_2O_3$ case, while another one corresponding to a non-well defined near-In-neighborhood, is present too in a small fraction. ©1999 Elsevier Science B.V. All rights reserved.

*Keywords:* FTIR; TPAD; PAC

## 1. Introduction

The use of $CH_4$ as a substitute for $NH_3$ in the removal of nitrogen oxides from oxygen rich streams has become of particular interest. Since Li and Armor [1] reported that Co-ZSM5 is an effective catalyst for this reaction, a great variety of materials have been studied [2] with the same purpose. The results obtained so far suggest that the most effective catalyst is Co-ferrierite, among other Co-zeolites [2,3]. The same authors concluded that the added effectiveness of Co-ferrierite over Co-ZSM5 should be associated with the availability of more sites for the $NO_x$ reduction which must be related to the difference in topology between these two classes of zeolites [4]. Ga-H-ZSM5 and In-H-ZSM5 [5] have also been reported as effective catalysts, being more reactive and selective than Co-ZSM5 under a dry atmosphere over 500°C. Loughram and Resasco [6], concluded that both metallic and acid sites are necessary to achieve high catalytic activity through a two-step bifunctional mechanism. Kintaichi et al. [7], Hamada et al. [8] and Satsuma et al. [9], using different hydrocarbons as $NO_x$ reducing agents in the presence of excess oxygen over several catalysts, also claimed a dependence of the catalytic behavior on the acidic properties of the solids.

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PII: S0920-5861(99)00217-5

The present work has been aimed at better defining the role of the Indium structure and the acid properties of In-H-ZSM5 in the reaction under study. To attain this goal, we performed TPAD, FTIR and PAC studies on a series of In-H-ZSM5 with different Si/Al ratios. With the same purpose, we correlated the kinetic behavior of these samples with the surface characterization results.

## 2. Experimental

### 2.1. Sample preparation

Three ZSM5 zeolites with Si/Al = 17, 27 and 50 were obtained by hydrothermal synthesis using tetrapropil ammonium hydroxide (TPA) as template [10]. The ammonium form of the catalyst was prepared by ion exchange with ammonium chloride 1M at 80°C for 40 h. In-H-ZSM5 samples were prepared using $NH_4$-ZSM5 zeolites by ion exchange with $InCl_3$ followed by calcination in air at 500°C during 10 h.

In all samples the quantity of In introduced (in atoms) was two times the number of Al atoms in the zeolite. The remaining In in the zeolite after the ion-exchange was estimated from the intensity on $^{111}$In-radioactive probes in the samples. We found the following values: 2.5(3), 1.5(2) and 1.6(2)% w/w for Si/Al = 17, 27 and 50, respectively. However, the relevant values of In-concentration should be considered from In-species different from $In_2O_3$ determined in the present work (see Section 3.2 and Table 2).

### 2.2. TPAD studies

Temperature Programmed Desorption data of ammonium for $NH_4$-Zeolites were collected with an INSTRELEC programmer, which admits to change the heat slope during the run. The slope was 10–20°C/min and a nitrogen flow of 20 ml/min was used. The desorbed products were analyzed using an FID detector.

### 2.3. FTIR studies

Infrared analysis of H-Zeolites and In-H-Zeolites were performed on a JASCO 5300 spectrometer in the lattice vibration region using KBr 0.05% wafer technique. Pyridine adsorption experiments with In-H-ZSM5 samples were carried out using a thermostaticized cell with $CaF_2$ windows connected to a vacuum line, with a self-supported wafer.

### 2.4. Catalytic experiments

Steady-state kinetic experiments were performed using a single-pass flow reactor made of fused silica with an inside diameter of 5 mm and 300 mm long operating at atmospheric pressure, loaded with 0.5 g of catalyst. 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, balance in helium. Temperature ranged between 300 and 650°C.

### 2.5. Perturbed angular correlation (PAC) technique

The time differential observation of the perturbed angular correlation of gamma-rays emitted from radioactive $^{111}$In allows us to characterize different In species by means of hyperfine interactions. The principle of the application of PAC to In compounds consists in determining the hyperfine interaction between the nuclear quadrupole moment and the electric field gradient (EFG) produced by all extranuclear charges.

The method relies on the fact that, due to the conservation of angular momentum, the direction of emission of a particle (photon) in a nuclear decay is strictly correlated with the orientation of the nuclear spin. Since nuclear spins are normally randomly oriented, ‘interaction’ on the spatial correlation is lost. However, if an angular correlation with the direction of first emission of the cascade is performed, an anisotropy pattern is obtained. This angular correlation can be perturbed via the interaction of nuclear moments with extranuclear fields, provided the nucleus remains in the intermediate excited state for a sufficient long time.

A perturbation of the angular correlation can be reach with electric fields gradients. 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. Inequivalent probe sites in the unit cell or inequivalent sites due to the coexistence of several phases in the sample lead to a superimposing of 'perturbation functions' ($A_{22}G_{22}(t)$ in Fig. 4), which are fitted in order to obtain characteristic parameters for each probe site.

When a set of probes have very similar near-neighborhoods, a finite frequency distribution around a mean 'precession frequency' due to inhomogeneities can be obtained. If the EFG tensor deviates from axial symmetry, then the intensities and precession frequencies ($\omega_Q$) are also function of the asymmetry parameter ($\eta$). These 'inhomogeneities' can be produced by $^{111}$In-probes located in very small crystallites.

## 3. Results and discussion

### 3.1. Reaction experiments

Reaction results are depicted in Fig. 1a ($NO_x$ conversion to $N_2$) and Fig. 1b ($CH_4$ conversion). Among the samples studied, it can be seen that In exchanged on $NH_4$-ZSM5 with Si/Al = 27 is the most active catalyst in both cases. 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).

With respect to the decrease of NO conversion above 550°C, it is generally accepted that $NO_x$ conversion has a maximum with temperature due to two factors: the $CH_4$ consumption due to deep oxidation with oxygen and/or the shift to the left of $NO + 1/2\ O_2 = NO_2$ equilibrium at high temperatures.

An important issue to be addressed is the water tolerance of In-H-ZSM5 catalysts. It is known [11,12] that water has two negative effects on the activity of zeolitic catalysts during the $NO_x$ SCR reaction: a reversible poisoning effect, which takes place under reaction conditions at relatively low temperatures (300–450°C); and an irreversible effect, due to hydrothermal dealumination at higher temperatures. For In-H-ZSM5 catalysts, the first effect is mainly due to the coordination of water molecules to zeolite Lewis acid sites, which strongly inhibit the $NO_2$ formation step [11].

On the other hand, as far as we know there are no literature data on hydrothermal dealumination on In-H-ZSM5 catalysts. It would be expected that the higher the Si/Al ratio of the catalyst, the stronger the hydrothermal stability. Previous results, however, show that is not the case for H-mordenite catalysts, since solids having 5.9; 7.3; 11.0 and 16.9 Si/Al ratios show similar activity decay after 2 h of hydrothermal treatments at 650°C [12].

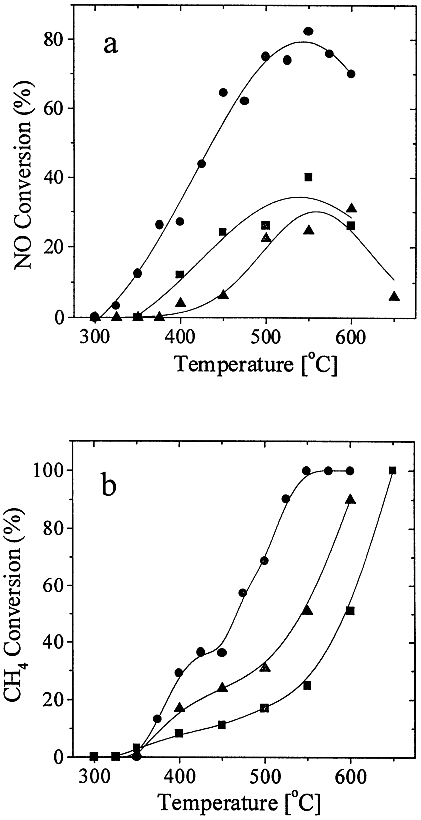

Fig. 1. NO (a) and $CH_4$ (b) conversion on In-H-ZSM5 (0.25 g) with Si/Al ratio 17 (■), 27 (●) and 50 (▲). $CH_4$: 1000 ppm, NO: 1000 ppm, $O_2$: 10%. Total flow rate: 100 $cm^3\ min^{-1}$.

The following TPAD, FTIR and PAC characterizations are helpful to study the different In species present in these catalysts, the interactions with the zeolitic structure, and their role in the reaction under study.

### 3.2. TPAD and FTIR studies

Temperature-Programmed Ammonium Desorption (TPAD) experiments, and FTIR of pyridine desorbed under vacuum at different temperatures were performed in order to study the acidic properties of the parent samples and the effect of In exchange on the

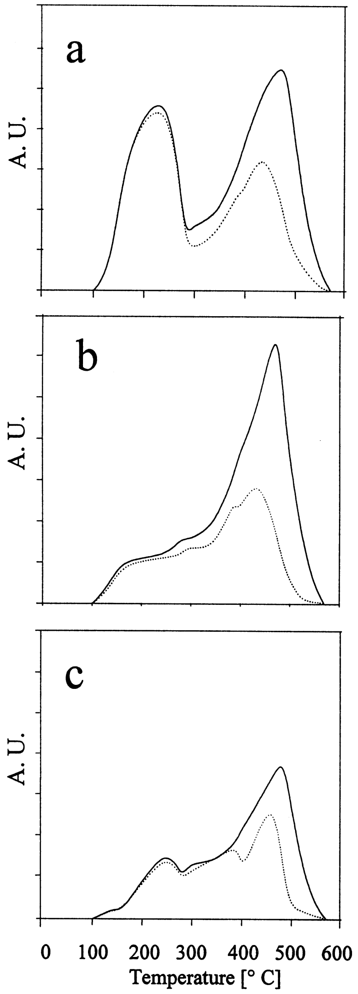

Fig. 2. Temperature programmed ammonia desorption from $NH_4$-ZSM5 (solid lines) and In-$NH_4$-ZSM5 zeolites (dotted lines), with Si/Al ratio (a) 17, (b) 27 and (c) 50.

nature and strength of the acid sites. Fig. 2 shows TPAD spectra of the three parent samples ($NH_4$-ZSM5 with Si/Al = 17, 27 and 50) as compared with the same materials after In exchange. The parent sample with Si/Al = 17 shows two stages of ammonia desorption (Fig. 2a), the first at ca. 200°C (l-peak) and the second at c.a. 500°C (h-peak). It is known from the literature that the h-peak corresponds to the interaction of ammonia with strong Brönsted acidic sites. The other parent samples show mainly the h-peak (Fig. 2b,c).

TDPAD of In-exchanged samples indicates that the ionic exchange is incomplete, since the h-peak is still present in these samples, being however smaller and shifted to lower temperatures. The spectra shapes are similar to those of the parent samples. The observed temperature shift indicates that In ions were incorporated as counter ion blocking preferentially the stronger Brönsted acid sites, the remaining protons having weak or medium acidic strength. The exchanged In species generate new and strong acceptor electron sites, as indicated by the FTIR results shown below.

Table 1
Ratio of Brönsted to Lewis sites (B/L), calculated from the FTIR spectra after Pyridine desorption at 250°C, 350°C and 400°C of the H- zeolites and InH-zeolites.

| Py mmol $g^{-1}$ ratio | H-ZSM5 | | | In-H-ZSM5 | | |
|---|---|---|---|---|---|---|
| | B/L | | | B/L | | |
| Temp. Desorp.,°C | 250 | 350 | 400 | 250 | 350 | 400 |
| Ratio Si/Al | | | | | | |
| 17 | 50.4 | 16.6 | 8.6 | 4.7 | 5.14 | 3.14 |
| 27 | 31.9 | 25.0 | 22.2 | 1.2 | 1.44 | 1.01 |
| 50 | 32.8 | 5.5 | 4.3 | 5.4 | 3.86 | 2.52 |

According the IR studies, an absorption band for OH-groups (Si-OH) with maximum at 3740 $cm^{-1}$ was observed for H- and In-H- containing zeolites, whereas the band at 3610 (bridging OH- groups) is present in H-Z. The introduction of In species decreases the intensity of the band at 3610 $cm^{-1}$. The number of Lewis sites increases as Brönsted sites decrease upon the introduction of In as we report in Table 1.

Taking into account our TPAD experiments, perhaps the IR data of pyridine desorbed at different temperatures, was comparable with $NH_3$-TPD obtained by Choi et al [13]. In this way, In-containing zeolite showed more pyridine retained at high temperature (by interaction with Lewis sites) than H-zeolites, in correspondence with the increasing Cu content and increasing h-peak for ammonia desorption in TPD analysis reported by Choi [13].

Fig. 3 shows FTIR spectra of Pyridine adsorbed at room temperature and 3 Torr and desorbed at 400°C and $10^{-4}$ Torr for H-Zeolites [10] (Fig. 3a) and In-H-Zeolites (Fig. 3b), respectively. In all of the In-exchanged samples it can be observed the presence of both Brönsted and Lewis sites. In Table 1 the ratio of Brönsted to Lewis sites (B/L), calculated from the FTIR spectra after Pyridine desorption at 250°C, 350°C and 400°C, are summarized. It can be seen that this ratio is smaller for the In-exchanged samples

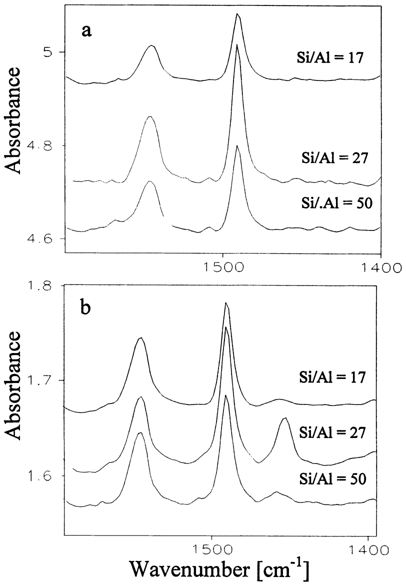

Fig. 3. (a) FTIR spectra of Pyridine adsorbed at room temperature and 3 Torr and desorbed at 400°C and $10^{-4}$ Torr for H-ZSM5 with Si/Al ratio 17, 27 and 50. (b) FTIR spectra of Pyridine adsorbed at room temperature and 3 Torr and desorbed at 400°C and $10^{-4}$ Torr for In-H-ZSM5 with Si/Al ratio 17, 27 and 50.

compared with the parent zeolites. 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 $\mathrm{cm}^{-1}$, 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 $NO_x$.

It must be pointed out here that the FTIR of In-H-ZSM5 zeolites in the finger-print zone of the MFI material (400–1200 $\mathrm{cm}^{-1}$) does not show evidence of $In_2O_3$ species. However, the results obtained by PAC characterization (see below) clearly indicate the presence of small crystals of the oxide, neither detected by FTIR nor by XRD.

### 3.3. Perturbed angular correlation experiments

The PAC experiments were performed in order to determine the number and concentration of inequivalent In-sites at the same temperature in which the catalysts exhibit the maximum activity. All spectra indicate, at least, the presence of three different hyperfine interaction associates with two different In sites. Two of them (HI1 and HI2 in Table 2) have the same parameters of $^{111}$In in $In_2O_3$ oxide [14] and constitute the 72, 58 and 49 % of all the In-sites in the zeolites with Si/Al ratio of 17, 27 and 50 respectively. Slight differences with the pure $In_2O_3$ case 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 In-species with a short-range order. The In-species different form $In_2O_3$ present in samples with Si/Al = 17 and 50 are similar and both different from that with Si/Al = 27 (see Table 2). Taking into account the catalytic performance of the catalysts (Fig. 1a), this last In-specie, only present in the sample with Si/Al = 27, should be associated with the catalytic active specie for the SCR of $NO_x$.

Table 2
Hyperfine fitted parameters of PAC spectra of In-H-ZSM5 samples

| Ratio Si/Al | In-site | Population $f$ (%) | Frequency $\omega_Q$ (Mrad $s^{-1}$) | Assimetry $\eta$ | Distribution (%) |
|---|---|---|---|---|---|
| | HI1-$In_2O_3$ | 30 (12) | 27.5 (3) | 0 | 7 (2) |
| 17 | HI2-$In_2O_3$ | 42 (9) | 19.5(3) | 1 | 13(3) |
| | | 28 (12) | 41 (1) | 0.3 (1) | 10 (5) |
| | HI1-$In_2O_3$ | 17 (3) | 24.5 (2) | 0.13 (4) | 1.5 (1) |
| 27 | HI2-$In_2O_3$ | 41 (8) | 19.0 (1) | 0.69 (1) | 2.6 (1) |
| | | 42 (4) | 28.4 (4) | 0.27 (3) | 8 (1) |
| | HI1-$In_2O_3$ | 18 (2) | 24.7 (1) | 0.22 (2) | 2 (1) |
| 50 | HI2-$In_2O_3$ | 31 (4) | 19.3 (3) | 0.77 (2) | 8 (2) |
| | | 51 (3) | 44 (1) | 0.56 (2) | 12 (2) |
| Pure $In_2O_3$ [14] | HI1-$In_2O_3$ | 20 (3) | 24.0 (5) | 0.22 (2) | 1 (1) |
| | HI2-$In_2O_3$ | 74 (3) | 17.9 (5) | 0.74 (1) | 4 (1) |

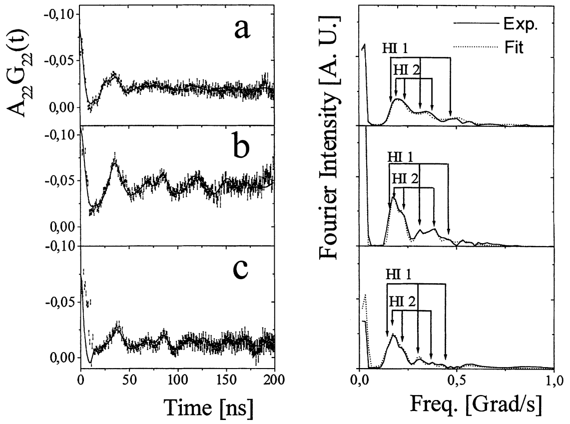

Fig. 4. PAC (left) and Fourier (right) spectra of In-H-ZSM5 samples measured at 500°C: (a) Si/Al = 17; (b) Si/Al = 27; (c) Si/Al = 50.

## 4. Conclusions

The synthesized ZSM5 zeolites have two distinguishable exchange sites; one of them is associated with slightly bonded ammonium, while the other is associated with strongly bonded ammonium. The concentration of these sites depends on the Si/Al ratios of the samples. Indium mainly interacts with the stronger bonded ones, especially in the case of Si/Al = 27.

According to TPAD and FTIR studies, indium is distributed inside zeolite channels, interacting with Brönsted acid sites. In 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, stronger Lewis sites. Of all 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.

After calcination at 500°C, PAC results reveal the presence of small $In_2O_3$ crystals, even when they are neither detected by FTIR nor by XRD. Taking into account the sensitivity of the electric field gradient with distance, the crystal size should be smaller than 5 nm. The crystallites are highly dispersed on the three InH-ZSM5 studied, and their relative concentration is 72, 58 and 49% (on total In basis) for ZSM5 zeolites with Si/Al ratio of 17, 27 and 50, respectively Fig. 4.

The remaining fraction of In-species (other than $In_2O_3$) may be associated with very highly dispersed phases. The indium local environment inhomogeneities is 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 the form of very highly dispersed phases containing strong Lewis sites formed during the ionic exchange process. Also, the ability of the PAC technique in characterizing and quantifying very highly dispersed phases is demonstrated.

## Acknowledgements

This work was partially supported by Fundación Antorchas, and CICpBA, Argentina and the Third World Academy of Sciences (TWAS) under grant RGA No. 97-057, Italy. Thanks are also given to CONICET, CONICOR and to Universidad Nacional del Litoral CAI+D program for their partial support.

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