In,Fe-zeolites: Active and stable catalysts for the SCR of NO$_x$—Kinetics, characterization and deactivation studies

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Abstract

In this work, the addition of Fe_2O_3 to InH-zeolites (ZSM5 and mordenite) is investigated for the selective catalytic reduction of NO$_x$ with both methane and butane as reducing agents. When Fe is added to InHMOR and methane is used, the NO$_x$ to N_2 conversion increases from 25% to 55% at 20,000 h^{-1} and 500 °C. An increase is also observed when butane is employed but to a lower extent. The role of Fe could be ascribed to an improvement of the NO to NO_2 reaction rate. The presence of iron oxides also improves durability in the presence of 2% water. The catalyst InFeHMOR undergoes a fast initial inhibition after which a reasonable NO$_x$ conversion (25%) remains constant during 125 h. TPR, XRD and LRS characterizations indicate that Fe_2O_3 and Fe_3O_4 are the iron species present, while InO^+ at exchange sites and small amounts of In_2O_3 are also present. The kinetic plots for the NO$_x$ selective catalytic reduction (SCR) with methane with the InFeHMOR catalyst show fractional orders for the NO concentration and ca. first order for methane.

1. Introduction

Catalysts based on metal-zeolites have been widely studied as candidates for the abatement of nitrogen oxide emissions. The selective catalytic reduction (SCR) of NO$_x$ with hydrocarbons is an alternative way to replace the technology that uses ammonia as reductant.

Particularly, there has been much effort to develop active and selective catalysts for the selective catalytic reduction of NO$_x$ with methane in the presence of excess oxygen, water vapor and SO$_2$. Only a few elements such as Co, Pd, Ga and In either supported or exchanged in zeolites are able to activate the relatively stable methane molecule [1–3]. However, the activity of these catalysts is drastically diminished in the presence of water vapor in concentrations of practical relevance. In order to improve the water tolerance, the addition of a noble metal (Pt, Rh, and Ir) to InHZSM5 results in a more resistant catalyst [4,5]. Montes and co-workers [6] found a similar effect in PdCo-zeolites. In our group, satisfactory results were achieved by incorporating Pt on Co- or In-exchanged zeolites [7–9].

On the other hand, Fe-zeolites have been extensively studied proving to be active and stable catalysts when isobutane is used as a reducing agent [10]. According to Requejo et al. [11] Fe^{2+} and Fe^{3+} cations and Fe_2O_3 clusters are the species involved in the said reaction when FeHZSM5 is the catalyst used. Likewise, it has been found that solids based on Cu-, Ce- or Fe-exchanged zeolites are active only when hydrocarbons with two carbons or more (C2+) are used as reduction agents [12]. Most catalysts lose their activity in an excess of water vapor, and only a few catalysts based on Fe are active and stable to SCR in the presence of water vapor.

Wang et al. [13] found that the direct incorporation of iron oxide to InHZSM5 improved the activity and durability of the catalyst, even in the presence of water vapor. In a similar way, Sowade and co-workers [14,15] have recently reported that CeO_2 promotes the In-ZSM5 activity and the resistance to water deactivation. They observed that In-ZSM5 catalysts with different active site structures exhibit different responses to promotion by ceria. The most intense promotional effects were found with sites that catalyze unselective methane oxidation in the absence of CeO_2 (intrazeolite InO_xCl_y species, extrazeolite

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In_2O_3 aggregates, probably active at the border with the zeolite). This is at variance with respect to intrazeolite indium oxo species, which are often considered as the most important active sites in In-ZSM5 SCR catalysts but which are not so upon promotion with CeO_2.

The present work reports results obtained from the addition of Fe to the InH-zeolite. It analyzes the catalytic behavior of bimetallic samples prepared on two different zeolitic supports (HZSM5 and HMOR), using methane or butane as reducing agent. The catalysts stability is also studied in the presence of steam. The nature of the species present in the monometallic and bimetallic samples and their relation with the catalytic activity is studied by means of different techniques such as temperature-programmed reduction (TPR), X-ray diffraction (XRD) and Raman spectroscopy (LRS). A kinetic study is also performed to determine reaction rate order and kinetic constants, together with a simulation of the reaction behavior at different space velocities.

2. Experimental

2.1. Catalysts preparation

InHMOR and FeHMOR were prepared by ion exchange of a commercial mordenite, NH_4MOR (Zeolyst CBV-21A, Si/Al = 10), with solutions of indium and iron, respectively. In order to prepare FeHMOR, zeolite powder (2 g) was ion exchanged in 300 ml of a 0.01-M $Fe(NO_3)_3$ solution. The mixture was stirred for 24 h at room temperature and afterwards it was filtered several times, washed and dried at 120 °C for 8 h. The InHMOR sample was prepared by ion exchange using 70 ml of a 0.05-M $In(NO_3)_3$ solution.

The InFeHZSM5 and InFeHMOR bimetallic catalysts were prepared from a mechanical mixture of 2 g of zeolite with 0.16 g of Fe_2O_3 in an agate mortar and then, 15 ml of a 0.04-M $In(NO_3)_3$ solution were added. The slurry was stirred at 80 °C upto the complete evaporation of water. FeHMOR was calcined at 450 °C while the samples containing indium were calcined at 700 °C to complete the exchange [13].

2.2. Catalytic activity measurement

The activity was measured in a fixed-bed quartz reactor. The concentrations were analyzed by an on-line gas chromatograph equipped with a column filled with 5 A zeolite. So as to analyze the concentrations of O_2, N_2 and CH_4. The reaction conditions were similar to those found in the gaseous effluents of combustion: 1000 ppm of NO, 1000 ppm of CH_4 or 125 ppm of C_4H_{10}, 2% of O_2 in He and GHSV = 20,000 h^{-1}. The more active catalysts were tested in the presence of 2% of water in the feed. In order to test the stability, the InFeHMOR catalyst was monitored during 125 h of time-on-stream under wet conditions at 500 °C.

2.3. Determination of the kinetic parameters

The kinetic study was carried out in a flow reactor, which was the same one used in the catalytic activity evaluation.

InFeHMOR was used because it was the catalyst with the greatest activity, selectivity and water resistance. The temperature range selected was between 300–350 °C under dry conditions and 400–450 °C when water was also fed, in order to have conversions lower than 10%. The CH_4 and NO concentrations were varied between 500 ppm and 2000 ppm, and the O_2 concentration was maintained at 2%. The NO reduction and the methane oxidation rates were determined under differential conditions whose conversions did not have to exceed 10% [16].

The following power rate law equations are proposed:

$$r_{NO} = k_1' p_{NO}^a p_{CH_4}^b \quad \text{reduction rates of NO,} \quad \text{where } k_1' = k_1 p_{O_2}^e \tag{1}$$

$$r_{CH_4} = k_2' p_{NO}^c p_{CH_4}^d \quad \text{oxidation rate of } CH_4, \quad \text{where } k_2' = k_2 p_{O_2}^f \tag{2}$$

It is necessary to point out that the oxygen concentration is included in k' because it is in excess. The calculated kinetic parameters were used to simulate NO_x and CH_4 conversions at different spatial velocities.

2.4. Temperature-programmed reduction experiments

The characterization was carried out using an 5% H_2 in Ar stream. The heating ramp was 10 °C/min from 25 °C to 900 °C for all the samples. Before the reduction, the samples were calcined in air at 500 °C.

2.5. X-ray diffraction

The X-ray diffraction measures were taken using a XD-D1 model Shimadzu diffractometer operated with Cu Kα radiation at 30 kV and 40 mA, using a scanning rate of 1° min^{-1}. The database employed was the one provided by the manufacturer.

2.6. Raman spectroscopy

The spectra were obtained with a TRS-600-SZP Jasco Laser Raman instrument equipped with charged-coupled device (CCD) with a detector cooled at 153 K using liquid nitrogen. The power of the laser was 30 mW.

3. Results and discussion

3.1. Catalytic activity evaluation

Fig. 1A and B shows the catalytic behavior of the monometallic samples, Fe and In exchanged on the NH_4MOR zeolite. The NO to N_2 conversion was evaluated using methane or butane as a reducing agent; the CH_4 conversion was included in the figure.

The FeHMOR catalyst was active but unselective, as much with C_4H_{10} as with CH_4, the conversion to N_2 being less than 12% (Fig. 1A). Sachtler and co-workers [10] found similar results when they studied the behavior of Fe in different zeolitic
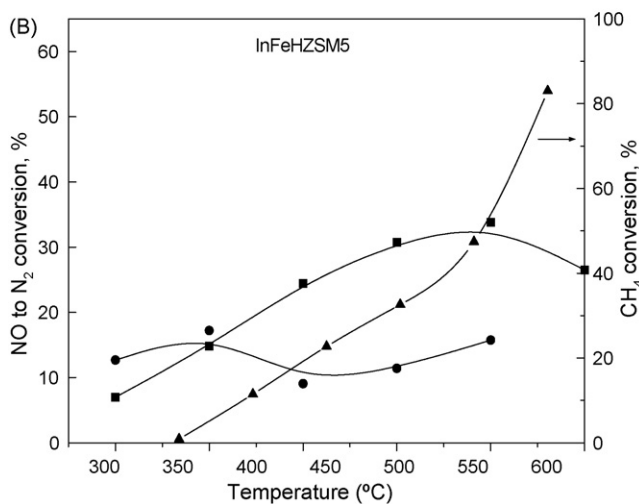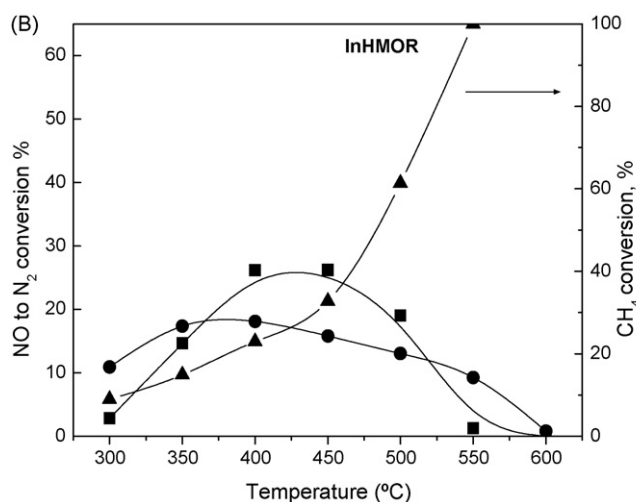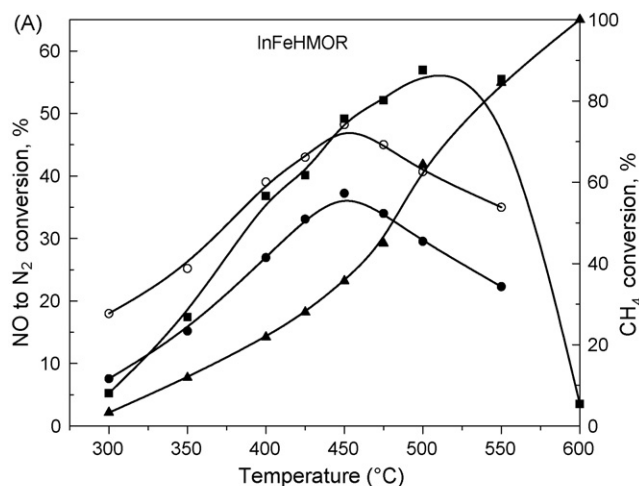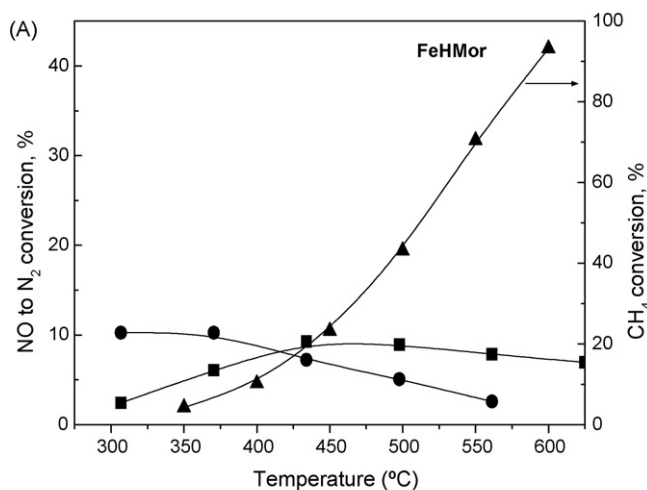
Fig. 1. Catalytic behavior in HC-SCR of NO_x. NO to N_2 conversion with CH_4 (■), C_4H_{10} (●), CH_4 conversion (▲), reaction conditions: 1000 ppm NO, 1000 ppm CH_4, 125 ppm C_4H_{10}, 2% O_2 in He, GHSV = 20,000 h^{-1}.

Fig. 2. Selective catalytic reduction of NO_x with HC. Conversion of NO to N_2 with CH_4 (■), C_4H_{10} (●), CH_4 conversion (▲), reaction conditions: same as in Fig. 1.

supports. With FeHMOR, they observed that the conversion to N_2 was less than 10%, a very low value with respect to the one reached with Fe-MFI, in which the conversion to N_2 was 76% using isobutane as reducing agent.

In the InHMOR catalyst (Fig. 1B), the conversion from NO_x to N_2 was 25% with CH_4 and 18% when C_4H_{10} was used as a reductant.

The InFeHMOR bimetallic sample (Fig. 2A) shows an increase in the reducing activity compared with the mono-metallic InHMOR catalyst. The maximum NO to N_2 conversion was 57% at 500 °C corresponding to 67% methane conversion. When the butane was used as a reductant, the maximum conversion to N_2 was 37% and 48% using a carbon-to-nitrogen molar ratio of 0.5 and 1.0, respectively (Fig. 2A).

According to the literature, indium is attached to zeolite cation sites as InO^+ species, which can be introduced via aqueous ion exchanged [15]. An accepted reaction mechanism for the SCR of NO_x by methane with In catalysts proposes one first step, in which NO is oxidized to NO_2 on Brönsted acid sites and/or In_2O_3 clusters, followed by the reaction of NO_2 and CH_4 on InO^+ active sites. The incorporation of Fe_2O_3 to

InHMOR can promote NO oxidation thus improving N_2 production. Wang et al. [13] found almost 100% NO conversion at 500 °C in the In–Fe_2O_3/H-ZSM5 catalyst, but using a low spatial velocity of 3600 h^{-1}. In a similar way, Berndt et al. [14] added 8 wt% Ce_2O_3 to InHMOR and improved the N_2 conversion from 30% (4InMOR) to 80% (8Ce4InMOR) at 24,000 h^{-1}.

On the other hand, butane was a worse reducing agent than methane, both in the InMOR sample as in InFeMOR (Fig. 1B and Fig. 2A). Butane is a molecule less stable than methane against oxidation and its greater size hinders its access to the InO^+ active sites inside the zeolite structure. In addition, the presence of Fe_2O_3 on the zeolite surface favors the oxidation of butane impairing the reduction of NO_x.

The reducing activity was influenced by the support, because the InFeHZSM5 sample, prepared with NH_4ZSM5 (Fig. 2B), showed a maximum conversion to N_2 of 30% with methane and less than 20% with butane. Berndt et al. [14] using MFI as support and optimizing the incorporation of indium, achieved a catalyst (2Ce2InHMFI) reaching a 65% NO conversion to N_2 under wet conditions.

The effect of adding 2% water in the feed was evaluated on InHMOR and InFeHMOR catalysts using methane as reducing agent (Fig. 3A and B). While the deactivation suffered by InHMOR was severe (the conversion of NO in the presence of H_2O decreased to 5%), the InFe sample was only partially deactivated showing a maximum conversion to N_2 of 30% at 550 °C.

In addition, the hydrothermal stability of the InFeHMOR catalyst has been studied under wet reaction conditions. The constant temperature NO reduction test was made at 500 °C. The incorporation of 2% water to the feed stream caused an initial fast decay of CH_4 and NO conversions due to the adsorption of water on the InO^+ active sites. But the NO conversion value reached around 23% conversion remained constant for 70 h. When the concentration of water was increased to 10%, the NO to N_2 conversion was progressively decreased to less than 5% and the activity did not recover after removing the water. Berndt et al. [14] with their 8Ce13InHMFI catalyst reported a residual NO_x conversion of 50% after 160 hs

but using wet air (10% H_2O at 500 °C) ageing, not under reaction conditions.

3.2. Kinetic study

The reaction orders were obtained by varying the concentration of one of the reactants while maintaining the others constant at 325 °C.

Fig. 4 shows linear regressions for the order reaction calculations. From Fig. 4A and B the reaction orders and the k' kinetic constants are obtained. The reaction orders are in line with those previously obtained for the H-Mordenite [16] and InZSM5 [17] catalysts.

When water (2%) was added to the feed, the reaction order for the NO concentration with respect to the NO reaction rate increased from 0.62 to 0.96 (Fig. 4C). This result seems to be originated in the effect of water reported in the literature [17], which is the inhibition of NO_x adsorption through the competition of H_2O and NO_x for the same adsorption sites.

The reaction orders indicated above are also in agreement with those reported by Sowade et al. [18] under similar reaction conditions, for their Ce/In-ZSM5 catalyst, except for the CH_4 order with respect to the NO reduction rate. While they obtained an order of 0.35, our value is ca. 1.2. Most probably the different nature of the catalysts affects the reaction steps in which CH_4 is involved.

Table 1 presents the data found for each one of the empirical reaction orders as well as the reaction constants for the NO reduction rate and the CH_4 oxidation rate. It is important to point out that in the case of added water, only the orders for NO were obtained. Comparing orders *a* and *c*, it can preliminarily be said that the water added in the feed has an effect on both the NO reduction mechanism and the CH_4 oxidation mechanism.

Fig. 4D depicts simulation results in which the calculated kinetic constants are used. As seen, the NO_x conversion increases upto ca. 65%, reaching a constant value. It can also be seen that further increases in the W/F ratio do not result in increases in the NO_x conversion, because methane is no longer available.

3.3. Catalysts characterization

The concentration of Fe in FeNH$_4$MOR was determined using atomic absorption analysis, and the approximate concentration of In on InNH$_4$MOR was obtained by EDAX. These values are shown in Table 2.

The profiles obtained with TPR are shown in Fig. 5. The maximum temperatures and the consumption of H_2 calculated from the thermogram are presented in Table 2. In the calcined FeHMOR sample (Fig. 5A profile a) a small peak at 74 °C is observed which is probably due to the reduction of absorbed species on the surface (e.g. O_2 adsorbed species). Two strong peaks at 240 °C and 326 °C can be assigned to the reduction of Fe^{3+} to Fe^{2+} (cations and/or oxocations) at different sites in the framework. The H_2/Fe ratio for this region is 0.52, which would indicate that all the iron is initially found as Fe^{3+} species. The reduction of Fe^{2+} exchanged ions to Fe^0 cannot be observed
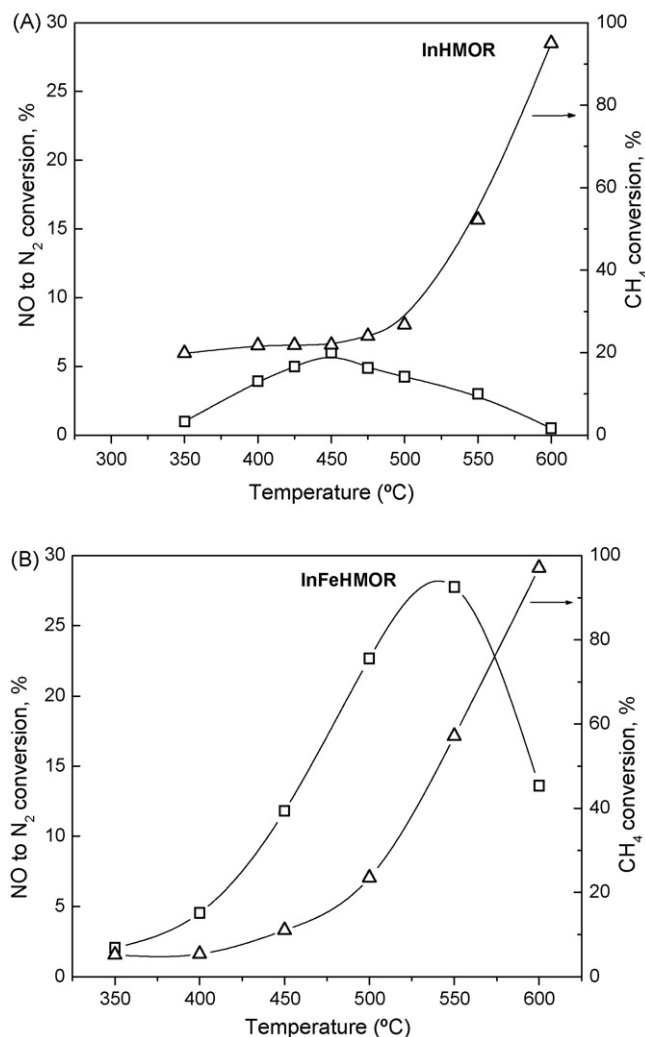

Fig. 3. Selective catalytic reduction of NO_x with HC with addition of H_2O. Conversion of NO to N_2 with CH_4 (□); conversion of CH_4 (△). Reaction conditions: 1000 ppm NO, 1000 ppm CH_4, 2% O_2 in He, 2% of H_2O, GHSV = 20,000 h^{-1}.
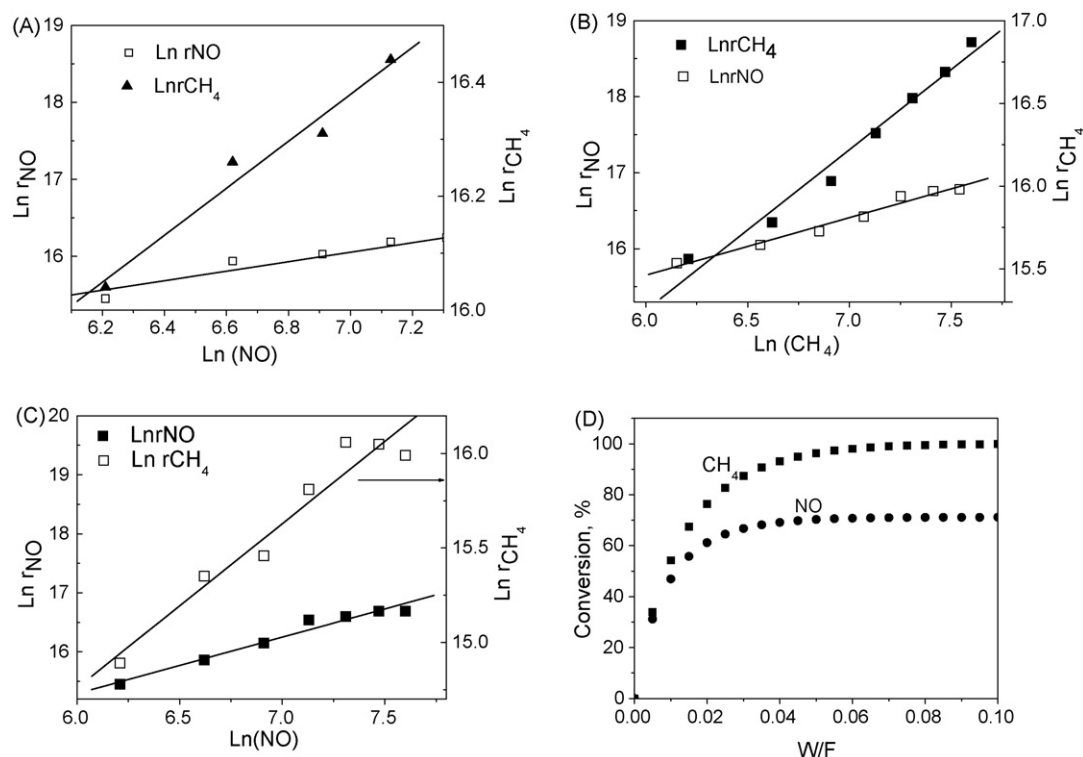
Fig. 4. Kinetic plots for the CH_4-SCR of NO on InFeHMOR. (A) Under dry conditions at 325 °C, NO orders. (B) Under dry conditions, CH_4 orders. (C) O with 2% of water, NO orders. (D) Simulation results using the calculated kinetic parameters, where (W/F) g cm^{-3} min.

because it occurs at temperatures above 900 °C [19–21]. Finally, a broad peak at 530 °C would correspond to the reduction of FeO_x highly dispersed clusters [20]. After the samples are used in the chemical reaction, the reducibility of Fe decreases in all regions.

For InHMOR (Fig. 5B), the main peak is centered at 220 °C and corresponds to the reduction of exchanged species InO^+Z^- to In^+Z^-. The ionic indium oxo species InO^+ were introduced via aqueous ion exchange from the $In(NO_3)_3$ solution. The shoulder observed around 350 °C suggests the presence of small amounts of In_2O_3 crystals, which could be formed during the calcination process [7,14].

For InFeHMOR (Fig. 5C), two small peaks can be observed at 222 °C and 314 °C and another more intense one at 438 °C. The first two peaks could correspond to InO^+ species and In_2O_3 clusters, according to what was observed in the InHMOR sample. If we take into account the H_2 moles consumed at these first two reduction peaks, we obtain $H_2/In = 1.14$. This value would indicate that FeO_x species are also reduced. Then, a $H_2/Fe = 1.08$ ratio is obtained, lower than 1.5 which is the

necessary one to reduce Fe_2O_3 oxide to metallic Fe. This would indicate that not all the Fe present in the solid is as Fe^{3+} or else that not all the Fe^{3+} present in the solid is reduced to Fe^0. Loobre et al. [22] reported that the Fe_2O_3 bulk reduces in two steps, first towards Fe_3O_4 at 420 °C and then, to Fe^0 at 700 °C via FeO. However, when they reduced 3 wt% Fe/SiO_2, they obtained a single wide reduction peak between 450 °C and 600 °C with a $H_2/Fe = 0.5$ ratio. The Fe (Fe^{2+}) oxide remains stable. There were no modifications in the profiles after the sample was exposed to the reaction gases, showing a very stable behavior.

Comparing the bimetallic system in another zeolitic structure, InFeHZSM5 (Fig. 5D), the main peak in the calcined sample appears at 530 °C, and at lower temperatures a shoulder around 400 °C can be observed, corresponding to the reduction of In_2O_3 and Fe_2O_3 clusters. The absence of a peak around 200 °C would indicate that In is present as In_2O_3, or that the InO^+ species are reduced at higher temperatures.

The results of DRX are shown in Fig. 6. The patterns (b) obtained for the InFeHMOR catalyst after it was used in the chemical reaction with water are compared to the original support HMOR, pattern (a). The signals corresponding to the different iron oxides can be observed: the three main peaks of Fe_2O_3 at 32.7°, 35.1° and 53.6°, respectively. The sign at 40.4° can be assigned to FeO and the one at 62° corresponds to Fe_3O_4. In_2O_3 has its most intense peak at 30.6°, which cannot be seen because it coincides with a peak from the spectra of the zeolite. However, at 49° there is another sign of In_2O_3, which confirms its presence in the sample [23].

Table 1
Empirical parameters of the following kinetic equations^a $r_{NO} = k'_1 p^a_{NO} p^b_{CH_4}$, $r_{CH_4} = k'_2 p^c_{NO} p^d_{CH_4}$

| | Kinetic parameters | | | | | |
	a	b	c	d	k'_1	k'_2
0% of H_2O	0.62	1.24	0.45	0.97	0.25	5.94
2% of H_2O	0.96	–	0.85	–	–	–

^{a} The units of kinetic constants k'_1 and k'_2 correspond to concentrations in ppm and time in min.

Table 2
Temperature-programmed reduction

Catalyst[a]	Treatment[b]	T max (°C) consumption of H_2/Metal		
FeNH$_4$MOR 1.76%Fe	Calc. 450 °C	240 (0.18)	326 (0.34)	530 (0.30)
	Used with C_4H_{10} and CH_4	210 (0.13)	324 (0.26)	425 (0.20)
InNH$_4$MOR 3.84%In	Calc. 700 °C	219 (0.70)	–	–
	Used with C_4H_{10} and CH_4	213 (0.60)	–	–
InFeHMOR 7%Fe 5%In	Calc. 700°	222 (0.16)	314 (0.13)	438 (0.77)
	Used with C_4H_{10} and CH_4	219 (0.14)	326 (0.15)	444 (0.77)
InFeHZSM5 14% Fe 5% In	Calc. 700 °C		403 (0.13)	530 (0.80)
	Used with C_4H_{10} and CH_4			483 (0.53)

[a] Metal concentrations (wt%).
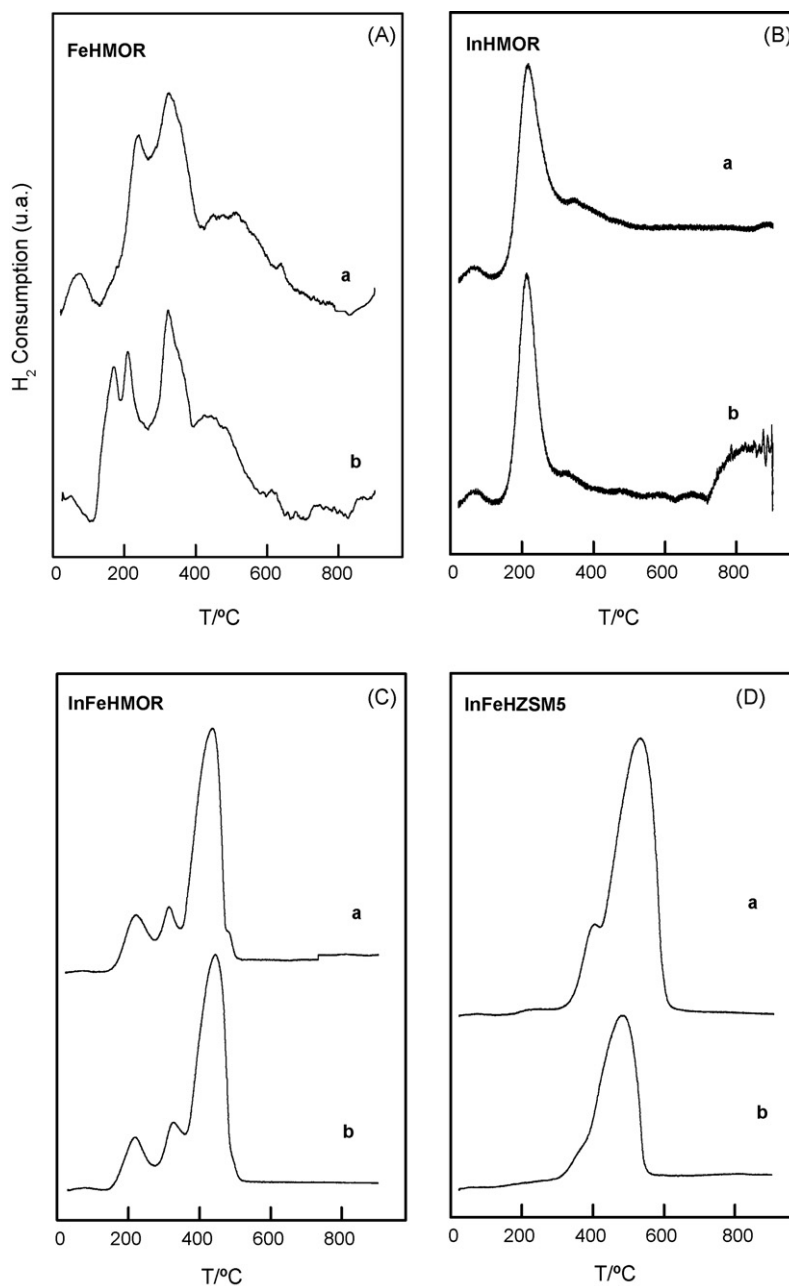[b] Treatment of the samples before the TPR.

Fig. 5. TPR of M-zeolite: (a) fresh and calcined and (b) used with C_4H_{10} and CH_4.
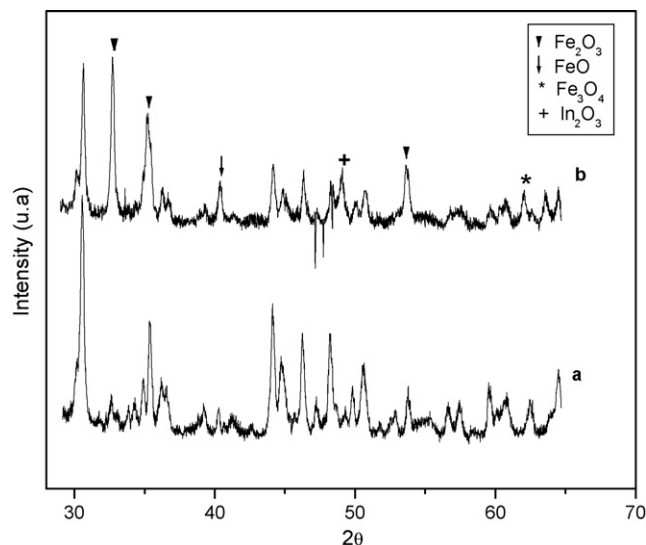
Fig. 6. XRD of (a) calcined HMOR and (b) InFeHMOR used in the chemical reaction with water.
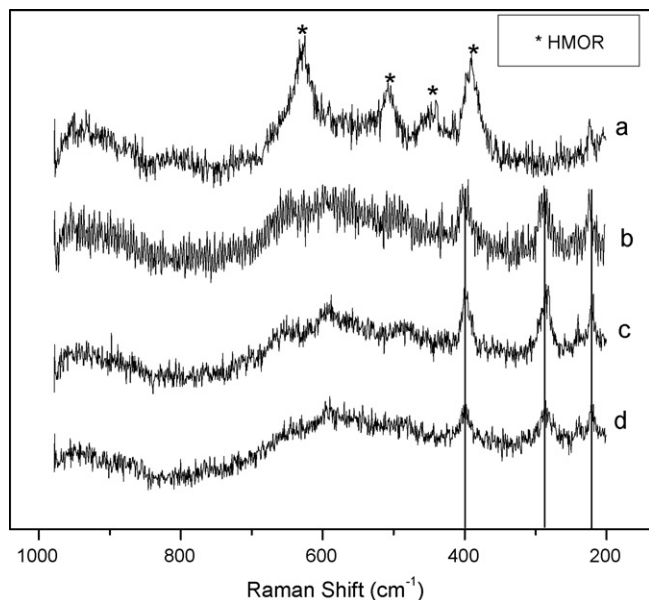

Fig. 7. Raman spectroscopy: (a) InHMOR, (b) calcined InFeHMOR, (c) used InFeHZSM5 and (d) calcined InFeHZSM5.

The Raman spectroscopy spectra are presented in Fig. 7. In the calcined InHMOR catalyst, we can observe the bands corresponding to HMOR at $390 \, cm^{-1}$, $441 \, cm^{-1}$, $506 \, cm^{-1}$ and $626 \, cm^{-1}$ [24]. In the sample of calcined and used InFeHZSM5, and for calcined InFeHMOR, the main bands are at $203 \, cm^{-1}$, $292 \, cm^{-1}$ and $410 \, cm^{-1}$ that can be assigned to α-Fe_2O_3 [25].

4. Conclusions

A higher activity and selectivity on NO reduction can be clearly observed in InFeHMOR than in monometallic catalysts both with methane and butane as hydrocarbon, probably due to a synergic effect between In and Fe on the

support structure. The synergic effect observed for the bimetallic catalyst can be originated in the capacity of the Fe oxides to oxidize NO to NO_2, and that of the InO^+ sites to complete the reduction with the hydrocarbon both in the presence and absence of H_2O.

It can also be concluded that the presence of Fe decreases the deactivation caused by the presence of water (2%) in the feed, and that after an initial decay due to water adsorption on active sites, the activity remains constant for over 125 h.

Nitric oxide and methane reaction rates showed to be ca. first order for methane and fractional for NO when a dry feed was used. For wet reaction conditions, both methane and NO orders changed, probably due to the water adsorption on the InO^+ active sites.

Acknowledgements

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