Microporous and Mesoporous Materials 222 (2016) 9–22

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Exchanged lanthanum in InHMOR and its impact on the catalytic performance of InHMOR. Spectroscopic, volumetric and microscopic studies

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ARTICLE INFO

Article history:
Received 26 June 2015
Received in revised form
16 September 2015
Accepted 24 September 2015
Available online 9 October 2015

Keywords:
Indium-mordenite
Lanthanum-mordenite
Dealumination
Zeolite hydrothermal stability
NO_x-SCR

ABSTRACT

The incorporation of lanthanum by ion exchange into InHMordenite was studied in order to investigate the modification of the physicochemical properties of the InHM catalysts. The prepared solids, LaInHM and InHM, were treated under rigorous reaction conditions, i.e. 25 h of TOS with addition of 10% of water and 500 °C. The structural changes of the catalysts were followed by spectroscopic, volumetric and microscopic studies. The presence of lanthanum in the InHM acts like a protection for the zeolite structure avoiding the formation of EFAl species, but the alteration of the indium environment into the matrix leads to a reduction of the catalytic yield of the InHM catalyst. In fact the XPS results revealed that the concentration of the indium active sites $(InO)^+$ in LaInHM is lower than in the InHM catalyst, while the remaining indium species interact strongly with Lanthanum. After the reaction, a decrease of In active site in the LaInHM catalyst was observed, suggesting a closer interaction In–La which was later corroborated by TEM microscopy. On the other hand, a steric factor between the side channels of the mordenite and the hydrated cation of La during the exchange process locates lanthanum in outer position, with the consequent loss of pore volume and area specific. The lanthanum exchanged ions protect the deactivation process by structure collapse, but negatively affect the activity of the InHM catalyst.

1. Introduction

It is well-known that zeolites as catalysts are complex materials formed by different components which give its characteristic properties to the zeolite. The different types of zeolitic structures together with the vast number of combinations of elements that can be associated to these matrices result in a vast array of catalysts that may be actives for many industrial reactions. The role of such components can be purely catalytic; they can act as stabilizing agents or just provide particular physical properties to the zeolitic support. For the catalytic goals the incorporation of active metals by different methods conduces to complex interactions between the guest components and the zeolitic matrix with the consequent improvement in the global catalytic performance of the modified zeolite. Nevertheless, in all cases the zeolitic catalysts undergo changes during its use under reaction conditions. The inside zeolite transformations can range from the loss of crystallinity, the migration of the metals from their original positions, the agglomeration of active particles sites, the changes on the strength and distribution of acid sites to pore blockage. By now, it is known that zeolites are not stable under rigorous conditions such as high temperature gas streams containing water, and it is for this reason that the use of zeolite-based catalysts is limited.

Many efforts have been made in order to explain the deactivation mechanisms of the technical relevant zeolites (MFI, MOR, FER, BEA, Y) [1,2], and to improve the durability of these materials. But drawing general conclusions is difficult, due to the extensive possibilities of combinations between structures, zeolite guest components (with different natures and contents), preparation methods, and conditions of the pretreatments and the reactions. These different combinations as regards materials and procedures conduce to different authors reaching to highly controversial findings when studying similar materials.

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http://dx.doi.org/10.1016/j.micromeso.2015.09.042
1387-1811/

They all agree that exposure of zeolitic catalysts to water vapor at high temperatures irreversibly depresses the activity because some structural changes occur in the solids. Among them: (i) Dealumination, i.e., tetrahedral Al^{3+} ion removal from the zeolite lattice, (ii) Formation of metal oxides, loss of the dispersion and migration or sinterization of exchanged cations to highly coordinated non-accessible locations.

Several authors have studied zeolite deactivation in which the active site is the exchanged cobalt, but none of these studies evaluate the catalysts for more than 50 h on stream [3–8]. Towards further improvements, bimetallic catalysts were also proposed [9–15]. However, the durability of zeolite-based catalysts is not long enough yet to make its use economically feasible for industrial process.

Y zeolites are extensively used in the fluid catalytic cracking (FCC) of petroleum distillates so they have been exhaustively studied. It has been found that Rare Earth (RE) ions exchanged into the Y zeolite play an important role in the stabilization of such structure. These cations improve the acidity, the cracking activity, and the thermal stability [16,17]. A probable mechanism which may conduce to enhance the durability of these catalysts is the formation of lanthanum-hydroxyl species in zeolite channels, following thermally induced hydrolysis of the $[RE(H_2O)_n]^{3+}$ cations upon calcination [18] and their migration to smaller cages [19–23]. The thermal stability of HY zeolite is also improved by lanthanum exchange and to a lesser extent by cerium exchange. The reason is probably related to the increase in the ionic field within the crystal, but it cannot be solely explained by this effect. Thermal stability of LaHY catalyst is higher than cerium zeolites, fact that can be related to the particular properties of the rare earth cations, but it is difficult to establish what the relevant properties of the involved rare earth are [23].

On the other hand, the zeolites modified by the addition of La were studied by theoretical methods in order to corroborate the hydrothermal stability. In fact, Bao and co-workers [24,25] reported a density functional calculation (DFT) to the improvement in hydrothermal stability of La-modified ZSM-5. They investigate the location and binding of lanthanum cations, i.e., $La(OH)^{2+}$ on H-ZSM-5 and they found that the charges on both Al and O atoms in La-ZSM-5 show an increase compared to H-form zeolite, which would undoubtedly lead to a stronger mutual interaction and, hence, enhance the stability of the aluminum tetrahedron anion $[AlO_4]^-$. Moreover, $La(OH)^{2+}$ seems to have thickened the zeolite framework, which can effectively retard the process of dealumination. Yang et al. also studied by DFT the hydrothermal stabilities of different Metal/ZSM-5 zeolites and they concluded that the binding energies of the metal cations, which decreased as La/ZSM-5 > Ca/ZSM-5 > Mg/ZSM-5 > K/ZSM-5 > Rb/ZSM-5 > Na/ZSM-5 > Zn/ZSM-5 > H/ZSM-5, determined the relative hydrothermal stabilities of different metal exchanged ZSM-5 zeolites [26].

Additionally the high catalytic activity of zeolites modified with indium for the selective catalytic reduction (SCR) of NO_x with methane have been well-documented by several authors [27–33]. Different preparation methods of In-Zeolites (MOR, FER, ZSM-5) catalysts together with the addition of different co-cations were reported. Some of the bimetallic formulations yielded better results than monometallic catalysts but the reaction mechanism and the nature of the active sites became more complex. Therefore, the interaction between the species present in the zeolitic matrix became the focus of many research studies and significant progress has been achieved in this field [34–40]. However, the common point among all these authors' conclusions resulted that the ion $(InO)^+$ exchanged into the zeolitic matrix is the active site, while the co-cation may improve the catalytic performance. However the hydrothermal stability of In-zeolites has been hardly studied.

In this vein, the main aim of this work is to perform a detailed characterization study of La and In co-exchanged mordenite, in order to investigate both the La species generated into the zeolite matrix and their influence on the exchanged Indium. To achieve this aim XRD, pyridine desorption, XPS, FTIR and TEM techniques were applied in order to understand better both surface and bulk properties of the La,In mordenite samples. In addition, taking into account that In-zeolites are active and selective catalysts for the SCR of NO_x with CH_4, and that lanthanum could improve the stability of the mordenite structure [8], this reaction was performed to evaluate probably stabilizing properties as well as possible synergic effects between La and In in a similar way with the La,Co-Mordenite catalytic system [8]. Nevertheless, this study could be of interest to be applied in other catalytic reactions.

2. Experimental

2.1. Catalyst synthesis

The catalysts were prepared by ion exchange starting from Na-mordenite (NaM) (Zeolyst CBV 10A, Si/Al = 6.5). The ion exchanged form H-mordenite (HM) was prepared following the procedure reported by Gutierrez et al. [41]. The InHM catalyst containing 0.5 wt% of indium was prepared by wet impregnation conventional method with $In(NO_3)_3$ on HM support. Then the InHM solid was pretreated by the following steps: (i) heating in air flow at 500 °C for 10 h, (ii) reduction at 500 °C for 2 h with pure hydrogen and (iii) calcination with pure O_2 at 500 °C for 2 h. After each step the solid was flushed with pure He for 30 min.

Aliquots of HM and InHM were contacted with a $La(NO_3)_3$ aqueous solution during 36 h at RT for ion exchange of La and finally LaHM and LaInHM solids were obtained. All La-containing catalysts were treated in flowing oxygen for 10 h at 500 °C. Table 1 shows the composition of the prepared catalyst.

2.2. Catalyst characterization

2.2.1. Elements quantification

Atomic concentrations in the solid materials were determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES). The measurements were performed in a Perkin Elmer Optima 2100 DV. Samples were dissolved using a mixture of perchloric and nitric acids.

2.2.2. X-ray photoelectron spectroscopy (XPS)

The X-ray Photoelectron analysis (XPS) was performed with an Axis Ultra DLD (Kratos Tech.). The spectra were excited by the monochromatized AlKα source (1486.6 eV) run at 15 kV and 10 mA. For the individual peak regions, pass energy of 20 eV was used. Survey spectrum was measured at 160 eV pass energy.

Table 1
Compositions of the synthesized catalysts.

Catalyst	In (wt%)[a]	La (wt%)[a]	%IE[b]	La/In[c]
LaHM	–	1.85	14.6	–
InHM	0.5	–	2.3	–
LaInHM	0.5	0.96	9.8	0.63

[a] Analyzed using inductively coupled plasma technique (ICP).
[b] Ion exchange rate (%IE) assuming that a stoichiometric exchange process take place with 3 monovalent ammonium ions being replaced by one $La(OH)^{2+}$ ion and one monovalent $(InO)^+$ ion.
[c] Atomic ratio.