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Supported catalysts for DeNO$_x$ reaction based on iron clays

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Abstract

Different clays have been employed as supports for iron oxide based catalysts prepared by the impregnation method. A basic characterization of the catalysts synthesized has been performed, which includes comparisons between the supports and iron-containing catalysts at bulk and surface levels. The characterization results are correlated with conversion levels achieved during NO$_x$ reduction with propene over the iron clay catalysts. Comparison with the catalytic behaviour obtained over an alumina-supported iron oxide catalyst reveals the promising properties of iron clay catalysts for DeNO$_x$ reactions.

Keywords: Clay catalysts; Iron active phase; Nitrogen oxides removal

1. Introduction

Iron is an element of great interest in diverse fields such as metallurgy, biology, geology and industrial processes in which significant developments involving iron or iron oxides materials like coloured pigments, catalysts, magnetic materials or ceramics have been carried out. This technological relevance has motivated the study of iron properties, focussing the attention over the nature of active states and its chemistry. Among the latter, most important characteristics are related to its redox properties, polymerisation capacity and acidity [1]. An important objective in this respect is related to the study of the behaviour of iron in solution, because almost all iron compounds can be tailored from solutions. Despite numerous studies of processes involved in the aqueous chemistry of iron, the mechanism of the iron hydrolysis is not fully understood. The versatility of iron chemistry in solution arises from the existence of two stable oxidation states, from the high reactivity of iron complexes and the sensitivity of the hydrolysis reaction to relatively minor changes in the experimental conditions [2–4].

Recent applications of iron involved the synthesis of heterogeneous catalysts. Their synthesis may be carried out incorporating the metal to the structure of the support, as in iron zeolites, depositing it over the chosen solid (mainly silicic or aluminic materials) or creating a new structure, as in pillaring of smectitic clays with iron polycations. The reactions in which these solids have been employed are quite different: benzene oxidation, ethylbenzene dehydrogenation, methanol conversion or NO$_x$ reduction. The elimination of NO$_x$ has become one of the greatest challenges in environmental protection. These compounds, which are essentially originated from thermal combustion of fossil fuels in stationary sources and engines of vehicles, are important atmospheric pollutants, being involved in acid rain, ozone destruction and photochemical pollution [5,6]. For these reasons the NO$_x$ emissions must be controlled and severe regulations have been implemented worldwide. Taking this in mind, several technologies have been developed in order to decrease the harmful NO$_x$ emissions; among them, catalytic removal has shown to be among most efficient ones, in particular the catalytic reduction employing either ammonia or hydrocarbons as reductants [5,6].

The aim of this article is to analyse the preparation and catalytic activity of supported catalysts based on Fe oxide prepared by impregnation of different clays, employing as supports an Al$_{13}$ pillared clay and an acid activated metakaolin while an alumina sample was also employed as a reference support. All these solids were tested in the catalytic reduction of NO$_x$ using propene as the reducing

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agent. For comparing the efficiency of the different systems for the reaction we mainly focus our attention on the characterization of the solids; textural and bulk analyses having been employed for this aim.

2. Experimental

The Fe impregnated solids were prepared by the incipient wetness impregnation method, a conventional method employed for synthesizing supported catalysts [7]. The iron component was incorporated over the supports by employing the ferric acetylacetonate complex, $Fe(acac)_3$, as precursor. The amount of precursor was calculated to obtain a ca. 8 wt.% of Fe_2O_3 in the final solids. The salt was dissolved in the amount of acetone appropriate to achieve conditions close to incipient wetness. The solids obtained were first dried at 70 °C overnight and then heated under air at 500 °C during 4 h, employing a heating rate of 1 °C/min.

The supports employed were an Al_{13} pillared clay, an acid activated metakaolin and a commercial alumina. The Al_{13} pillared clay was prepared from a natural saponite, whose characterization has been described in a previous work [8]. The pillaring process was performed by a conventional procedure [9]. The initial Al-polycation was prepared by hydrolysis of $AlCl_3{\cdot}6H_2O$ precursor with diluted NaOH with a ratio $OH^-/Al^{3+} = 2.2$, followed by ageing at room temperature for 24 h. This solution was added to previously prepared clay suspensions (ratio mmol Al^{3+}/g clay $= 5$) obtaining a new suspension which, after 24 h ageing, was washed by centrifugation and dialysis. The solid obtained was dried at 70 °C and heated under air at 500 °C during 4 h employing a heating rate of 1 °C/min. The acid activated metakaolin was prepared from a natural kaolin described in a previous paper [10]. The metakaolin was prepared by calcination of the purified kaolin at 600 °C for 10 h, employing a heating rate of 10 °C/min. This metakaolin was submitted to acid activation, a conventional method for improving the surface and acid properties of clays [11]. The acid solution employed was 6 M HCl and was added to the metakaolin with a ratio of 30 mL/g. The suspension was kept at 90 °C under reflux conditions for 6 h with constant stirring. The solid obtained was separated by centrifugation, washed with distilled water until no chloride anions could be detected, dried at 50 °C and heated at 500 °C under the same conditions employed for the former support. The last support employed was a commercial γ-alumina (Spheralite 505), chosen as reference material. This material was supplied by Procatalyse and, as done for the other supports, it was submitted to calcination at 500 °C before impregnation. The final samples are hereafter referred to as *Fe/support*, where the supports are denoted Al_{13} for the pillared clay, MK for the acid activated metakaolin and Al_2O_3 for the commercial alumina.

Elemental chemical analyses of the solids were performed by Activation Laboratories Ltd., Ancaster, Ont., Canada, using inductively coupled plasma spectroscopy (ICPS) and atomic absorption spectroscopy (AAS). The X-ray powder diffraction patterns were carried out with a Siemens D-500 diffractometer, at 40 kV and 30 mA (1200 W), employing Cu Kα filtered radiation. Textural analyses were carried out from the corresponding nitrogen adsorption–desorption isotherms carried out at 77 K, employing a static volumetric apparatus for this purpose (Micromeritics ASAP 2010 adsorption analyser). Prior to these measurements, the samples were degassed for 1 h at room temperature, and then at 110 °C up to a pressure below 50 μmHg. Transmission electron microscopy (TEM) was performed using a Zeiss-902 microscope. Samples were ground and dispersed in ethanol by using an ultrasonic apparatus; then, a drop of the suspension was placed in a Cu grid and air dried before the study.

The catalysts were tested in the NO_x reduction reaction employing propene as reductant. The spatial velocity employed was GHSV $= 19{,}000\,h^{-1}$ and the feed composition of 0.1% C_3H_6 and 0.9% NO in Ar (v/v) was employed. The products of the reaction were analysed by infrared spectroscopy using a Perkin-Elmer 1725X FTIR spectrometer using a multiple reflection transmission cell (Infrared Analysis Inc.). In all cases, the samples were taken to the measurement temperature with a ramp of 5 °C/min and stabilized for 45 min prior to analysis, in order to ensure stationary conditions. The conversion of NO_x was calculated as the ratio between the NO_x consumption and the NO_x feed.

3. Results and discussion

The structural characterization of the natural clays employed as supports in this work has been extensively described in previous reports [8,10]. In Table 1, the chemical composition of supports and Fe impregnated solids are summarized. The different nature of the supports employed, with the metakaolin displaying a high silica content while Al_{13} is a magnesic silicate containing alumina pillars, is reflected in the chemical composition. All the samples synthesized have an iron content quite similar, 7–8% Fe_2O_3; considering the structural amount of Fe_2O_3 present in the original clays, amounts very close to 7% are fixed in all impregnations. In this sense, it must be noted that the impregnation method permits to control the amount of active phase incorporated, differences between the three solids being likely related to

Table 1
Chemical composition of the supports and Fe impregnated solids

Samples	SiO_2	Al_2O_3	Fe_2O_3	MgO
Al_{13}	53.54	14.33	1.07	28.98
MK	89.08	7.86	0.35	0.34
Al_2O_3	–	98.00	–	–
Fe/Al_{13}	50.19	13.56	8.27	26.91
Fe/MK	82.49	7.87	7.11	1.02
Fe/Al_2O_3	–	93.04	7.26	–

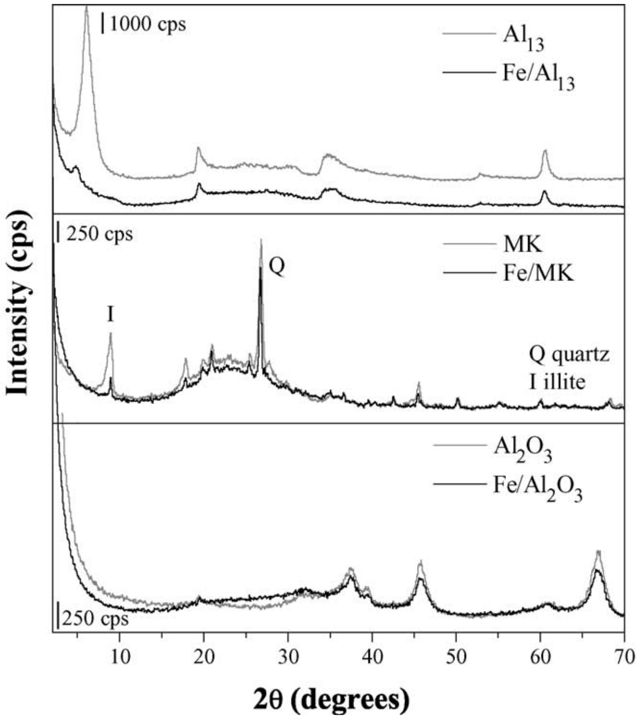

Fig. 1. Diffraction patterns of the supports and iron impregnated samples.

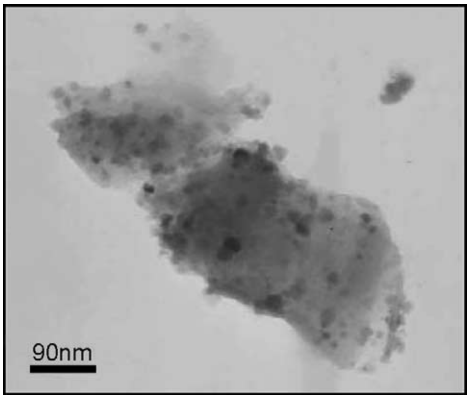

Fig. 2. TEM image obtained for the iron pillared clay.

their different water content during the various steps of the synthesis procedure.

The structural characteristics of the supports are not quite modified upon iron incorporation by impregnation. Thus, the X-ray diffraction patterns of the iron-containing solids show the same reflections as the support samples (Fig. 1). This behaviour means that the supports are quite stable; even the pillared clay maintains its layered ordered structure, its basal plane distance remaining constant at 18.7 Å. Noteworthy, although the iron percent in the samples is quite high, the diffraction patterns show no evidence with respect to the formation of any crystalline phase of iron oxide or iron oxihydroxide, as could be expected to be present after calcining the solids at 500 °C. This effect may be due to the formation of small iron oxide particles very disperse over the supports, as can be seen in Fig. 2 where the TEM image shows small dark zones attributable to iron-containing particles over the pillared clay particles.

Table 2
Surface properties of the supports and Fe impregnated solids

Samples	S_{BET} (m^2/g)	S_{MP} (m^2/g)	S_{EXT} (m^2/g)
Al_{13}	162	124	38
MK	150	75	75
Al_2O_3	185	–	185
Fe/Al_{13}	217	116	101
Fe/MK	30	5	25
Fe/Al_2O_3	191	–	191

The surface properties of the solids are summarized in Table 2. All supports have analogous specific surface area values, 150–180 m^2/g, but they differ in their porosity properties. The MK and the pillared clay present microporosity, which corresponds to 50 and 75%, respectively, of the total area, while the commercial alumina is not a porous material. When these supports are impregnated with the iron precursor, their surface properties can become modified as a function of the support material employed. Thus, the iron pillared clay presents a high surface area, 217 m^2/g, higher than the original support, which may be explained by the incorporation of the Fe-complexes to the internal galleries of the pillared clay, expanding these galleries during the elimination of the gases generated by combustion of the organic moieties during the calcination process. The microporosity surface is also higher, ca. of 60% of the total area, which indicates that the impregnation method induces relatively minor changes in the surface properties of this support. In contrast, the metakaolin suffers an important modification after iron incorporation, its surface area is reduced from 150 to 30 m^2/g while the microporosity almost disappears. These data reveal the low stability of the metakaolin as catalytic support. It is an unstable solid which is converted into low surface area silicates during the deposition of an active phase by impregnation, probably due to the sintering of the particles during the synthesis process. This behaviour can explain the fact that metakaolin is not usually employed as catalytic support. Thus, some works can be found on the employment of acid activated kaolins directly as catalysts, but not as catalyst supports, and mainly used for acid-catalysed reactions, due to the improvement of the acidic and textural properties achieved during the acid treatment [12–14]. The iron impregnated alumina sample presents a surface area quite similar to the original support. This material is quite stable, its textural and structural properties do not appreciably change as a consequence of the impregnation process, which justifies its common use as catalytic support [15,16].

The catalytic properties of the iron clay samples were studied for NO_x reduction employing a hydrocarbon, namely propene, as reductant agent. The reaction monitored was $NO_x + C_3H_6$ under stoichiometric conditions, where the expected products could likely be CO_2, H_2O and N_2. Accord-

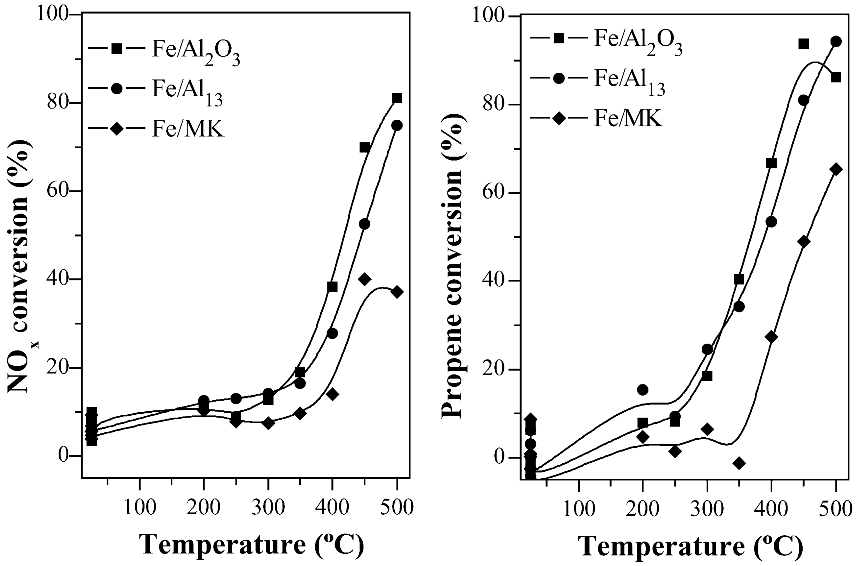

Fig. 3. NO_x and propene conversion levels observed for the iron impregnated clay samples in comparison with a Fe/Al_2O_3 reference catalyst.

ingly, the effluent analysis detected those products although a small amount of NH_3 was also detected as byproduct in concentration below 500 ppm. The NO_x conversions for the samples studied are shown in Fig. 3, along with the respective hydrocarbon conversions. The Fe/Al_{13} and Fe/Al_2O_3 catalysts exhibit high NO_x conversion levels, values close to 80% being achieved at 500 °C. However, differences between them are somewhat greater at 450 °C, at which the Fe/Al_2O_3 achieves a conversion level of 70% whereas the Fe/Al_{13} only reaches 50%. This difference does not appear to correlate closely with the hydrocarbon conversion levels comparatively attained by the samples, levels higher than 90% being achieved in both cases at the mentioned temperatures. Such slight differences in the activities of Fe/Al_{13} and Fe/Al_2O_3 may be due to differential influences of reaction intermediates in each case, in turn attributable to small changes in the physicochemical properties of the iron oxide particles present in each case as a consequence of differences in the dispersion levels obtained for the incorporated metal. This hypothesis, rather than attribution of the observed differences to changes in the support nature, is mainly based on the fact that this reaction has been shown to be mainly influenced by the chemical and electronic properties of the active iron oxide phase of the catalysts [17].

The behaviour of Fe/MK is quite different to that exhibited by the other systems. Its NO_x conversion is quite lower, only 40% being achieved, while the propene conversion does not reach 65%. The structural collapse evidenced in the textural analysis of this system certainly plays a significant role on this catalytic behaviour. In contrast, the high acidity of this support, mainly Brönsted acidity created by the acid activation treatment, does not appear to have a particular role in improving the catalytic behaviour of the final impregnated catalysts.

4. Conclusions

These results show the most optimum behaviour of the alumina as catalytic support, particularly at lower reaction temperatures. Nevertheless, the high conversion levels reached by the iron pillared clay opens a promising way to obtain functional catalysts for this reaction from pillared clays. In contrast, the kaolinitic material does not appear suitable for this reaction. The loss of its original surface properties after the impregnation process may be the reason of its low catalytic activity.

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