Effect of preparation conditions on the characteristics of Fe^{3+}–K10 clay catalysts

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Mössbauer spectroscopy and IR techniques were employed to characterize the iron-impregnated montmorillonite K10 clay catalysts, prepared by using acetonitrile or water solutions of iron(III) chloride. Samples prepared in a non-aqueous medium consisted of comparable amounts of α-Fe_2O_3 and FeOOH, whereas those prepared in an aqueous medium showed only FeOOH-type species. The higher catalytic activity obtained using a non-aqueous medium for alkylation of arenes with benzyl chloride is attributed to the additional Lewis-type acidic sites associated with iron oxide.

KEY WORDS: Fe^{3+}–K10 clay catalyst; nature of active sites; Mössbauer and IR spectroscopy.

1. Introduction

Lewis acid-impregnated montmorillonites (K10) are known to show high catalytic activity for Friedel–Crafts reactions [1–3], and among these catalysts Fe^{3+}–K10 are found to be superior to Al^{3+}–K10 samples. It is reported that the solvent used for impregnation purposes may significantly affect the catalytic properties of such materials [4–7]. In the earlier reported studies, it was demonstrated that the catalysts prepared using an acetonitrile solution of iron(III) chloride exhibited exceptionally high activity of Fe^{3+}–K10 catalyst for the Beckmann rearrangement of diaryl ketoximes [8], as well as for Friedel–Crafts benzylation of arenes [9], compared with a catalyst prepared in an aqueous medium. It has also been shown that the temperature at which a catalyst is activated prior to its use has considerable influence on its activity for benzylation reaction using benzyl chloride [10]. The present study aims to identify the influence of such preparation conditions on the catalytically active sites. Mössbauer and infrared spectroscopy are employed to characterize the Fe-impregnated K10 catalysts prepared through different routes. The effect of activation of these catalysts at different temperatures (120, 280 or 550 °C) has been evaluated.

2. Experimental

Montmorillonite K10 was obtained from Süd-Chemie, Germany. The main components (wt%) of the clay were Al_2O_3 (14.6), SiO_2 (67.6) and MgO (1.8). Three iron-impregnated catalysts, identified as K10 Fe-OO, K10 Fe-OA and K10 Fe-AA, were prepared by procedures described earlier [10]. A sample of clay was added slowly to a solution of $FeCl_3$ in dry acetonitrile followed by filtration and washing, first with acetonitrile and then with benzene. The same procedure was followed for preparing K10 Fe-OA, except that de-ionized water was employed for final washing. In the case of K10 Fe-AA, water was used for preparing $FeCl_3$ solution as well as for washing. These catalysts were activated at 120, 280 or 550 °C for 5 h, preserved under dry environment, and were used after an overnight activation at 120 °C.

^{57}Fe Mössbauer spectra were recorded in transmission mode using a spectrometer, working in the conventional constant acceleration mode and employing a ^{57}Co source in an Rh matrix. The absorbers were made using 270 mg of catalyst on a 2 cm diameter holder. IR spectra were recorded using a Bomem FTIR at a resolution of 4 cm^{-1}. Samples mixed with KBr and pressed into thin pellets were used.

3. Results and discussion

The Fe^{3+} content of K10 Fe-OO, K10 Fe-OA, K10 Fe-AA and K10 clay samples was found to be 4.63, 3.27, 3.19 and 1.97 wt%, respectively. The surface area of different samples, as evaluated from the isotherms of nitrogen adsorption at −196 °C, was found to be almost similar with a value at $220 \pm 20\,m^2\,g^{-1}$.

While the natural K10 clay showed no catalytic activity, the Fe-impregnated samples were active for benzylation of benzene, the reaction rate depending on

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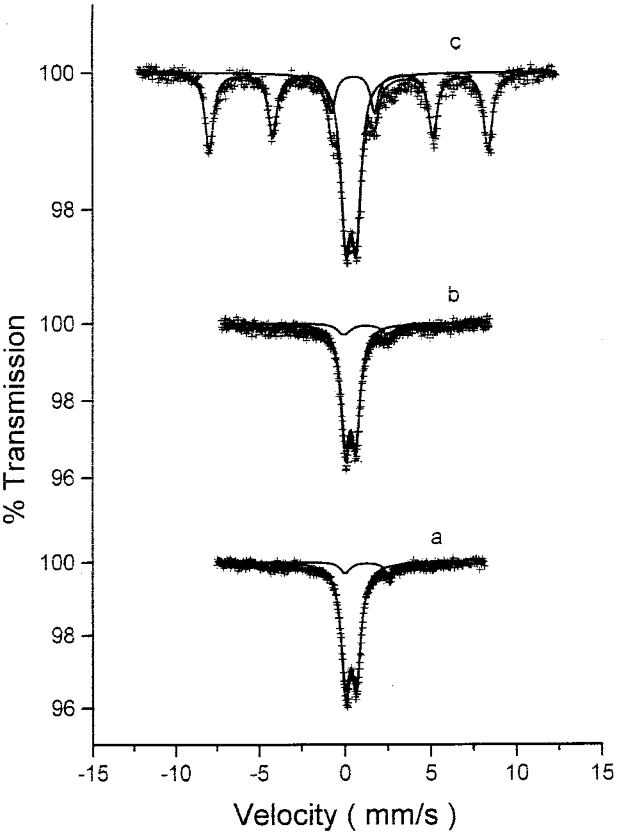

Figure 1. Mössbauer spectra of Fe–K10 montmorillonite prepared under different conditions and calcined at 120 °C. (a) K10 Fe-AA, (b) K10 Fe-OA, (c) K10 Fe-OO.

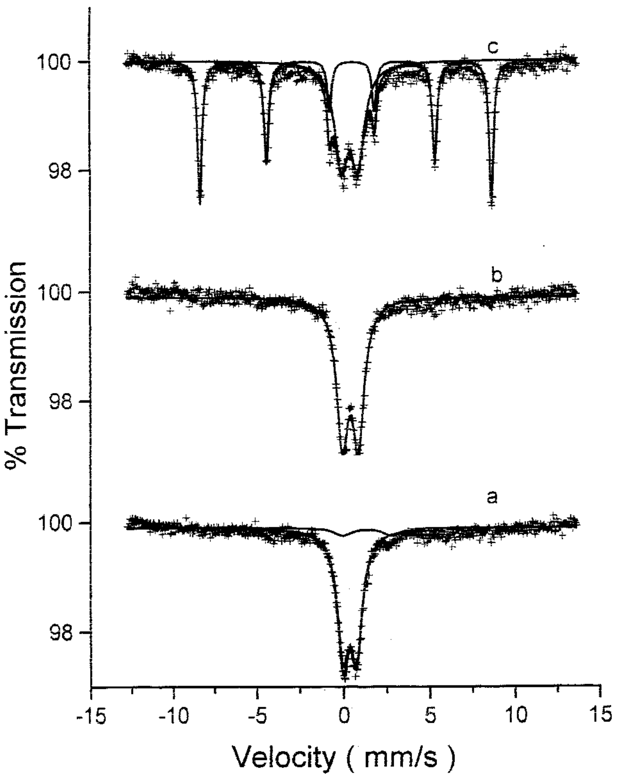

Figure 2. Mössbauer spectra of Fe–K10 montmorillonite prepared under different conditions and calcined at 550 °C. (a) K10 Fe-AA, (b) K10 Fe-OA, (c) K10 Fe-OO.

the conditions of sample preparation. These results are described elsewhere in detail [10]. In general, the samples prepared in organic medium exhibited a higher rate of reaction. The typical values of the rate constant (k) for benzylation of benzene at 40 °C using Fe-OO and Fe-AA samples, both calcined at 120 °C, are found to be 4.4×10^{-3} and $9.2 \times 10^{-5}\,\mathrm{min}^{-1}$ respectively. Similarly, for the samples calcined at 550 °C, the typical values of k using Fe-OO and Fe-AA catalysts at 40 °C were found to be 2.3×10^{-4} and $2.3 \times 10^{-5}\,\mathrm{min}^{-1}$, respectively. It may be mentioned again that the natural K10 clay shows negligible catalytic activity. This is because a small quantity of iron in this case exists in the form of isomorphic substitution in the matrix and is not accessible to the reactants.

Figures 1 and 2 show the room temperature Mössbauer patterns of Fe^{3+}–K10 samples prepared under different conditions and calcined at 120 and 550 °C, respectively. The results of the analysis are given in table 1. The continuous line in these figures represents the best theoretical fit to the data. These results show that the iron in exchanged K10 clay may exist in different charge and magnetic states depending upon the preparation condition. The samples prepared in an organic (acetonitrile) medium show the presence of two distinct forms of iron atoms in the Fe^{3+} charge state. The Fe^{3+}

Table 1
Mössbauer parameters of Fe^{3+}–K10 montmorrillonite catalysts

Sample	IS[a] (mm/s)	QS[b] (mm/s)	HPF (kOe)	% Area
K10 Fe-AA-120				
Ferric	0.36	0.62	–	91
Ferrous	1.25	2.68	–	9
K10 Fe-AA-550				
Ferric	0.36	0.78	–	95
Ferrous	1.35	2.76	–	5
K10 Fe-OA-120				
Ferric	0.36	0.60	–	89
Ferrous	1.20	2.70	–	11
K10 Fe-OA-550				
Ferric	0.34	0.91	–	~100
K10 Fe-OO-120[c]				
Ferric (magnetic)	0.29	0.20	503	53
Ferric (paramagnetic)	0.36	0.59	–	47
K10 Fe-OO-550				
Ferric (magnetic)	0.27	0.22	525	51
Ferric (paramagnetic)	0.37	0.97	–	49

[a] IS is with respect to α-Fe at room temperature.

[b] For the paramagnetic spectrum QS equals the quadrupole spectrum, whereas for the six-line magnetic pattern QS represents the quadrupole shift and $QS = \{(S_{56}-S_{12})/2\}$, where S_{56} means the separation between the sixth and fifth peaks in the sextet pattern.

[c] A small amount of ferrous exists in the FeOO-120 sample, which has been ignored while fitting the data. This does not appreciably affect the other parameters on the conclusions of this study.

atoms in the first form are in the magnetically ordered state at room temperature, as shown by a six-line pattern. These are characterized by a chemical isomeric shift (IS) of 0.26 ± 0.02 mm/s with respect to α-Fe, a nuclear hyperfine field (HPF) of 500 to 525 kOe and a quadrupolar shift of $\cong 0.25 \pm 0.05$ mm/s (see table 1). These Mössbauer parameters are close to those for α-Fe_2O_3 [11] or to a somewhat off-stoichiometric form of this oxide. The second type of Fe^{3+} sites have $IS = 0.36 \pm 0.02$ mm/s and a quadrupole splitting (QS) in the range 0.60–1.0 mm/s. This form of iron atoms can be identified with oxyhydroxide of iron (β-FeOOH) or an off-stoichiometric form of this compound. An increase in the QS value of β-FeOOH for samples heated to 550 °C compared with those of 120 °C (see table 1) implies that the charge distribution around Fe has become asymmetric. It is suggested that this loss of symmetry around Fe^{3+} sites may have a direct bearing on the activity of a particular catalyst.

The Mössbauer spectra of K10 Fe-AA samples calcined at 120 °C (figure 1(a)) or at 550 °C (figure 2(a)) have a small amount of Fe^{2+} species. On the other hand, Fe^{2+} gets nearly suppressed in the K10 Fe-OA sample calcined at 550 °C. The Mössbauer parameters of the predominant phase correspond to a high-spin Fe^{3+} state and are close to those of oxyhydroxide of iron (β-FeOOH) or its off-stoichiometric form. The smaller component ($\sim$10%) having $IS = 1.25 \pm 0.2$ mm/s and $QS \simeq 2.7$ mm/s is typical of high-spin Fe^{2+} species. Considering the comparatively poor activity of the K10 Fe-AA sample as mentioned above, we infer that the iron in oxyhydroxide form is catalytically less active than its oxide form.

It may be stressed that the patterns in figures 1(c) and 2(c) cannot arise from the particles of different sizes, because (i) the isomeric shifts from the two spectra are appreciably different, and (ii) any particle-size distribution should also have a range where relaxation features in Mössbauer spectra should be manifested. In none of the K10 Fe-OO samples, calcined at different temperatures, could relaxation features be seen. We thus attribute the magnetically split spectra to Fe species in the α-Fe_2O_3 form, and the paramagnetic doublet to β-FeOOH.

Figure 3 shows IR spectra of an Fe^{3+}–K10 clay sample prepared under aqueous (curves c, d) and organic (curves e, f) media. Spectra of an iron-free clay sample, recorded without any pretreatment except oven drying, are also included in this figure (curves a, b) for comparison. While spectra a, c and e represent the samples pretreated at 120 °C, spectra b, d and f refer to the samples calcinated at 550 °C. The IR spectra in figure 3 are similar to the earlier reported IR spectra of montmorillonite clays [12]. In the hydroxyl region, the absorption bands at 3620 and 917 cm^{-1} are normally assigned to the stretching and deformation vibrations of structural hydroxyl groups, which are directed towards vacant octahedral positions. The broad bands at 3400 and 1650 cm^{-1}, on the other hand, arise due to stretching and deformation vibrations, respectively, of adsorbed water molecules. A comparison of data in figures 3(c)–(f) reveals that preparation in an organic medium not only prevents the development of structural hydroxy groups, but also minimizes the occlusion of molecular water in between the clay layers. These findings are in general agreement with those obtained from our Mössbauer studies described in the previous section. We may thus conclude that the Lewis acid sites associated with iron oxide species incorporated into K10 play a dominant role in the promotion of catalytic activity. It is suggested that the sample preparation in organic medium helps in the stabilization of these α-Fe_2O_3 species. In addition, higher iron content in the K10 Fe-OO sample, as mentioned above, may also lead to an increased number of active catalytic sites.

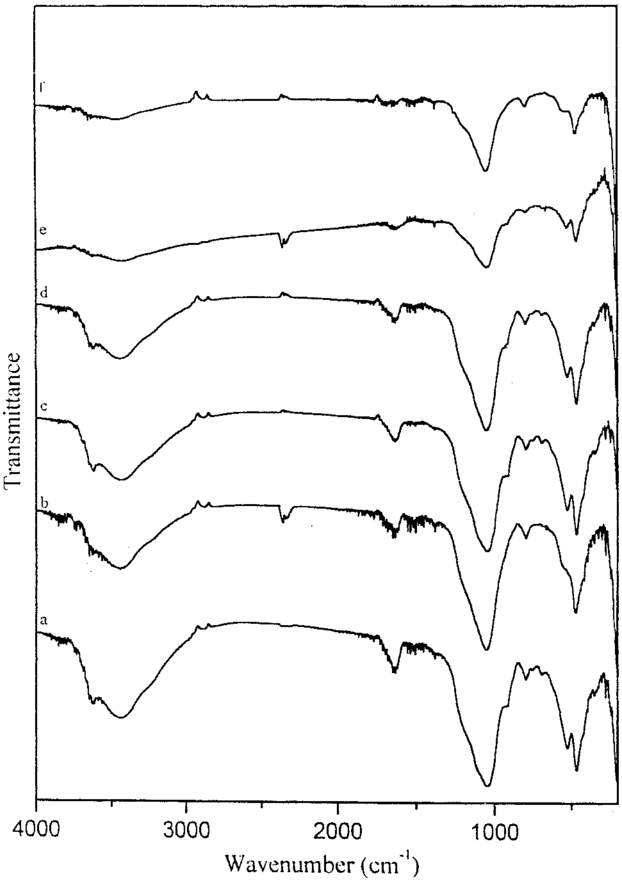

Figure 3. Infrared spectra of Fe–K10 montmorillonite samples, prepared and calcined under different conditions. Spectra a, c and e show IR bands of clay K10, K10 Fe-AA and K10 Fe-OO samples, respectively, all calcined at 120 °C. Spectra b, d and f are corresponding data for K10, K10 Fe-AA and K10 Fe-OO samples calcined at 550 °C.

4. Conclusions

It is concluded that in a catalyst prepared through an aqueous route only FeOOH formation takes place and no Fe_2O_3 is formed even after heating at 550 °C. On the other hand, following the acetonitrile procedure, Fe_2O_3 and FeOOH are termed in comparable proportions even under low-temperature activation conditions. The relative concentration of the oxide phase increases slightly on raising the activation temperature.

The benzylation of an arene using benzyl chloride is classically a Lewis acid catalyzed reaction. In the context of the high activity of Fe-exchanged K10, Cseri *et al.* [3] have postulated a radical cation mechanism. We suggest that both Fe_2O_3 and β-FeOOH may serve as independent catalytic sites, the ligand structure around Fe^{3+} playing a crucial role in deciding their catalytic behavior. The observed changes in catalytic activity as a function of sample preparation or pretreatment conditions may thus be ascribed to a transformation in the phases of the above-mentioned species, as is revealed by Mössbauer data.

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