

Mg–Fe Hydrotalcite as a Catalyst for the Reduction of Aromatic Nitro Compounds with Hydrazine Hydrate

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Catalysts consisting of mixed oxides of Fe³⁺ and Mg²⁺ were prepared by decarbonation of Mg–Fe hydrotalcite-like precursors. They show high activity and selectivity for the selective reduction of aromatic nitro compounds under mild reaction conditions. They are regenerable and can be recycled without any loss of activity. The solids were characterized by XRD, XPS, and Mössbauer spectroscopy. From Mössbauer spectroscopy the solid appears as a well-dispersed ferrihydrite phase supported by a MgFeO matrix, and only Fe³⁺ ions in ferrihydrite can be reversibly reduced by hydrazine and reoxidized by the nitro compound. This observation and the value of the slope of the Hammett plot suggest that the mechanism is similar to that reported for iron oxides. The activity is proportional to the fractional surface of iron oxide, and at equal surface area, MgFe oxides are more active than iron oxides and form negligible amounts of hydroxylamine intermediates. © 2000 Academic

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Key Words: selective hydrogenation; hydrazine hydrate; nitro aromatics; Mössbauer spectroscopy; H-transfer catalysis; hydrotalcites.

INTRODUCTION

The selective reduction of organic nitro compounds is widely used at the industrial scale (1). When the substrate contains several reactive groups, selective reduction becomes particularly difficult. Intermediates often formed in the process are hydroxylamines which are toxic and unstable and can yield colored azo and azoxy products (2, 3). It was recently reported that the disproportionation of hydroxylamines can be efficiently catalyzed by small additions of vanadium promoters to Pd or Pt/C (3, 5). Another efficient catalyst is Pt/TiO₂, reaching 99.3% yield in the hydrogenation of chloronitrobenzene to chloraniline, with a very low concentration (<1%) of intermediates during the reaction (6).

Selective reduction can also be obtained by hydrogen transfer which is an easy, safe, and highly selective method

(7). Indeed, aromatic amines, widely used as intermediates for dyes, photographic, pharmaceutical, and agricultural chemicals, and antioxidants are easily prepared by reduction of aromatic nitro compounds using this method and Pt/C, Pd/C, or Raney nickel catalysts (8). An ecofriendly alternative to the still commonly practiced reduction using iron or sulfides is the use of a hydrazine hydrate as a hydrogen donor (Scheme 1) in the presence of an inexpensive heterogeneous catalyst such as iron oxide hydroxide (9–13). It has however to be remarked that hydroxylamines are also formed, with selectivities reaching 40% in this process catalyzed by iron oxides when electron-attractive substituents are present on the aromatic ring (12).

We reported recently that Mg–Fe hydrotalcite after activation at moderate temperatures was a highly active, selective, reusable, and regenerable catalyst for this class of reactions (14). The choice of Mg–Fe hydrotalcite-like material as a precursor was based on two well-known properties of hydrotalcites: their ability to form mixed oxides with very high surface areas upon activation in air or nitrogen at 723 K and their ability to be regenerated since the structure and surface area can be restored after reactivation in nitrogen at 723 K (15, 16).

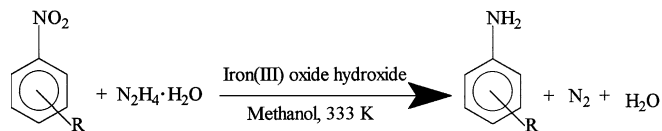
We report here a detailed investigation of this system, in comparison with the iron oxide hydroxides described earlier by Lauwiner *et al.* (12) and Benz *et al.* (17).

EXPERIMENTAL

(1) Catalyst Preparation

Mg–Fe hydrotalcite-like material was obtained from Mg(NO₃)₂, Fe(NO₃)₃ (Mg-to-Fe ratio in the solution of 3), and NaOH + Na₂CO₃ by coprecipitation at low supersaturation (pH 9, 293 K) as described by Cavani *et al.* (15). The catalysts were dried at 333 K. The solids thus prepared showed a Mg/Fe ratio of 1.66 and a typical hydrotalcite-like XRD pattern without any other phase. The solid prepared as such had a low surface area (88 m²/g), but after activation in nitrogen at 723 K it exhibited a very high surface area (220 m²/g) and formed a solid solution

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SCHEME 1

of iron oxide in MgO: by XRD only a MgO pattern was detected, as reported earlier by Shen *et al* (16).

(2) Characterization Techniques

X-ray powder diffraction patterns were recorded on a Phillips instrument using $\text{CuK}\alpha_1$ radiation. XPS measurements were performed using $\text{AlK}\alpha$ radiation at 1486.6 eV. The reference for the energies was $\text{C}_{1s} = 284.6$ eV. The integrated areas of the lines corresponding to Mg_{1s} (binding energy: 1303.2 eV), Fe_{2p_3} (710.8 eV) were compared taking into account the factors of sensitivity of these elements. The kinetic energies corresponding to these transitions are rather different and correspond to different depths of analysis: superficial layers for Mg, but deep analysis for Fe if we take into account the small size of the crystals after heat treatment. Therefore, this analysis is only semiquantitative.

The textural analysis was performed on a homemade volumetric system, driven by a computer. The isotherm for N_2 adsorption at 77 K was determined on solids activated at 723 K in nitrogen or air and then desorbed *in situ* at 473 K in vacuum.

The solids were also investigated by Mössbauer spectroscopy using a 2 GBq $^{57}\text{Co}/\text{Rh}$ source. Wafers (0.12 g of fresh hydrotalcite) were mounted in a cell equipped with beryllium windows to record the spectra in a controlled atmosphere after *in situ* activation. The spectra were recorded at 298 and 333 K or for some of them at 4.2 K. The hyperfine parameters were determined by computer fitting with a precision of about 0.02 mm/s. The isomer shifts are reported with respect to $\alpha\text{-Fe}$.

(3) Catalytic Measurements

The potential of these catalysts was tested for reduction of a variety of nitro aromatics (Aldrich) using a three-neck glass flask equipped with a condenser as a batch reactor. The standard reaction conditions used in the kinetic studies with *p*-nitrotoluene were 0.01 mol of substrate, methanol (25 ml) as the solvent, 333 K as the reaction temperature obtained with an oil bath, 900 rpm as the stirring speed, and catalyst weight before activation of 0.3 g. Since the solid loses 50% of its weight during activation at 623–823 K, the effective mass of the catalyst used in the reaction was 0.15 g.

To avoid diffusional limitations, the solid was crushed below 50 μm . The catalyst was activated in N_2 (100 ml/min) at 723 K for 3 h using a ramp of 10 K/min. After cooling, the

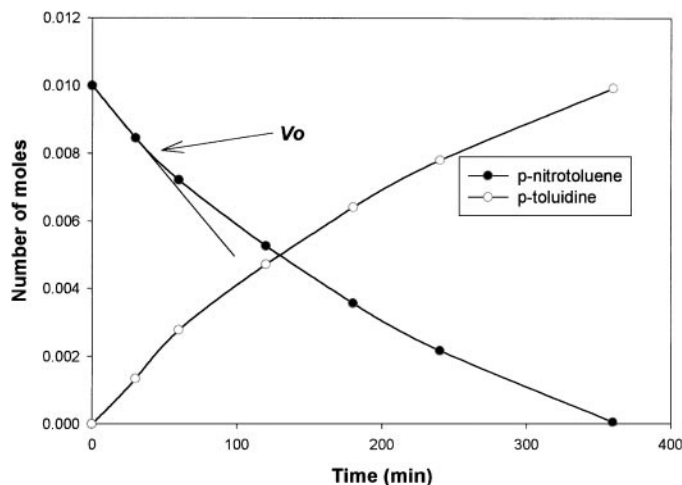


FIG. 1. Concentration profile for the reduction of *p*-nitrotoluene by hydrazine hydrate and an activated hydrotalcite-like MgFe catalyst at 333 K.

catalyst was transferred to the reactor containing the solvent and the nitro aromatic substrate at the reaction temperature. Hydrazine hydrate (0.05 mol) was then slowly added.

Aliquots were taken periodically and analyzed by GLC using a Perkin Elmer instrument equipped with a Supelcowax 10MT column (length 30 m, internal diameter 0.25 mm). The catalyst was found to be 100% selective. Apart from aniline, no other product was observed; in particular, dehalogenation was not noticed, and the carbon balance was respected for partial conversions. Since hydroxylamines were not found in the analysis of the products and the carbon balance was respected, it was concluded that they were not formed, or in trace amounts only. This is a remarkable difference from earlier work on iron oxides (12).

RESULTS

(1) Catalytic Results

(a) *Kinetic study on nitrotoluene hydrogenation.* A typical result of hydrogenation of *p*-nitrotoluene by hydrated hydrazine on activated hydrotalcite is reported in Fig. 1.

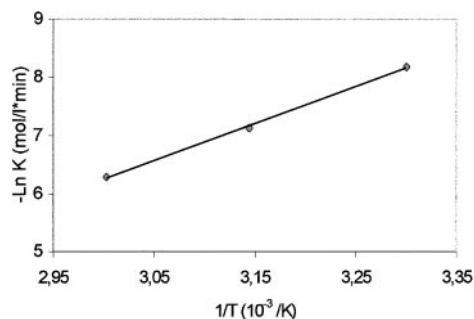


FIG. 2. Arrhenius plot for the hydrogenation of *p*-nitrotoluene on MgFe hydrotalcite-like catalysts.

TABLE 1
Surface Areas and Composition of FeMg Hydrotalcites
Activated in Different Conditions

HDT-MgFe treatment	at.% Mg from XPS Mg _{1s}	at.% Fe from XPS Fe _{2p_{3/2}}	BET area (m ² /g)	S _{Fe} (m ² /g)
Fresh	74	26	88	23
423 K	72	28	99	28
623 K	71	29	174	50
723 K	63	37	202	75
823 K	57	43	138	59
Catalyst after 2nd cycle	62	38	96	36
Regenerated catalyst (723 K)	59	41	142	58

The rate is practically constant and decreases slightly with conversion, which suggests a small inhibition by the products of reaction, most probably by water. The inhibition is related to the type of substrate and is negligible for *p*-methoxynitrobenzene, for instance. Lauwiner *et al.* (12) also reported a zero order for iron oxides, in this range of concentrations of the nitro compound. The initial rate can be measured from this plot and has been used to determine the activation energy (Fig. 2), equal to 53 kJ/mol for the reduction of nitrotoluene.

The solid was calcined at different temperatures to change the degree of segregation of iron oxides at the surface, and the amount of Fe was measured by XPS. The surface areas occupied by Fe oxides was then estimated, assuming that this was equal to the total surface area multiplied by the Fe surface content. The results of these measurements are reported in Table 1. The initial rate is indeed proportional to this Fe surface content (Fig. 3).

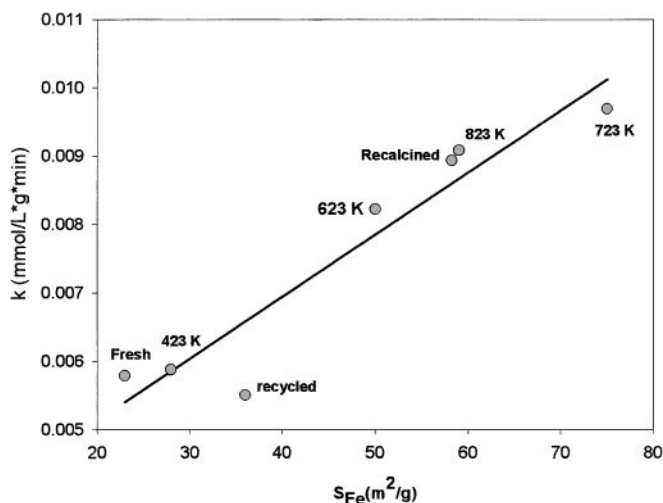


FIG. 3. Initial activities at 333 K for the reduction of *p*-nitrotoluene as a function of the iron oxide surface area for catalysts calcined at the temperatures quoted on the figure, recycled, and regenerated.

TABLE 2
Reusability of the Catalyst for
4-Chloronitrobenzene Reduction

Run	Time (h)	% Conversion
1	3	100
2	3	83
3	3	57
4 ^a	3	100

Note. Reaction conditions: 1 g of nitro compound, 12 ml of methanol, 0.16 g of catalyst (after activation at 723 K in nitrogen flow), reaction temperature 333 K, 1 ml of hydrazine hydrate added dropwise over a 30-min period, and stirring speed 900 rpm.

^a Catalyst regenerated at 723 K and used again.

Recycling of the catalyst was investigated with two substrates: *p*-chloronitrobenzene (Table 2) and *p*-nitrotoluene (Fig. 4). It was found that the catalyst was getting deactivated after each run. However, a reactivation in nitrogen at 723 K restored the original activity. The main cause of the deactivation was hydration of the catalyst by the water in hydrazine hydrate and the reaction product which induces a decrease in surface area due to the reformation of an hydrotalcite-like structure (Table 2). This behavior of calcined hydrotalcites is well-known and is reversible as can be seen here.

(b) *Effect of substituents.* The reaction was investigated on a series of nitro compounds, listed in Table 3. Good results were obtained, even with electron-attracting substituents, since high yields could be obtained in a reasonable amount of time. The interesting characteristic of the FeMg systems is that hydroxylamines were not detected in the products and are therefore readily converted into the corresponding anilines.

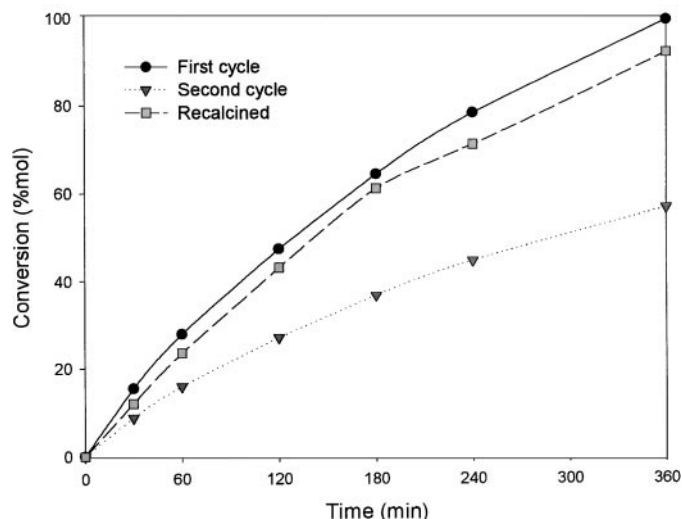


FIG. 4. Activities of the fresh, recycled, and regenerated catalysts.

TABLE 3

Reduction of Aromatic Nitro Compounds with Hydrazine Hydrate in the Presence of Iron(III) Oxide–MgO Catalysts Prepared from Parent Hydrotalcite-like Material

Nitro compound	Time (h)	% Yield
4-Chloronitrobenzene	3	100
4-Bromonitrotoluene	2	100
4-Nitrotoluene	6	99
2-Nitrotoluene	6	99
4-Methoxy-nitrotoluene	6	96
1,3-Dinitrobenzene	1.5	100
Nitrobenzene	5	100

Note. Reaction conditions as in Table 2.

A Hammett plot, $\log k/k_0 = \sigma \rho$, was established using the initial rates which represent here rate constants since the reaction order is zero. The plot represented in Fig. 5 gives a straight line with a good correlation coefficient (0.96) and a slope of $\rho = 0.69$, indicative of an anionic charge on the transition state. The value observed here is very close to that of 0.546 for iron oxides (12), therefore suggesting a common mechanism.

(2) Characterization by Mössbauer Spectroscopy

The spectrum of the fresh unactivated catalyst is presented in Fig. 6: this spectrum can be fitted with two doublets whose calculated parameters are reported in Table 4. The spectrum of the same compound at 4.2 K (Fig. 7) consisted of two hyperfine six-lines patterns and of a quadrupolar doublet with a splitting comparable to that of one of the doublets identified at room temperature (0.52 mm/s). The $\text{Fe}^{3+}(1)$ species which showed no magnetic ordering down to 4.2 K has been attributed to isolated ions in the hydrotalcite lattice. The other species has been attributed to ferrihydrite $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ from the value of the magnetic fields of the magnetic subspectra observed

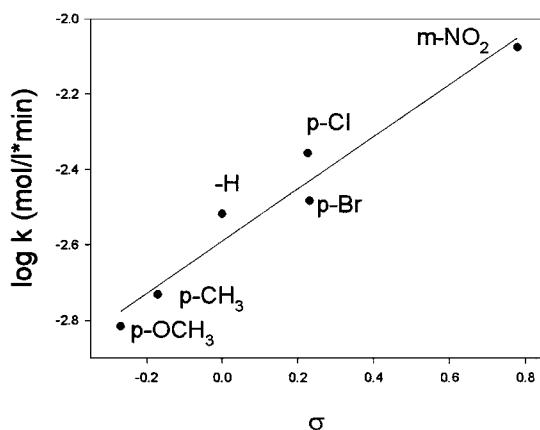


FIG. 5. Hammett plot for the hydrogenation of some substituted nitro aromatics at 333 K.

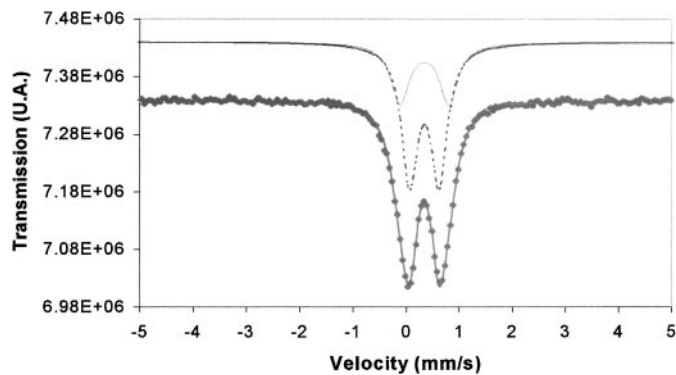


FIG. 6. Mössbauer spectrum of the fresh FeMg catalyst recorded at 298 K. Fit of the experimental data, the subspectra are in dotted lines.

at 4.2 K (18). The observation for that last species of a quadrupolar subspectrum at room temperature has been attributed to superparamagnetic behavior in relation to a very small size of the particles.

After the sample underwent activation at 723 K under nitrogen, the spectrum recorded at 298 K showed some broadening due to a lower crystallinity of the sample. It could be fitted again with two doublets that have been attributed to the Fe^{3+} in MgO and in small ferric oxide particle since this latter phase is the product of the dehydration and dehydroxylation of the ferrihydrite (19). The relative ratios of the two doublets increased slightly, which could correspond to a small segregation of part of the iron localized in the hydrotalcite lattice before activation (Table 4).

The sample after activation was contacted with hydrazine hydrate at 333 K and studied by Mössbauer spectroscopy (Fig. 8). The spectrum obtained was fitted with three doublets. Two of these doublets corresponded to the ferric doublet identified before reduction and the third one, in a smaller amount, to ferrous cations (Table 4). The comparison of the relative ratios of the ferric doublets used to fit the spectra before and after reduction showed that the reduction concerned only the species in the supported iron oxide

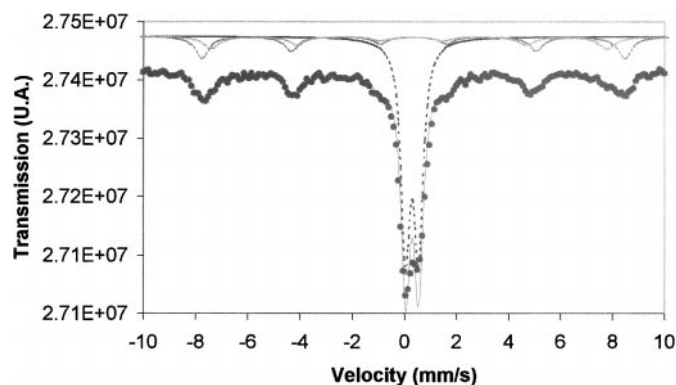


FIG. 7. Mössbauer spectrum of the fresh catalyst recorded at 4.2 K.

TABLE 4
Mössbauer Parameters for the MgFe Samples Treated in Different Conditions

Sample	Recording temperature T (K)	Site	δ	W (mm s ⁻¹)	Δ	H (kOe)	Spectral contribution (%)
Fresh	298	Fe ³⁺ (1)	0.33	0.37	0.55		67
		Fe ³⁺ (2)	0.33	0.42	0.92		33
Fresh	4.2	Fe ³⁺ (1)	0.30	0.41	0.51		65
		Fe ³⁺ (2a)	0.35	0.63	-0.01	504	20
		Fe ³⁺ (2b)	0.25	0.72	-0.09	472	15
Calcined at 723 K	298	Fe ³⁺ (3)	0.31	0.45	0.69		59
		Fe ³⁺ (4)	0.35	0.50	1.26		41
Calcined at 723 K	333	Fe ³⁺ (3)	0.27	0.49	0.73		60
		Fe ³⁺ (4)	0.23	0.52	1.32		40
Reduced by hydrazine	333	Fe ³⁺ (3)	0.27	0.72	0.58		59
		Fe ³⁺ (4a)	0.28	0.69	1.29		35
		Fe ²⁺ (4b)	1.16	0.74	1.80		6
Reoxydized by nitrotoluene	333	Fe ³⁺ (3)	0.27	0.50	0.67		60
		Fe ³⁺ (4)	0.24	0.52	1.23		40
Reduced a second time	333	Fe ³⁺ (3)	0.27	0.66	0.59		60
		Fe ³⁺ (4a)	0.26	0.64	1.22		35
		Fe ²⁺ (4b)	1.13	0.88	1.88		5

particles. The sample was then contacted with nitrotoluene and its Mössbauer spectrum recorded. The spectrum of the solid showed only the two ferric doublets identified before reduction with again the same relative ratio. A second reduction with hydrazine hydrate was performed and we observed that it led to the same pattern as that obtained after the first reduction, confirming that the redox mechanism is well reversible (Table 4).

DISCUSSION

The Mössbauer study demonstrates that the fresh solid contains the same ferrihydrite phase reported as the active phase for iron oxides. After activation, this phase is however converted to γ -Fe₂O₃ which should be the active phase in the case of MgFe systems. As for iron oxides (17) the reaction follows a redox mechanism in which Fe³⁺ is reduced to Fe²⁺ by hydrazine and reoxidized to Fe³⁺ by the nitroaromatic. The main difference between the two catalytic systems is a much higher dispersion of the active phase on MgFe hydrotalcite, as evidenced by the fact that the sextets characteristic of the magnetic phase are observed at room temperature in the case of bulk oxides, and only at 4.2 K in the present case.

The close values of the ρ coefficient of the Hammett relation, 0.54 and 0.69, respectively, show that the mechanism of reduction of the nitro compounds is very similar on iron oxide hydroxides and activated FeMg hydrotalcites. The positive value suggests a mechanism in which the transition state is negatively charged. Indeed, the classical mechanism

of hydrogenation with hydrazine (20) is a redox mechanism involving anionic species which can be written as shown in Scheme 2.

The activities for nitrotoluene hydrogenation measured here at 333 K on FeMg hydrotalcites can be compared to those reported by Benz *et al.* (17) at 328 K for iron oxide hydroxides. For the pure iron oxides, the activity is proportional to the BET surface area and a value of 5.3×10^{-6} mol/min/m² can be calculated from a comparison of the different phases, while the value extracted from Fig. 3 is about 24×10^{-6} mol/min/m². At equal surface areas these hydrotalcites are then more active than iron oxides.

This higher activity can also account for the lower selectivity observed for hydroxylamines. The accumulation of hydroxylamines supposes that the rate of formation of this product is slower than its rate of hydrogenation, thus that the slow step of the reaction is the hydrogenation of hydroxylamine. On activated MgFe hydrotalcite, a higher specific rate of aniline formation is observed; therefore, the slow step of the reaction has been accelerated. This induces a lower selectivity for hydroxylamines. Since the hydrogenation of hydroxylamine also involves a carbanion, it can be speculated that the higher activity is related to a higher basicity of the surface.

In conclusion, the reduction of nitro compounds to the corresponding amines with hydrazine hydrate can be efficiently catalyzed using activated FeMg hydrotalcites. These catalysts can be regenerated and then recycled very easily. One of their features is their very low selectivity into undesired intermediate products such as hydroxylamines.

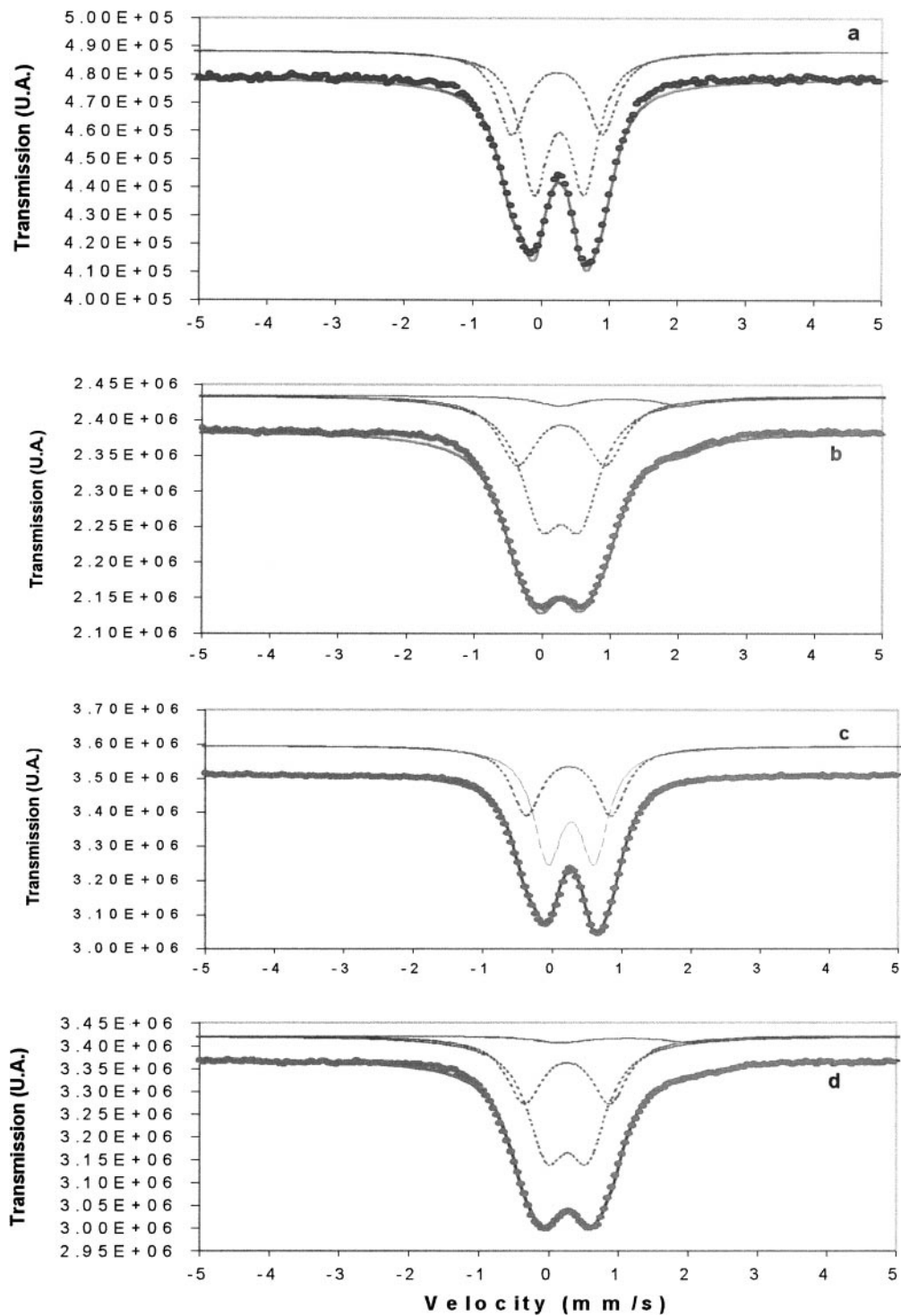
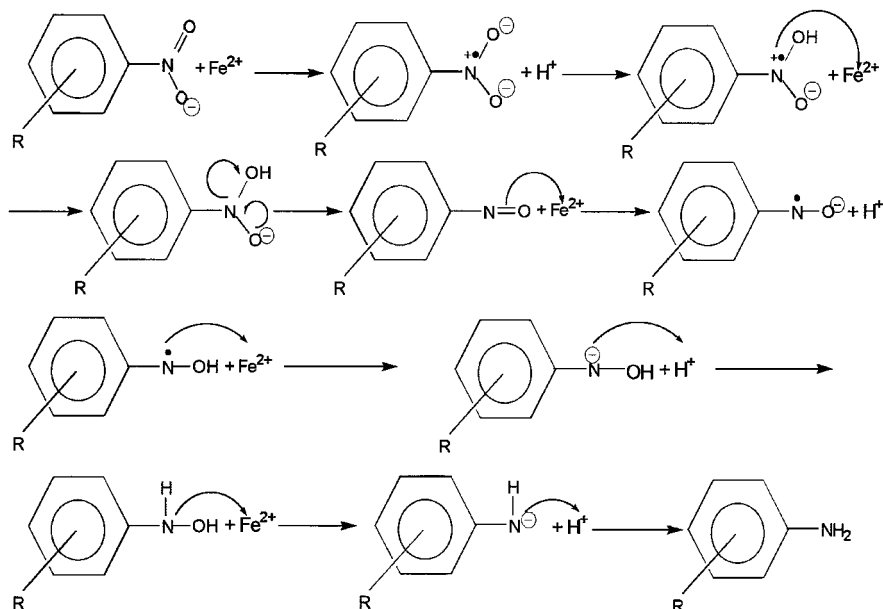
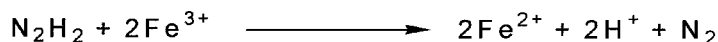
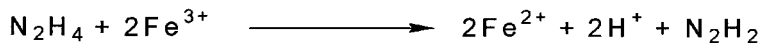


FIG. 8. Mössbauer spectra recorded at 333 K of the MgFe catalyst treated in nitrogen at 723 K (a), reduced by hydrazine hydrate at 333 K (b), reoxidized by 2-nitrotoluene at 333 K (c), reduced again by hydrazine hydrate (d).



SCHEME 2. Reduction of aromatic nitro compounds on activated MgFe hydrotalcite.

This process combines the advantages of being safe and clean and operating at atmospheric pressure with cheap catalysts, in a multipurpose reactor.

ACKNOWLEDGMENTS

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