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Reduction of Aromatic Nitro Compounds with Hydrazine Hydrate in the Presence of the Iron(III) Oxide-MgO Catalyst Prepared from a Mg-Fe Hydrotalcite Precursor

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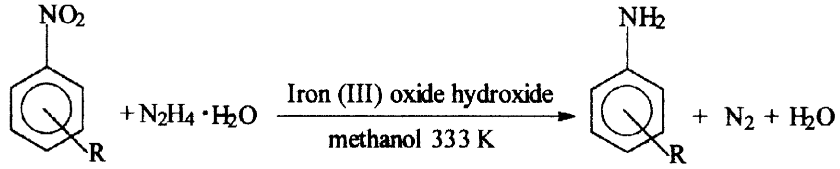
Abstract: Iron(III) oxide-MgO catalyst prepared from a Mg-Fe hydrotalcite precursor shows high activity and selectivity for reduction of aromatic nitro compounds under mild reaction conditions. The catalyst is reusable and regenerable. © 1998 Elsevier Science Ltd. All rights reserved.

Reduction of organic compounds is widely practised both in laboratory and in industry. Hydrogen transfer reduction is one of the easiest, safest and highly selective method of carrying out the reduction[2]. Aromatic amines, widely used as intermediate for dyes, photographic, pharmaceutical and agricultural chemicals and antioxidants can be easily prepared by reduction of aromatic nitro compounds using this method. An ecofriendly alternative to the commonly practised reduction by means of iron and acid or sulphides is the use of hydrazine hydrate as hydrogen donor in the presence of an inexpensive heterogeneous catalyst such as iron oxide hydroxide[3].



In this communication we report for the first time that iron(III) oxide-MgO catalyst prepared from a Mg-Fe hydrotalcite precursor is highly active, selective, reusable and regenerable catalysts for this class of reaction. The choice of a Mg-Fe hydrotalcite-like material as the precursor is based on the following properties of hydrotalcites : i. the activation of hydrotalcite like materials in air or nitrogen at 723 K gives mixed oxides of large surface area; this is essential to optimize this reaction[3]; ii. these catalysts can be regenerated number of times without loss of structure and surface area after simple re-activation in nitrogen at 723 K.

The Mg-Fe hydrotalcite-like material (Mg to Fe ratio 3) was obtained from $Mg(NO_3)_2$, $Fe(NO_3)_3$ and $NaOH+Na_2CO_3$ by coprecipitation at low supersaturation (pH 9, 293 K)[4]. The catalyst was dried at 333 K. The solid thus prepared showed a typical hydrotalcite-like pattern by XRD without any other phase. The solid thus prepared has a very low surface area (< 30 m^2/g). However, after activation in nitrogen flow the solid has a very high surface area (220 m^2/g) and forms a solid solution of iron oxide in MgO (by XRD only MgO pattern is detected).

The potential of these catalysts was tested for reduction of a variety of nitroaromatics (Table 1). The catalyst was found to be highly active and 100% selective. No dehalogenation or demethylation was observed.

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Table 1. Reduction of Aromatic Nitro Compounds with Hydrazine Hydrate in Presence of Iron(III) oxide-MgO Catalysts Prepared from Parent Hydrotalcite like Material[a]

Nitro compound	Time (h)	% Conversion[b]
4-Chloronitrobenzene	3	100
4-Nitrotoluene	6	99
2-Nitrotoluene	6	99
4-Methoxy-nitrobenzene	6	96
Nitrobenzene	5	100

[a] : Reaction Conditions : nitro compound 1g , methanol 12 ml, catalyst 0.16 g, (activated at 723 K in nitrogen flow), reaction temperature 333 K, hydrazine hydrate 1 ml added dropwise over 30 min period, stirring speed 900 rpm

[b] : determined by G.L.C.

The reusability of the catalyst was checked for the reduction of 4-chloronitrobenzene (Table 2). It was found that the catalyst became deactivated after each run. However, a reactivation in nitrogen at 723 K restored the original activity. The main cause of the deactivation was the decrease in the surface area due to hydration of the catalyst by water in hydrazine hydrate and water formed in the reaction. This behaviour of calcinated hydrotalcites is well known and is reversible, as seen here.

Table 2. Reusability of the Catalyst for 4-chloronitrobenzene Reduction[c]

Run	Time (h)	% Conversion
1	3	100
2	3	83
3	3	57
4[d]	3	100

[c] Reaction conditions same as in Table 1 . The catalyst was filtered, washed with excess of methanol and used as such for subsequent run. [d] After reactivation at 723 K.

Further work is in progress to understand the mechanism of the reaction over these catalysts and to check if the basicity of these catalysts has any role to play.

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