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# Catalytic transfer reduction (CTR) of alkyl alkyl, alkyl aryl, cyclic and unsaturated ketones over calcined Mg–Al hydrotalcites

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## Abstract

Calcined Mg–Al hydrotalcites are very efficient catalysts in the vapor phase transfer reduction of a wide variety of ketones to afford corresponding alcohols. Aryl alkyl ketones were converted to aryl alkenes in excellent yields at 548 K. The catalytic activity of calcined hydrotalcites is attributed to the co-existence of acid–base pair sites, with strong basic sites, which can promote transfer hydrogenation. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Catalytic transfer reduction; Mg–Al hydrotalcites; Ketone

## 1. Introduction

Catalytic transfer reduction (CTR) is found to be an efficient and selective method to synthesize different alcohols. Several attempts have been made to reduce ketones by CTR over oxide catalysts [1–3]. Kijenski et al. demonstrated the practical potential of hydrogen transfer over magnesia in the reduction of a wide variety of ketones using 2-propanol as a hydrogen donor [4]. They used magnesia also for the reduction of epoxides, nitro compounds and nitriles [5]. It is generally believed that hydrogen exchange over oxides occurs according to the mechanism of the Meerwein–Ponndorf–Verley type [2].

In continuation with our ongoing research on transfer hydrogenation reactions herein, we report the vapor phase transfer hydrogenation of a wide variety of ketones using *iso*-propanol as a hydrogen donor over MgO–Al<sub>2</sub>O<sub>3</sub> catalysts prepared from a Mg–Al

hydrotalcite-like precursors [6–10]. It is known that layered double hydroxides of the hydrotalcite type upon calcination at temperature above 400°C gives highly dispersed mixed metal oxides with a larger surface area, uniform particle size and pronounced basic properties [11]. A detailed description of synthesis, characterization and various applications of hydrotalcites have been reported elsewhere [12]. Recently, it has been found that properly activated Mg–Al hydrotalcite is an efficient catalyst for the MPV reduction of ketones and oppeneaur oxidation of alcohols in liquid phase [13,14].

## 2. Experimental

### 2.1. Catalyst preparation

Two separate solutions, one containing Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (115.38 g, 0.45 mol) and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (56.27 g, 0.15 mol) in 300 ml of distilled water and another containing NaOH (30 g, 0.75 mol) and Na<sub>2</sub>CO<sub>3</sub>

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Table 1  
Physico-chemical characteristics of Mg–Al hydrotalcites

Mg <sup>II</sup> :Al <sup>III</sup> molar ratio of samples	Mg <sup>II</sup> /Al <sup>III</sup> atomic ratio <sup>a</sup>	Unit cell parameters		Specific surface area (m <sup>2</sup> /g <sup>b</sup> )
		<i>a</i>	<i>b</i>	
3:1	2.75	3.062	23.331	126
4:1	3.75	3.073	23.599	178
5:1	4.79	3.088	23.915	139
MgO	–	–	–	145

<sup>a</sup> ICPEs.

<sup>b</sup> Calcined at 450°C/12 h.

(15 g, 0.141 mol) in 200 ml of distilled water were prepared at room temperature. The metal nitrate solution was added to the second solution at a rate of 60 ml/h maintaining the pH 9–9.5. The resulting precipitate was digested at 65°C for 30 min with stirring and washed with distilled water many times until the pH of the filtrate became 7. The catalyst (Mg–Al hydrotalcite, atomic ratio = 3) was filtered and dried at 110°C and calcined in air at 450°C for 6 h and stored in sealed ampoules.

## 2.2. Catalyst characterization

The characterization of LDHs and calcined-layered double hydroxides (CLDHs) were carried out using XRD, thermogravimetry and BET surface area measurements. The ICPEs (Inductively coupled plasma emission spectrometry) method was adopted to estimate the ratios of the M<sup>II</sup> and M<sup>III</sup> ions in LDHs.

## 2.3. Transfer hydrogenation of different ketones

Transfer hydrogenation reactions were carried out in vapor phase in a fixed bed down flow silica reactor.

Table 2  
Effect of acceptor:donor molar ratio on the conversion of cyclohexanone over calcined Mg–Al hydrotalcite<sup>a</sup>

<i>iso</i> -Propanol:ketone molar ratio	Conversion to alcohol (%)
1	35
2	48
3	59
4	60

<sup>a</sup> Reaction conditions: reaction temperature = 448 K; flow rate = 3 ml/h; time on stream = 1 h; catalyst MgAl HT (Mg/Al = 3) = 2 g.

Table 3  
Transfer hydrogenation of cyclohexanone at different temperatures over calcined Mg–Al hydrotalcite<sup>a</sup>

Temperature (K)	Conversion to alcohol (%)
448	59
458	76
473	100

<sup>a</sup> Reaction conditions: donor:acceptor ratio = 3; flow rate = 3 ml/h, time on stream = 1 h; catalyst MgAl HT (Mg/Al = 3) = 2 g.

Table 4  
Transfer hydrogenation of different ketones over calcined Mg–Al (ratio = 3) hydrotalcite at 473 K<sup>a</sup>

Ketone	Conversion to alcohol (%)
Methyl ethyl ketone	100
Methyl <i>iso</i> -propyl ketone	100
Methyl <i>iso</i> -butyl ketone	95
Di- <i>iso</i> -propyl ketone	82
Cyclopentanone	100
Cyclohexanone	100
Cyclohexenone	67 <sup>b</sup>
Cinamaldehyde	62 <sup>c</sup>
Benzophenone	31
Acetophenone	32 <sup>d</sup>
Propiophenone	34
4- <i>iso</i> -Propylacetophenone	36
Nonanone	57

<sup>a</sup> Reaction conditions: reaction temperature = 473 K; donor:acceptor ratio = 3; flow rate = 3 ml/h; time on stream = 1 h; catalyst MgAl HT (Mg/Al = 3) = 2 g.

<sup>b</sup> At 423 K, 100% conversion is obtained and saturated alcohol (12% selectivity) is also formed.

<sup>c</sup> At 423 K, 100% conversion is obtained and saturated alcohol (10% selectivity) is also formed.

<sup>d</sup> At 548 K, dehydration of alcohol takes place to afford styrene in excellent yield (100%).

Two grams of the catalyst (as pellets 10–20 mesh) was loaded in the middle of the reactor fitted with a thermocouple for temperature measurements. The catalyst was activated in a stream of air at 450°C for 6 h and brought down to the reaction temperature under nitrogen flow. The reaction mixture (ketone and *iso*-propanol, 1:3 mol ratio) was introduced at the top of the reactor by means of an infusion pump. The products were collected in a water-cooled condenser and analyzed by a gas chromatograph fitted with a capillary column and flame ionization detector. The identity of the products was established by the comparison of retention times of authentic samples and also by GC-MS and GC-IR.

### 3. Results and discussion

#### 3.1. Physico-chemical characteristics of hydrotalcites

All the hydrotalcite samples exhibited the typical XRD patterns of the hydrotalcite structure with

intense sharp and symmetric peaks for (003), (006), (110) and (113) planes. The typical IR, TG and DTA patterns also substantiated the formation of layered double hydroxides (LDHs). The important physico-chemical characteristics of LDHs are presented in Table 1. A detailed account of the physico-chemical characteristics of hydrotalcites is already reported elsewhere [15].

#### 3.2. Transfer hydrogenation of different ketones

The effect of donor:acceptor (*iso*-propanol:ketone) molar ratio on the conversion of cyclohexanone to cyclohexanol was examined by varying the ratio from 1 to 4 (Table 2). Conversion increased sharply from 35 to 59% by varying the ratio from 1 to 3 and became constant. An optimum molar ratio of 3 was taken for further study. The effect of temperature on the conversion of cyclohexanone is shown in Table 3. Cyclohexanone conversion to cyclohexanol increases monotonously with increase in temperature and attained 100% conversion at 473 K. Reduction of different ketones to

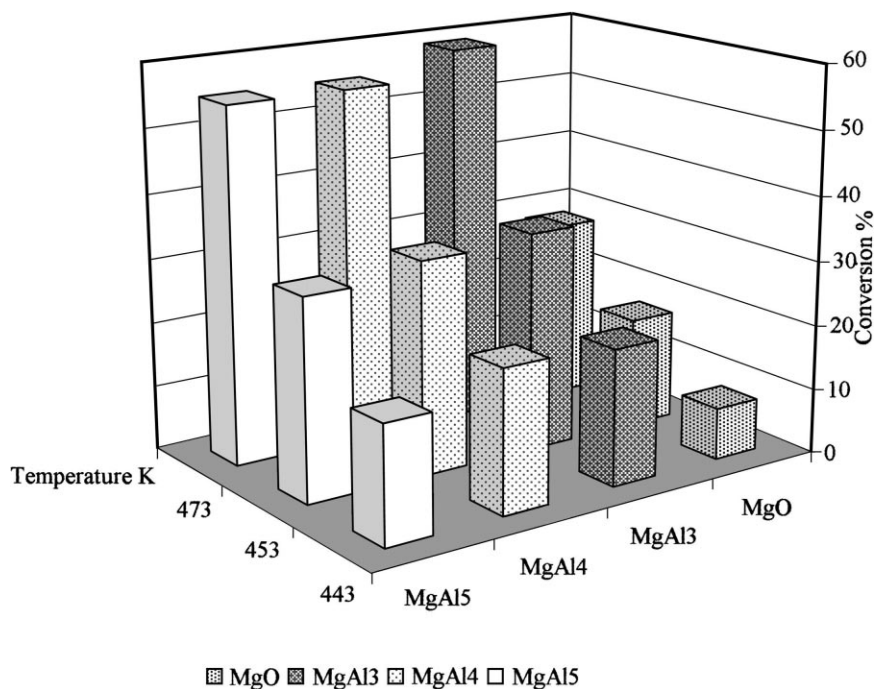


Fig. 1. Transfer hydrogenation of di-*iso*-propyl ketone at different temperatures over calcined Mg–Al hydrotalcites and pure MgO. Reaction conditions: reaction temperature = 443–473 K; donor:acceptor ratio = 3; flow rate = 3 ml/h; time on stream = 1 h; catalyst Mg–Al HT (Mg/Al = 3) = 2 g.

corresponding alcohols with *iso*-propanol over Mg–Al hydrotalcite is depicted in Table 4. Alkyl alkyl and cyclic ketones were reduced to corresponding alcohols in excellent yields. Also, the reduction of unsaturated carbonyl compounds, viz. cyclohexenone and cinnamaldehyde afforded the corresponding unsaturated alcohols in good yields. At 523 K, 100% conversion was obtained in the case of both the ketones, however, an appreciable amount of saturated alcohol (12% in the case of cyclohexenone and 10% in the case of cinnamyl alcohol) being also formed. In the hydrogenation of aryl alkyl ketones, viz. acetophenone and propiophenone, corresponding aryl alkenes were formed in excellent yields at higher temperatures by the dehydration of initially formed alcohols.

### 3.3. Comparison with MgO catalyst

A comparative study of different Mg–Al calcined hydrotalcites and MgO in the reduction of di-*iso*-propyl ketone is shown in Fig. 1. The catalytic activity of Mg–Al hydrotalcites was much better than that of pure MgO. In the case of Mg–Al hydrotalcites, the catalytic activity was not much affected by the change in Mg/Al atomic ratio due to the similarity of acid–base properties of calcined hydrotalcites with different Mg/Al ratios. Shen et al. from microcalorimetric measurements of NH<sub>3</sub> and CO<sub>2</sub> adsorption showed that calcined hydrotalcites with Mg/Al ratio from 3 to 12 exhibited similar surface acid–base properties [16]. Transfer hydrogenation reaction requires the presence of acid–base pair sites since *iso*-propanol is adsorbed on the basic site and ketone on the adjacent acidic sites before hydride ion transfer takes place [2]. It means that the total number and strength of basic sites are important in the transfer hydrogenation reaction. MgO can be considered as the most basic catalyst with practically zero acidity [17]. Calcined hydrotalcites can be viewed as possessing a pair of strong Lewis basic sites (O<sup>2-</sup> ions) and Lewis acid sites (coordinatively unsaturated Al<sup>3+</sup> ions) [18]. So, the presence of large number of active sites for the adsorption of *iso*-propanol and the co-existence of unsaturated aluminum sites makes hydrotalcites as efficient catalysts in transfer hydrogenation reactions compared to MgO. At higher temperatures, such acid–base pair sites can facilitate

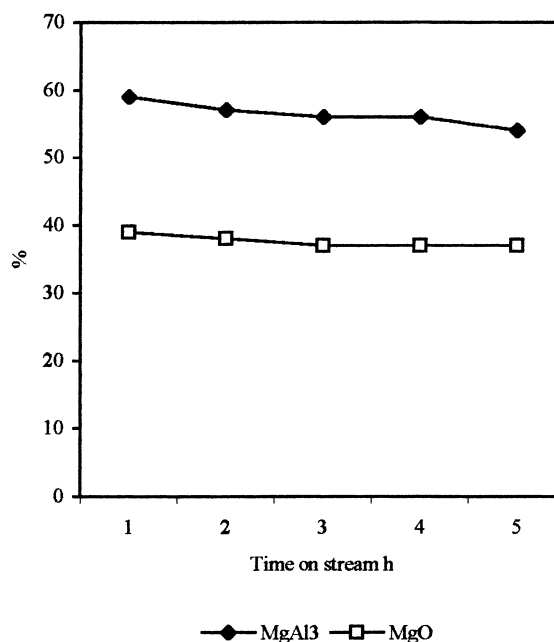


Fig. 2. Stability of calcined MgAlHT and MgO catalysts in the reduction of cyclohexanone. Reaction conditions: reaction temperature = 448 K; flow rate = 3 ml/h; donor:acceptor ratio = 3; catalyst MgAl HT (Mg/Al = 3) = 2 g.

reductive dehydration to alkenes as observed in the case of acetophenone and propiophenone.

The stability of the catalysts was established by allowing the reaction to proceed for a period of 5 h. In Fig. 2, the conversion of cyclohexanol is plotted as a function of time on stream over MgAl HT and MgO. It is evident from the plot that both the catalysts can retain stability even after a period of 5 h.

## 4. Conclusions

In conclusion, calcined Mg–Al hydrotalcites can be efficiently employed for the transfer hydrogen reduction of a wide variety of ketones. Their higher catalytic activity is attributed to the co-existence of acid–base pair sites, with strong basic sites which can promote transfer hydrogenation.

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