

Influence of acid–base properties of mixed oxides derived from hydrotalcite-like precursors in the transfer hydrogenation of propiophenone

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Received 15 September 1999; received in revised form 3 November 1999; accepted 14 December 1999

Abstract

Reductive dehydration of propiophenone to β -methylstyrene has been carried out over different calcined hydrotalcites viz MgAl, CoAl, NiAl, and CuAl under transfer hydrogenation conditions in the temperature range 498–548 K. The performance of calcined MgAl hydrotalcites is found to be much better than MgO and the physical mixture of MgO and Al₂O₃. It is found that selectivity of β -methylstyrene is improved upon the substitution of Mg²⁺ by Ni²⁺ or Cu²⁺ as a result of the formation of stronger acid sites. The overall conversion of propiophenone is influenced by the number and strength of basic sites whereas the selectivity of alkene is affected by the strength of acidic sites present on the catalyst surface. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Acid–base properties; Mixed oxides; Hydrotalcites; Transfer hydrogenation; Propiophenone

1. Introduction

Layered double hydroxides of hydrotalcite types, which are also known as anionic clays upon calcination above 400°C give highly dispersed mixed metal oxides of the M^{II}(M^{III})O periclase type with larger surface area and uniform particle size [1,2]. It has basic and redox properties depending on a wide variety of parameters such as the metal ion cations present,

their ratio in the layered matrices, the presence of alkali dopes, the nature of interlayer anions, and thermal treatments [3]. A detailed description of synthesis, characterization and various applications of hydrotalcites have been reported elsewhere [4]. These materials are found to be very active in various base-catalyzed organic transformations like the Knoevenagel condensations of aldehydes with active methylene compounds and the synthesis of chalcones and flavones [5–7].

A large number of basic catalysts have been employed for vapor phase transfer hydrogenation of carbonyl compounds in presence of hy-

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drogen donors like 2-propanol [8–10]. Kijenski et al. [11] used magnesia for the transfer hydrogenation of a wide variety of ketones. Recently, they employed magnesia modified with H_3BO_3 , H_3PO_4 and H_2SO_4 for the direct synthesis of aryl alkenes from aralkyl ketones under transfer hydrogenation conditions [12]. At temperatures above 523 K, transfer hydrogenation is accompanied by dehydration resulting in the formation of alkenes.

In the present work, we investigate the transfer hydrogenation of propiophenone with isopropanol as a hydrogen donor over a series of mixed metal oxides derived from hydrotalcite-like precursors. An attempt is made to correlate the observed catalytic properties with acid–base properties of the systems, taking into account the effect of interlayer anions, metal ions present and the ratio of metal (Mg/Al) ions.

2. Experimental

2.1. Catalyst synthesis

Analar-grade samples of metal nitrates were used to prepare aqueous solutions. A sequential precipitation method was adopted to prepare different layered double hydroxides (LDHs). To an aqueous solution containing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ mixed at the desired ratio, an aqueous solution of NaOH and Na_2CO_3 was added dropwise with stirring until the pH reached 10. The resulting slurry was stirred at 313 K for 18 h, then filtered and washed with deionised water until the pH of the water became neutral and dried at 373 K for 12 h. The calcined (723 K in air for 12 h) samples were stored in a desiccator before use. Similarly, other hydrotalcites were also synthesized starting from the corresponding metal nitrate solutions.

2.2. Characterization of catalysts

The characterization of LDHs and calcined-layered double hydroxides (CLDHs) were car-

ried out using XRD, thermogravimetry and BET surface-area measurements. The ICPES method was adopted to estimate the ratios of the M^{II} and M^{III} ions in LDHs.

2.3. Vapor phase reductive dehydration of propiophenone

Reductive dehydration reactions were carried out in vapor phase in a fixed bed down flow silica reactor. Two grams of the catalyst (as pellets 10–20 mesh) were 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 (propiophenone and isopropanol, 1:3 mole 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 properties

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 and broad

Table 1
Lattice parameters of different MgAl hydrotalcites

Sample	Lattice parameters (Å)	
	<i>a</i>	<i>c</i>
MgAl 3:1	3.062	23.331
MgAl 4:1	3.073	23.599
MgAl 5:1	3.088	23.915

Table 2
Physico-chemical characteristics of different calcined hydrotalcites

Catalysts	Cations	M ^{II} /M ^{IIIa}	XRD phase obtained	Surface area (m ² /g) ^b
MgAl ₃	Mg ²⁺ , Al ³⁺	2.75	MgO	126.1
MgAl ₄	Mg ²⁺ , Al ³⁺	3.75	MgO	178.5
MgAl ₅	Mg ²⁺ , Al ³⁺	4.79	MgO	139.0
CoAl ₃	Co ²⁺ , Al ³⁺	2.81	CoO	156.7
NiAl ₃	Ni ²⁺ , Al ³⁺	2.78	NiO	139.4
CuAl ₃	Cu ²⁺ , Al ³⁺	2.80	CuO	119.0

^aICPES.

^bDetermined by N₂ adsorption method, catalysts calcined at 450°C/12 h.

and asymmetric peaks for (102), (105), and (108) planes, which are characteristic of clay minerals possessing layered structure. The lattice parameters *a* and *c* calculated for MgAl hydrotalcites (Mg/Al = 3, 4, and 5) with a hexagonal crystal system is presented in Table 1. The typical IR, TG, and DTA patterns also substantiated the formation of LDHs. The important physico-chemical characteristics of LDHs calcined at 450°C are presented in Table 2. A detailed account of the physico-chemical characteristics of hydrotalcites is already reported elsewhere [13].

3.2. Acid–base properties of mixed oxides evaluated from cyclohexanol conversion reaction

Cyclohexanol conversion reaction is reported to be a little sensitive to redox properties of oxides and hence, can be conveniently used to evaluate acid–base properties of a series of oxides [14]. It is proposed that in the dehydration of secondary alcohols, dehydration is catalyzed by acidic sites, whereas the dehydrogenation is catalyzed by acid–base pair sites through a concerted mechanism [15]. Thus, the selectivity of cyclohexene formed as a result of dehydration which can be used as a measure of the acidity of the catalysts and the selectivity of cyclohexanone formed as a measure of their basicity. The result of cyclohexanol reaction over different catalysts is depicted in Table 3 for comparison. Based on the selectivity of cyclohexene and cyclohexanone, catalysts can be arranged in the increasing order of their acidity as MgO < MgAl₃ ≅ MgAl₄ ≅ MgAl₅ ≅ CoAl < MgO–Al₂O₃ < NiAl < CuAl.

3.3. Comparison of catalysts in the transfer hydrogen reduction of propiophenone

Conversion of propiophenone to β-methyl styrene via alcohol as an intermediate is shown

Table 3
Reaction of cyclohexanol over different catalysts at 300°C^a

Catalysts	M ^{II} /M ^{III} (ratio)	Conversion (%)	Selectivity of cyclohexene (%)	Selectivity of cyclohexanone (%)
MgAl ₃	3	35.1	9.1	90.9
MgAl ₄	4	34.8	10.8	89.2
MgAl ₅	5	33.0	11.1	88.9
MgAl S ^b	3	36.9	42.9	47.1
MgAl C ^c	3	39.0	45.6	44.4
CoAl	3	42.9	9.3	90.7
NiAl	3	49.1	91.8	8.2
CuAl	3	51.8	97.2	2.8
MgO	–	9.3	1.1	98.9
MgO–Al ₂ O ₃ ^d	3	46.8	73.9	24.1

^aReaction conditions: Flow rate = 3 ml/h, catalyst weight = 2 g, time on stream = 1 h.

^bInterlayer anions = sulfate.

^cInterlayer anions = chloride.

^dPhysical mixture of MgO and Al₂O₃.

in Fig. 1. It can be noted from the data presented in Table 4 that propiophenone conversion is more in the case of calcined MgAl HT (Mg/Al = 3). Substitution of magnesium by Ni and Cu resulted in a diminution in the propiophenone conversion. However, the alkene selectivity is improved upon the substitution of Mg^{2+} by Ni^{2+} or Cu^{2+} . This is evidently due to the formation of strong acid sites, which is reflected from the selectivity pattern of products in cyclohexanol reaction. Transfer hydrogenation reaction requires the presence of acid–base pair sites since isopropanol is adsorbed on the basic site and ketone on the adjacent acidic sites before hydride ion transfer takes place. So the presence of strong basic sites can enhance the hydride transfer from isopropanol to the ketone. The selectivity of alkenes formed depends directly on the rate of formation of alcohol from ketone, which is initiated by the adsorption of isopropanol on strong basic sites. From the temperature programmed desorption of CO_2 and NH_3 , Dumitriu et al. classified MgAl, CoAl, and NiAl on the basis of their acid–base properties. Considering the differential heat of CO_2 adsorption, the basic strength of these oxides decreases in the order $\text{MgAl} \cong \text{CoAl} > \text{NiAl}$. The concentration of basic sites (no. of meq/g) on the surface follows the order $\text{MgAl} > \text{NiAl} > \text{CoAl}$ [16]. From their studies, it is clear that there is not much difference in the no. of acid sites present on NiAl and CoAl, which is less than that found on the surface of MgAl. The acid strength, which was evaluated by the temperature corresponding to the maximum in the temperature profile, is greater in the case of NiAl followed by MgAl and CoAl. Hence, it can be concluded that overall conversion of propiophenone is influenced by the number and

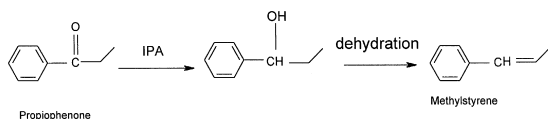


Fig. 1. Formation of β -methylstyrene by the reductive dehydration of propiophenone.

Table 4

The effect of metal ions present on the catalytic activity and product selectivity^a

Catalysts	Conversion (%)	Selectivity of alcohol (%)	Selectivity of alkene (%)
MgAl ^b	56	69	31
CoAl	54	77	23
NiAl	41	51	49
CuAl	36	47	53
MgO	49	97	3
MgO–Al ₂ O ₃ ^c	33	63	37

^aReaction conditions: Reaction temperature = 523 K, flow rate = 3 ml/h, donor:acceptor ratio = 3, time on stream = 1 h, catalyst = 2 g.

^bInterlayer anion = carbonate, metal atomic ratio = 3.

^cPhysical mixture of MgO and Al₂O₃.

strength of basic sites, whereas the selectivity of alkene is affected by the strength of acidic sites.

The activity of calcined MgAl hydrotalcites was compared with that of pure MgO and physical mixtures of MgO and Al₂O₃. The performance of calcined hydrotalcites is found to be much better than MgO and the physical mixture of MgO and Al₂O₃. Pure MgO displayed appreciable activity but the selectivity towards alkenes is poor. MgO can be considered as the most basic catalyst with practically zero acidity [17]. The incorporation of aluminium into MgO suppresses the formation of strongly basic sites that are normally present on the surface of magnesia. Calcined MgAl hydrotalcites can be viewed as possessing a pair of strong Lewis basic sites (O^{2-} ions) and Lewis acid sites (coordinatively unsaturated Al^{3+} ions) [15]. Lewis acidity is attributed to the dissolution of Al^{3+} in the oxide lattice during calcination around 450°C.

3.4. Effect of interlayer anions

The effect of interlayer anions on the conversion of propiophenone and the product selectivities are shown in Table 5. These results are in accordance with the fact that the residual sulfate and chloride anions increases the acidic character of the catalysts.

Table 5

Effect of interlayer anions (MgAl HT, Mg/Al = 3) on the catalytic activity and product selectivity^a

Interlayer anion	Conversion (%)	Selectivity of alcohol (%)	Selectivity of alkene (%)
CO ₃ ²⁻	56	69	31
SO ₄ ²⁻	52	66	34
Cl ⁻	48	60	40

^aReaction conditions: Reaction temperature = 523 K, flow rate = 3 ml/h, donor:acceptor ratio = 3, time on stream = 1 h.

3.5. Effect of Mg / Al atomic ratio

MgAl calcined hydrotalcites with three different compositions (Mg/Al = 3, 4, and 5) were compared in the transfer hydrogenation of propiophenone (Table 6). However, both the conversion and product selectivity are not much affected by the change in Mg/Al atomic ratio. The activity difference observed in the cyclohexanol conversion reaction support these results. Shen et al. [18] from microcalorimetric measurements of NH₃ and CO₂ adsorption showed that calcined hydrotalcites with Mg/Al ratio from 3 to 12 exhibited similar surface acid–base properties. The differential heats of adsorption on the hydrotalcite-derived samples were insensitive to the Mg/Al atomic ratio.

3.6. Effect of temperature

The effect of temperature on the conversion of propiophenone and product selectivity over calcined MgAl hydrotalcite is shown in Fig. 2. At 548 K, propiophenone is completely con-

Table 6

Effect of Mg/Al atomic ratio on the catalytic activity and product selectivity^a

Mg/Al ratio	Conversion (%)	Selectivity of alcohol (%)	Selectivity of alkene (%)
3	56	69	31
4	58	70	30
5	61	72	28

^aReaction conditions: Reaction temperature = 523 K, flow rate = 3 ml/h, donor:acceptor ratio = 3, time on stream = 1 h. Interlayer anion = carbonate.

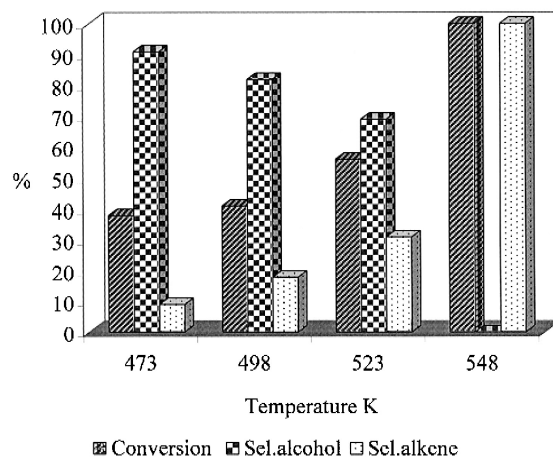


Fig. 2. The effect of temperature on the conversion of propiophenone and product selectivity over calcined MgAl hydrotalcite (Mg/Al = 3); Flow rate = 3 ml/h, donor:acceptor ratio = 3, time on stream = 1 h, catalyst = 2 g. (b) Interlayer anion = carbonate.

verted into corresponding alkene. Dehydration is predominant in the temperature range 523–548 K. In this temperature range, all the catalysts except pure MgO afforded β -methylstyrene as the sole product, which is formed by the reductive dehydration of propiophenone. In the case of pure MgO catalyst, no appreciable change in the conversion of propiophenone and selectivity of products was observed in the temperature 523–548 K.

4. Conclusions

Mixed metal oxides obtained by the calcination of hydrotalcite-like materials are found to be highly active in the reductive dehydration of propiophenone at 548 K under transfer hydrogenation conditions. Presence of strong basic sites favor reduction of ketone to corresponding alcohols, whereas the presence of moderately strong acidic sites favor dehydration of alcohol formed to alkene. The overall conversion of propiophenone is influenced by the number and strength of basic sites, whereas the selectivity of alkene is affected by the strength of acidic sites present on the catalyst surface.

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