Metal containing layered double hydroxides as efficient catalyst precursors for the selective conversion of acetone

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Abstract

Layered double hydroxides or hydrotalcite-like materials containing Ni, Co and Fe are prepared by coprecipitation technique. They are characterized by XRD, hydrogen and oxygen adsorption measurements, determination of acidity and surface area. Acetone conversion in presence of hydrogen has been carried out over these compounds at 373 K and at a pressure of 1 atm. They are found to be efficient catalysts in the selective conversion of acetone. NiMgAl selectively gives methyl isobutyl ketone (MIBK) whereas CoMgAl gives methyl isobutyl carbinol (MIBC) and FeMgAl produces mesityl oxide (MSO) which are all valuable chemicals. The formation of different products is related to the bifunctional nature of the catalysts involving both metallic and acid–base nature. The activity and product selectivity obtained are compared with those obtained over coprecipitated alumina-supported Ni, Co and Fe catalysts containing the same metal content. A mechanism of product formation is proposed. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Layered double hydroxides or hydrotalcite-like compounds are high-surface-area, homogeneous, basic, mixed hydroxides [1]. They are a class of precursors useful for the preparation of catalytically active oxides showing acid–base properties. Hydrotalcite-like materials are active in various condensation reactions of carbonyl compounds with activated methylenic com-

pounds known as Knovenagel, Michael, Claisen-Schmidt reactions and aldolizations in organic chemistry depending upon the nature of the compounds [2–5]. Metal containing hydrotalcites can be useful for the selective hydrogenation of organic molecules where both the metal as well as the acid–base nature of the catalysts take part in the reaction yielding value-added products [6–12]. Acetone hydrogenation is one such reaction to produce methyl isobutyl ketone (MIBK), an excellent solvent widely used in paint industry and an important reagent in dewaxing mineral oils [13]. Many reports are available for the production of MIBK from acetone over a variety of supported metal

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catalysts [14–18]. However, a high temperature (473 K) or a high pressure (10–100 atm) employed is a disadvantage of these processes. Recently, we have reported selective hydrogenation of acetone to MIBK over some selected Ni/Al_2O_3 catalysts at a relatively low temperature of 373 K and 1 atm [19]. In this communication we report the use of metal containing hydrotalcite-like compounds possessing acid–base nature in the conversion of acetone to yield value added products such as MIBK, mesityl oxide (MSO) and methyl isobutyl carbinol (MIBC). A comparison of the activity and selectivity of these catalysts with that of conventional supported metal catalysts has also been given.

2. Experimental

NiMgAl, CoMgAl and FeMgAl hydrotalcite-like precursors containing 30 wt.% Ni, Co and Fe, respectively, 10 wt.% Ni containing NiMgAl and MgAl without any metal, were prepared by coprecipitation technique at constant pH condition [1]. A mixture of 0.5 M solutions of the metal nitrate, magnesium nitrate and aluminium nitrate taken in a burette was added along with a stoichiometric equivalent of NaOH and Na_2CO_3 solution mixture, taken in another burette, to a beaker containing approximately 300 ml distilled water at a constant pH of 8 for NiMgAl and FeMgAl and at pH 7 for CoMgAl. The contents were continuously stirred during precipitation. The mixture of the precipitated hydroxide was filtered, washed, dried and sieved to 1000–1400 μm. The sieved sample was then calcined in air at 673 K for 15 h and reduced in flowing hydrogen (80 ml min^{-1}) at 723 K for 24 h. Hydrotalcite-like compounds have the general formula $[M_{1-x}^{II} M_x^{III}(OH)_2]^{x+}(A_{x/n})^{n-} \cdot mH_2O$. The composition of the materials was chosen in such a way that M^{II}/M^{III} molar ratio is 2.33 and $M^{III}/M^{II} + M^{III}(x)$ is 0.3 and hence represents a hydrotalcite-like compound (M =

cation, Ni, Co, Fe or Mg) [1]. The carbonate and hydroxide concentration were such that $CO_3^{2-}/M^{III} + M^{II} = 0.66$ and $OH^-/M^{III} + M^{II} = 2.25$. The metal (Ni, Co or Fe) concentration was determined by atomic absorption spectroscopy (AAS) and was found to be very close to the calculated value. Hence the same value is taken.

XRD patterns of the dried precipitates were taken with a Philips PW 1140 diffractometer using Ni-filtered Cu-Kα radiation ($\lambda = 1.540$ Å).

10 wt.% Ni/Al_2O_3, alumina- and magnesia-supported Ni, Co and Fe catalysts containing 30 wt.% metal were also prepared by coprecipitation technique following the procedure described elsewhere [20]. All the catalysts were calcined and reduced as described above.

Surface area of the catalysts was determined by N_2 adsorption at 77 K using a Micromerities Pulse Chemisorb Unit (Model 2700). Reducibility and metal area of the catalysts were determined from O_2 and H_2 uptake measurements using an all-glass high vacuum system. The detailed procedure for the measurements and calculation of metal area are described elsewhere [21,22].

Acidity of the catalysts were determined by stepwise temperature programmed desorption (STPD) of ammonia using a Micromeritics Pulse Chemisorb Unit (Model 2700) as described elsewhere [23].

Acetone hydrogenation was carried out in a fixed bed vertical down flow glass tubular reactor (10 mm i.d., 30 cm long) using approximately 0.5 g catalyst. Acetone was fed from the top using a motorized syringe at a controlled rate along with a regulated flow of hydrogen at 373 K and 1 atm. The liquid products obtained were collected in an ice-cooled trap and analyzed by a CIC gas chromatograph using a 5% Carbowax on Chromosorb W column (1/8 in. × 8 in.) in a programmed mode from 323–373 K at 10° min^{-1} and kept at 373 K for further 6 min. The products identified were 2-propanol (2-P), MIBK, MSO and MIBC.

3. Results and discussion

XRD patterns of the dried precipitates show (Fig. 1) characteristic peaks corresponding to hydrotalcite structure.

Table 1 gives the adsorption properties, acidity values obtained from STPD of ammonia and acetone conversion over the catalysts. All hydrotalcite-derived catalysts show high surface area when compared to alumina-supported catalysts as expected. The hydrotalcite-derived catalysts, except the Fe-containing sample, show lower reducibility and metal area than alumina-supported catalysts containing the same metal content. On the contrary, FeMgAl shows a higher metal area than Fe/Al_2O_3. Also, the reducibility of alumina-supported metal catalysts is in the order $NiAl > CoAl > FeAl$ whereas that of hydrotalcite-derived catalysts is in the order $FeMgAl > CoMgAl > NiMgAl$. These anomalies can be explained as follows.

In the case of coprecipitated alumina-supported metal catalysts, the strength of metal-support interaction is in the order $FeAl > CoAl > NiAl$ [22]. In other words, Fe forms a less reducible solid solution with alumina more easily than Co which again forms the same easier than Ni. Hence the order of reducibility is $NiAl > CoAl > FeAl$. The reverse order of reducibility of the hydrotalcite-derived samples can be attributed to the presence of Mg and also to the difference in the nature of metal substitution in the hydrotalcite structure. Addition of magnesium affects the reducibility of the catalysts by forming a metal oxide–magnesia (MO–MgO) solid solution [24–26]. It has been reported that MgO favours the dispersion and diffusion of Ni^{2+} ions into the underlying lattice, thus denying easy accessibility of the NiO surface to the reducing gas [25,26]. This is in addition to the metal–alumina interaction, which normally exists in coprecipitated supported metal catalysts [27]. This explains why the hydrotalcite-derived catalysts are less reducible than the alumina-supported catalysts. Nickel is known to interact with magnesia relatively easily than Co and Fe. Eventually its reducibility is affected to a greater extent than CoMgAl and FeMgAl. Also, in the hydrotalcite-like structure, Ni and Co substitute the M^{II} ion (Mg^{2+}) whereas Fe substitutes the M^{III} ion (Al^{3+}). Therefore at the same metal loading and at a constant value of x, FeMgAl contains a lower Al content than that present either in FeAl, CoMgAl or NiMgAl. This re-
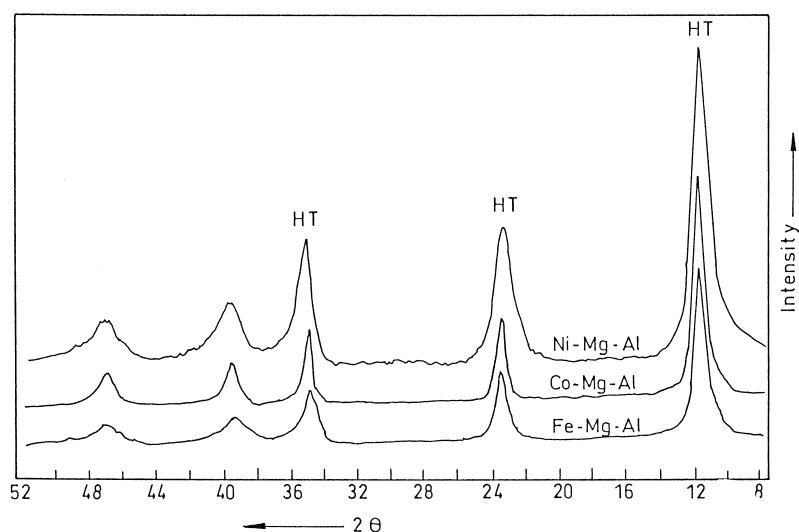

Fig. 1. XRD patterns of metal containing hydrotalcite-like compounds after precipitation and drying.

Table 1
Acidity, adsorption data and acetone conversion over different catalysts

Catalyst	Total acidity[a] (mmol NH_3 (g catalyst)$^{-1}$)	BET surface area (m^2 (g catalyst)$^{-1}$)	Metal area (m^2 (g catalyst)$^{-1}$)	% Reduction	Acetone[b] conversion (%)
10NiAl	0.663	290	2	61	54
10NiMgAl	0.685	330	0.5	20	45
30NiAl	0.696	251	11	78	86
30NiMgAl	0.708	309	1.7	15	48
30Ni/MgO	NM	NM	1	NM	82
30CoAl	0.799	195	4	66	31
30CoMgAl	0.815	293	1	19	18
30Co/MgO	NM	NM	NM	NM	44
30FeAl	0.611	187	1	50	0
30FeMgAl	0.550	202	2	24	18
30Fe/MgO	NM	NM	NM	NM	15
MgAl	0.255	400	–	–	0

[a]Total acidity determined from STPD of ammonia.
[b]Temperature = 373 K, acetone = 0.1227 mol h^{-1} (g catalyst)$^{-1}$, catalyst = 0.5 g, H/A = 1.6, NM = not measured.

duces the interaction between Fe and alumina in FeMgAl when compared to the same in CoMgAl. As a result, FeMgAl is more reducible than CoMgAl. Hence the observed order of reducibility.

Ni and Co containing hydrotalcite-derived catalysts show less acetone conversion than alumina- or magnesia-supported metal catalysts (Table 1). However, FeMgAl seems to be more active (18% conversion) than Fe/Al_2O_3 (no conversion), having the same iron content. The conversion variations over the catalysts can be understood if one remembers that acetone conversion takes place both on metal sites as well as on the acidic or basic sites of the catalyst [22]. In the presence of hydrogen, hydrogenation of acetone to 2-propanol over a metal site is more facile than condensation of acetone over an acid–base site. The hydrogenating property of Ni, Co and Fe decreases in the order Ni > Co > Fe [22,28]. Therefore, the low acetone conversion over NiMgAl and CoMgAl than over Ni and Co/Al_2O_3 can be attributed to their low reducibility and low available metal area. Fe being an inferior hydrogenating metal among the three, the higher acetone conversion over FeMgAl than on Fe/Al_2O_3 may be ascribed to the difference in the nature of Fe substitution in

the hydrotalcite structure as described earlier. Moreover, presence of magnesia can create new acid–base sites by forming an iron oxide–MgO solid solution where acetone can probably undergo a condensation reaction. The product selectivity obtained also supports this. This is further substantiated by the fact that an acetone conversion of about 15% is observed over 30% Fe/MgO. MgAl, where no metal is present, does not give any acetone conversion at the conditions studied here.

Fig. 2a and b show the product selectivity obtained over different catalysts. It is interesting to note the sharp selectivity differences obtained over hydrotalcite-derived catalysts when compared to simple supported metal catalysts. Al_2O_3- and MgO-supported catalysts preferentially give 2-P as the product whereas metal containing hydrotalcite-like catalysts give other products like MIBK, MIBC and MSO. For example, 10% Ni/Al_2O_3 gives 71% 2-P and 29% MIBK whereas 10% NiMgAl produces 56% MIBC, 38% MIBC and no 2-P. Almost 100% 2-P selectivity is obtained over 30% Ni/Al_2O_3. In contrast, there is hardly any 2-P formation over 30% NiMgAl where a 78% MIBK is obtained. Co/Al_2O_3 produces 100% 2-P whereas CoMgAl produces 100% MIBC. Fe/Al_2O_3 does
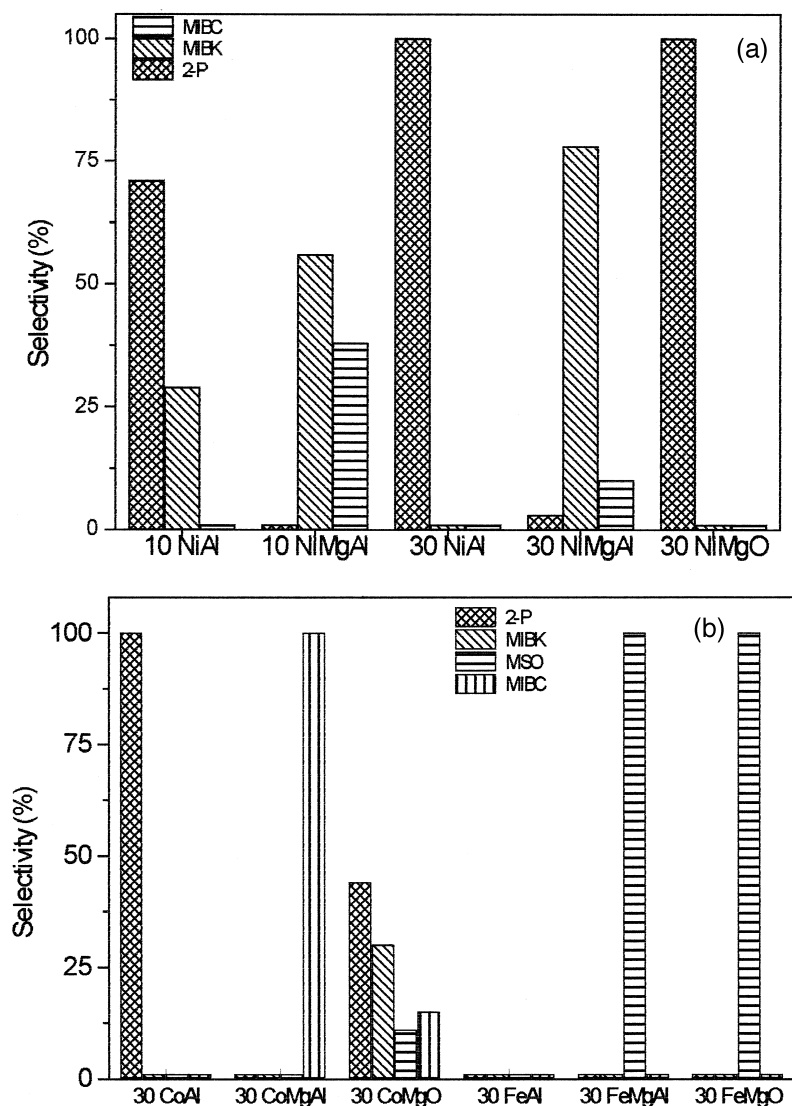
Fig. 2. (a and b) Acetone hydrogenation product selectivity over different catalysts. Acetone = 0.1227 mol h^{-1} (g catalyst)$^{-1}$, Temperature = 373 K. Weight of the catalyst = 0.5 g, H/A mole ratio = 1.6.

not give any product at 373 K, whereas FeMgAl gives 100% MSO at an acetone conversion of 18%.

Hydrogenation of acetone over a metal site gives 2-P as the primary product. Formation of other products involves an aldol condensation step in addition to hydrogenation [15,22]. The acidic or basic sites of the catalysts are involved in the aldol condensation step [29,30]. In other words, formation of products like MIBK, MSO

or MIBC is governed by the bifunctional nature of the catalysts. It is worthwhile to note that 78% MIBK at 48% acetone conversion could be obtained over 30% NiMgAl as against no MIBK formation over 30 wt.% Ni/Al$_2$O$_3$. This makes this a promising catalyst in the production of MIBK, which is a very valuable chemical.

The relatively low reducibility and hence the acid–base nature of hydrotalcite-like catalysts may be responsible for the selectivity difference

over them when compared to alumina-supported metal catalysts (see Table 1). These low reducible catalysts contain a metal–metal oxide interface where electron deficient sites such as oxygen vacancies or species like M^{n+} sites exist in close proximity to metallic hydrogenating sites. This metal–metal oxide interface can be created either by a partially reduced metal oxide or as a consequence of a metal–support interaction like the formation of a solid solution as mentioned earlier. The carbonyl group of acetone could be activated by attachment to the surface of these oxides through coordination of the O-atom to the M^{n+} surface site. The surface O^{2-} ion can act as a basic site to extract a methyl proton resulting in the formation of a nucleophile [31]. This nucleophilic species reacts with a neighbouring coordinated carbonyl centre in the presence of adsorbed hydrogen atoms on metallic sites to form a molecule of MIBK and water. This is schematically represented in Fig. 3. Thus the formation of MIBK is

due to a cooperative effect of both hydrogenating and acid–base properties of the catalyst. Co and Fe are not as good a hydrogenating metal as nickel. Moreover, carbonyl compounds are said to be adsorbed on nickel with a relatively weak acyl structure ($>C \overset{..}{=} O$) whereas on Co and Fe, it adsorbs via a strong alkoxy structure ($>C=O-M$) [32] and the strength of adsorption decreases in the order Fe > Co > Ni [33]. Therefore, it can be envisaged that the MIBK produced may undergo further hydrogenation to give MIBC over CoMgAl due to its low desorption rate from the catalyst surface. The much strongly adsorbed MIBK on FeMgAl in the presence of acid–base sites of the catalysts, undergoes dehydrogenation to yield MSO. It is evident that products like 2-P, MIBK and MIBC cannot be formed in the absence of metallic sites.

This tentative mechanistic pathway for the formation of MIBK is further corroborated by a similar observation over 10 wt.% Ni/Al_2O_3 impregnated catalyst [34]. When the catalyst
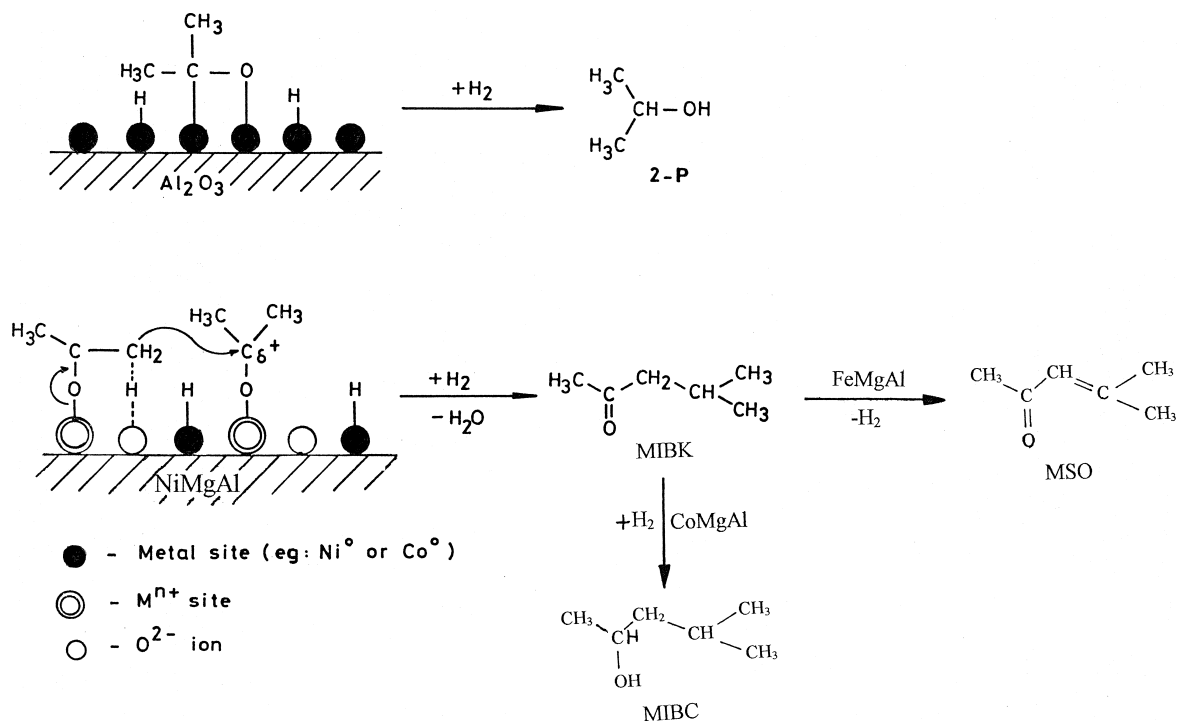

Fig. 3. Mechanism of different product formation in acetone conversion over different hydrotalcite-derived catalysts.

was reduced at 573 K for 3 h (low percentage reduction), it gave around 63% MIBK selectivity whereas no MIBK was produced over the same catalyst reduced at 723 K for 3 h (high percentage reduction). Only 2-P was produced at this condition.

Time-on-stream studies over the catalysts show no appreciable loss in activity for a period of 7 h.

4. Conclusion

In summary, metal containing hydrotalcite-like materials with acid–base properties are found to be useful and promising catalysts in the selective conversion of acetone to different valuable products like MIBK, MIBC or MSO, depending upon the nature of the metal present. NiMgAl hydrotalcite is found to be an efficient catalyst for the selective synthesis of MIBK from acetone at a relatively low temperature of 373 K. CoMgAl selectively gives MIBC whereas FeMgAl produces MSO from acetone at a relatively mild condition of 373 K and 1 atm. Normally these products are produced at a temperature as high as 473–573 K and at 10–100 atm. A mechanism of product formation is attempted.

Acknowledgements

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