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High activity of Mn-MgAl hydrotalcite in heterogeneously catalyzed liquid-phase selective oxidation of alkylaromatics to benzylic ketones with 1 atm of molecular oxygen

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Abstract

Mn-MgAl hydrotalcite, surface-enriched with Mn, was prepared by thermal decomposition of MgAl hydrotalcite followed by reconstruction of its structure in the presence of Mn(II) cations and atmospheric CO_2 as a guest inorganic anion through contacting the decomposed mass with aqueous Mn(II) nitrate solution. The Mn-MgAl hydrotalcite showed very high catalytic activity, stability, and reusability in the liquid-phase selective oxidation of a wide range of alkylaromatics to their corresponding benzylic ketones, using atmospheric pressure of molecular O_2 as a sole oxidant under solvent-free and mild reaction conditions. The catalytic performance of Mn-MgAl hydrotalcite was found to be much higher than that of Mn-containing hydrotalcites prepared by different methods or MgAl hydrotalcite catalysts containing various other transition metals and synthesized through similar procedures.

Keywords: Oxidation; Alkylaromatics; Benzylic ketones; Molecular oxygen; Mn-MgAl hydrotalcite

1. Introduction

Aromatic ketones are important chemical intermediates in the pharmaceutical, fragrance, flavor, dye, and agrochemical industries [1,2]. Conventionally, these are produced through electrophilic acylation of aromatic compounds catalyzed by homogeneous Lewis acids (e.g., $AlCl_3$, BF_3, $FeCl_3$, $ZnCl_2$, $SnCl_4$, $TiCl_4$) or strong protonic acids (e.g., H_2SO_4, HF), which leads to the formation of a large volume of toxic and corrosive wastes [3]. In the past, alternative ways were sought to produce benzylic ketones by oxidizing the methylene group of alkylaromatics using stoichiometric quantities of $KMnO_4$ as an oxidizing agent [4]. However, in the above stoichiometric oxidation, the volume of waste produced is also very large; moreover, the separation of reactants and products from the liquid reaction mixture is difficult. Recently, there has been increased interest in the development of clean and economical catalytic processes for the synthesis of value-added product ketones by benzylic oxidation of alkylaromatics [5–22].

The current industrial production of benzylic ketones is based on the oxidation of alkylbenzenes with molecular oxygen using cobalt cycloalkanecarboxylate or cobalt acetate as catalyst in acetic acid media [7]. However, this method suffers from the corrosive nature of the solvent and a homogeneous feature of the catalyst. Hence, the use of heterogeneous catalysts in the liquid-phase oxidation, particularly of neat substrate, is a subject of considerable interest from the standpoint of environmental consciousness, because losses of both solvent and catalyst on separation can lead to unacceptable levels of waste.

A number of transition metal-containing heterogeneous solids based on Ru, Cu, Fe, Co, and Mn has been reported for the liquid-phase oxidation of alkylaromatics to ketones by molecular O_2 [15–22]. However, these earlier-reported solid

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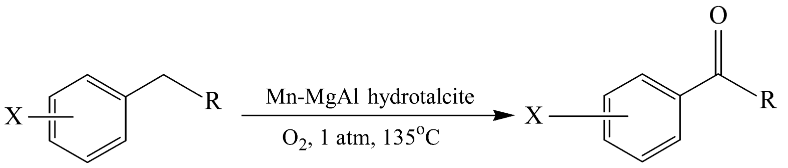


[where X = CH_3, C_6H_5, NH_2 or NO_2 and R = CH_3, C_3H_7 or C_6H_5]

Scheme 1.

catalysts suffer from limitations in the alkylaromatic oxidation reaction. The catalytic activity of Ru- and Cu-based heterogeneous solids is restricted only to doubly activated alkylaromatics, these catalysts being unable to oxidize ethylbenzene [15,17]. Although Fe- and Co-containing solids are active for ethylbenzene oxidation, the Fe porphyrin shows low acetophenone selectivity and inferior catalytic stability [18], and Co-based catalysts suffer from their poor reusability [19,20].

In contrast, the Mn-containing catalyst exhibits high activity in the ethylbenzene oxidation only after a long reaction period or at high oxygen pressure [21,22]. Among the various heterogeneous solids reported earlier, the catalytic performance of MnO_4^--exchanged MgAl hydrotalcite for the oxidation of ethylbenzene (which is difficult to oxidize due to the absence of an electron-donating aromatic ring-activating group under solvent-free reaction conditions) is interesting [22]. Choudhary et al. reported that $KMnO_4$, commonly used for oxidations, could be transformed into an active heterogeneous catalyst for oxidation of ethylbenzene to acetophenone by immobilization of MnO_4^- anions at the anion-exchange sites of highly basic MgAl hydrotalcite.

It is well known that the interlayer space of MgAl hydrotalcite, which is responsible for the accommodation of exchangeable anions, is very narrow (about 4 Å). Because MnO_4^- anion occupies the small interlayer space of hydrotalcite in MnO_4^--exchanged MgAl hydrotalcite, it is expected that the catalytically active Mn sites are only partially accessible even to a reactant as small as ethylbenzene. The low catalytic activity of MnO_4^--exchanged MgAl hydrotalcite in the ethylbenzene oxidation (TON, about 46 $\text{mol}\,\text{mol}^{-1}$) even at high oxygen pressure reported by Choudhary et al. seems to be the result of restricted accessibility of ethylbenzene through its narrow interlayer space [22]. Thus, to obtain maximum efficiency of Mn-containing hydrotalcite for the oxidation of a wide range of alkylaromatics by molecular oxygen, it is very important to heterogenize catalytically active Mn species into the hydrotalcite matrix in which most of the active sites will be accessible to even much larger reactants than ethylbenzene.

In this regard, we report here the synthesis of Mn-MgAl hydrotalcite, surface-enriched with Mn, by adopting the "memory effect" of hydrotalcite and its high oxidation activity for a wide range of alkylaromatics to their corresponding benzylic ketones by atmospheric pressure of molecular oxygen as the sole oxidant in the absence of any solvents and reducing reagents (Scheme 1). The catalytic activity of Mn-MgAl hydrotalcite in the ethylbenzene oxidation is compared with Mn-containing hydrotalcite/hydrotalcite-derived catalysts prepared by different methods and various other transition metals containing hydrotalcites synthesized by adopting the "memory effect" under identical experimental conditions. The reusability and stability of Mn-MgAl hydrotalcite for ethylbenzene oxidation is also investigated.

2. Experimental

Mn-MgAl hydrotalcites (prepared from MgAl hydrotalcites with Mg/Al molar ratios of 2.0–5.0 by providing Mn inputs of 0.25–1.0 mmol per g of hydrotalcite) were synthesized by adopting the "memory effect" of hydrotalcite [23,24]. In a typical procedure, a thermally decomposed hydrotalcite mass (calcined at 450 °C for 15 h) was reconstructed into the hydrotalcite structure along with Mn(II) cations by contacting with aqueous Mn(II) nitrate solution in the presence of atmospheric CO_2 (as a source of CO_3^{2-} anion) under stirring at room temperature for up to 12 h.

MgAl hydrotalcites with CO_3^{2-} as a guest inorganic anion were prepared by a modified version of the coprecipitation procedure reported in the literature [25]. In a typical method, a mixed aqueous solution of Mg^{2+} and Al^{3+} nitrates (with Mg/Al molar ratios of 2.0–5.0) were added dropwise to an aqueous Na_2CO_3 solution at 70 °C under vigorous stirring. The pH of the solution was adjusted to 10.5 ± 0.1 by adding aqueous NaOH solution, and the resulting gel-like material was aged at 90 °C for 12 h. The resultant slurry was then cooled to room temperature and separated by filtration, followed by washing with distilled water several times and drying at 100 °C for 20 h.

MnAl hydrotalcite with a Mn/Al molar ratio of 5.0 was synthesized by using CO_3^{2-} or NO_3^- as a guest inorganic anion in a procedure similar to that described above for the preparation of MgAl hydrotalcite.

MnO_4^--exchanged MgAl hydrotalcite with a MnO_4^- loading of 0.4 mmol per g of hydrotalcite was prepared by adopting the "memory effect" of hydrotalcite under stringent N_2 atmosphere at 80 °C for 5 days, to avoid the contact with atmospheric CO_2 during reconstruction, but otherwise similarly to the procedure reported previously [22]. Different transition metals, such as Ni-, Zn-, Cu-, Co-, Fe-, and Cr-containing MgAl hydrotalcites (prepared from MgAl hydrotalcite with a Mg/Al molar ratio of 5.0 by providing a metal input of 1.0 mmol per g of hydrotalcite) were synthesized following the procedure adopted for Mn-MgAl hydrotalcite. Mn/MgAl hydrotalcite or Mn/calcined MgAl hydrotalcite with a Mg/Al molar ratio of 5.0 was prepared by the conventional incipient wetness impregnation technique using an acetonic solution of Mn(II) nitrate.

Before catalytic use, all of the solid samples were treated further at 200 °C for 12 h. The phase(s) present in the different solid materials was confirmed by X-ray diffraction (XRD) (using a Mac Science M3X Model 1030 instrument equipped with a Cu$K\alpha$ radiations), surface area was measured by the N_2 adsorption–desorption method (using a Bell Japan Belsorp 28SA sorptometer), elemental analysis was performed on a Perkin-Elmer 240C elemental analyzer, surface composition was determined by a Shimadzu ESCA-3200 electron spectrometer, and the carbon analysis was conducted by a Perkin-Elmer 2400 Series II CHNS/O analyzer. The basicity of hydrotalcite and hydrotalcite-derived materials was measured by titrating them with nonaqueous benzoic acid using phenolphthalein ($pK_a = 9.3$) as an indicator.

H_2O_2 decomposition over the different hydrotalcite and hydrotalcite-derived catalysts was studied in a magnetically stirred glass reactor (capacity: 50 cm^3) at 60 °C by introducing 1 ml of 31% aqueous H_2O_2 solution in a reactor containing 0.1 g of powdered catalyst and 20 ml of distilled water and measuring quantitatively the amount of O_2 evolved in the H_2O_2 decomposition process ($H_2O_2 = H_2O + \frac{1}{2}O_2$) as a function of reaction time.

Catalytic oxidation of alkylaromatics in the absence of solvent over various Mn-based solids was carried out in a magnetically stirred glass reactor (capacity: 50 cm^3), equipped with a mercury thermometer and a reflux condenser. A continuous flow of oxygen (flow rate: 5.0 $cm^3\,min^{-1}$) was bubbled through a vigorously stirred liquid reaction mixture containing 100 mmol of alkylaromatics and the required amount of solid catalyst, in the form of fine powder, at 135 °C for up to 5 h. The reaction products (identified by comparing with the authentic samples) and unconverted alkylaromatics present in the reaction mixture were quantified by a gas chromatograph with a flame ionization detector using the internal standard method. TON was calculated based on mol of alkylaromatics converted per mol of Mn. The amount of ethylbenzene hydroperoxide in the reaction mixture was estimated by the standard iodometric titration method.

3. Results and discussion

3.1. Characterization of catalyst

XRD patterns of Mn-MgAl hydrotalcite (prepared from MgAl hydrotalcite with a Mg/Al molar ratio of 5 by providing Mn input of 1.0 mmol per g of hydrotalcite) obtained after various periods of reconstruction are presented in Fig. 1. XRD patterns of MnAl hydrotalcite prepared in the presence of CO_3^{2-} or NO_3^- as a guest inorganic anion, Mn/MgAl hydrotalcite, and Mn/calcined MgAl hydrotalcite are shown in Fig. 2. Figs. 1 and 2 show that by adopting the "memory effect" of hydrotalcite, Mn can be successfully incorporated into the hydrotalcite samples. In addition, the undesirable $MnCO_3$ phase observed in MnAl hydrotalcite prepared using CO_3^{2-} as a guest inorganic anion by the conventional coprecipitation method was not formed by adopting the postsynthesis method and the use of atmospheric CO_2 as a source of CO_3^{2-} guest inorganic anion for the incorporation of Mn into the MgAl hydrotalcite material (Figs. 1 and 2). The presence of CO_3^{2-} in the interlayer space of hydrotalcite is important for obtaining the sample with high basicity, which is beneficial for exhibiting the high alkylaromatic oxidation activity and/or ketone selectivity of the hydrotalcite-based catalysts [22]. The absence of $MnCO_3$ phase formation in the Mn-MgAl hydrotalcite prepared by the postsynthesis method seems to be due to the fact that the reconstruction of MgAl hydrotalcite leading to the incorporation of Mn into the hydrotalcite material is much faster than the formation of $MnCO_3$ from the reaction between aqueous Mn nitrate and atmospheric CO_2 under the present synthesis conditions. This seems to be due mainly to the presence of CO_2 in the aqueous phase at very low concentrations, as well as its high affinity to act as an interlayer anion for the reconstruction of hydrotalcite phase from its thermally decomposed mass.

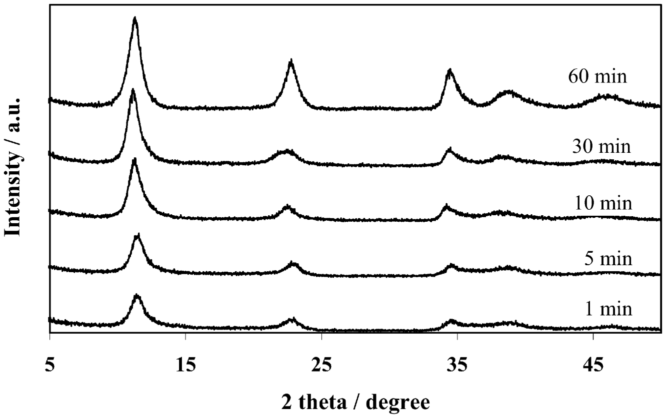


Fig. 1. X-ray diffraction patterns of Mn-MgAl hydrotalcite (prepared from MgAl hydrotalcite having Mg/Al molar ratio of 5.0 by providing Mn input of 1.0 mmol g^{-1} of hydrotalcite) obtained at different reconstruction time.

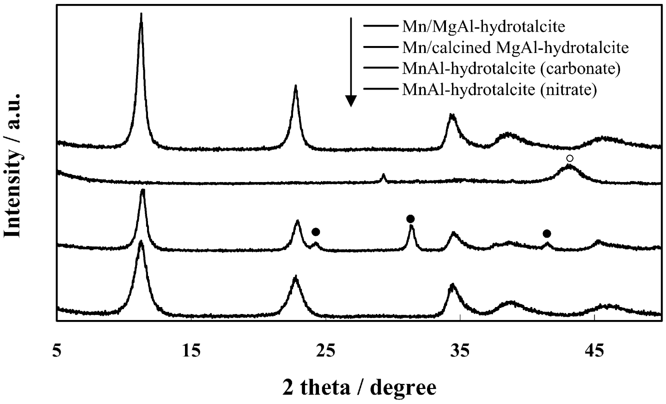


Fig. 2. X-ray diffraction patterns of MnAl hydrotalcite prepared in the presence of NO_3^- or CO_3^{2-} as a guest inorganic anion and Mn/MgAl hydrotalcite or Mn/calcined MgAl hydrotalcite (○, MgO phase; ●, $MnCO_3$ phase).

Fig. 3 shows the changes in metal content as a function of reconstruction period during the incorporation of Mn into MgAl hydrotalcite (with a Mg/Al ratio of 5 mol mol^{-1}). With increasing reconstruction time, the amount of Mn increased at the expense of Mg. A slight decrease in the Al content is also observed. This finding suggests that during reconstruction, a part

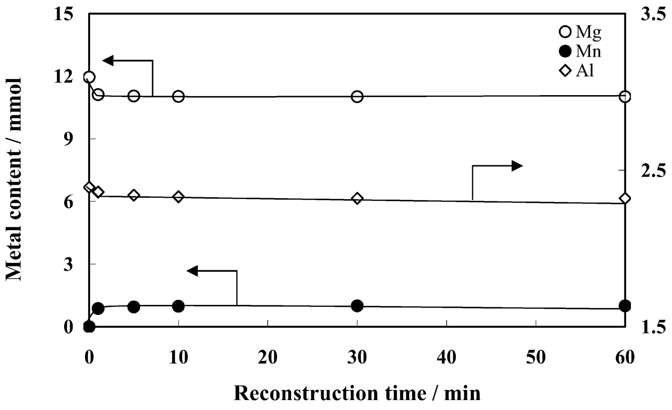


Fig. 3. Changes in the metal content in Mn-MgAl hydrotalcite (prepared from MgAl hydrotalcite having Mg/Al molar ratio of 5.0 by providing Mn input of 1.0 mmol g^{-1} of hydrotalcite) as a function of reconstruction time during the incorporation of Mn into MgAl hydrotalcite adopting the 'memory effect.'

of the Mg in MgAl hydrotalcite is replaced by Mn to form Mn-MgAl hydrotalcite. XPS analysis of the bulk and surface Mn compositions confirmed that in the Mn-MgAl hydrotalcite, Mn exists mostly on the surfaces of the hydrotalcite (Table 1). During the reconstruction process, Mg species present on the surfaces of MgAl hydrotalcite likely will be replaced by Mn, resulting in surface-enriched Mn in Mn-MgAl hydrotalcite.

The unusually drastic decrease in the BET surface area of magnesium–aluminum mixed oxide on contact with aqueous Mn(II) nitrate solution (from 134 to 31 $m^2\,g^{-1}$) suggests that during reconstruction of hydrotalcite from its thermally decomposed mass, the surface of the precursor material is covered by a dense layer, which seems to be Mn-MgAl hydrotalcite grown mostly over the surfaces of magnesium–aluminum mixed oxides. It is important to note that, in addition to the above phenomenon, another possible reason for the decreased surface area of the hydrotalcite material is simple rehydration, at least to some extent, as reported by Figueras et al. [26].

Comparison of XRD and ICP results reveals that the incorporation of Mn leading to the formation of Mn-MgAl hydrotalcite occurred very rapidly, even within 10 min of the reconstruction process (Figs. 1 and 3). However, the XRD peak intensities related to the hydrotalcite material increased gradually with increasing reconstruction time even after 10 min of reconstruction. This seems to be due to the continuous progress of reconstruction of MgAl hydrotalcite from its thermally decomposed mass even after complete incorporation of Mn into the hydrotalcite sample. This is expected because, compared with the amount of Mn used in the preparation of Mn-MgAl hydrotalcite, a large amount of Mg is present in the parent material. Thus, even after incorporation of the total amount of Mn, the replacement of equivalent amount of Mg into the hydrotalcite material means that a large amount of Mg is still available and seems to be gradually transformed into MgAl hydrotalcite material. This may be the reason for the progressive increase in the XRD peak intensities even after the complete incorporation of Mn into the MgAl hydrotalcite material. The gradual increases in the amount of carbon or, in other words, the amount of CO_3^{2-} (used mostly for the reconstruction of hydrotalcite from its thermally decomposed mass) with an increase in reconstruction time also support the above reaction pathway (Fig. 4). However, even after 12 h of reconstruction, the amount of CO_3^{2-} in Mn-MgAl hydrotalcite did not reach its theoretical value. This finding indicates that the reconstructed material contains

Table 1
Physicochemical properties of various Mn-containing hydrotalcite-based basic solids

Catalysts	Bulk Mn/[(Mn + Mg + Al) or (Mn + Al)] molar ratio	Surface Mn/(Mn + Mg + Al) molar ratio	BET surface area ($m^2\,g^{-1}$)	Basic sites (μmol g^{-1})[i]	$t_{1/2}$ for H_2O_2 decomposition (min)[j]
Mn-MgAl hydrotalcite (Mg/Al = 1.75)[a]	0.081	0.203	29	41	7.2
Mn-MgAl hydrotalcite (Mg/Al = 2.69)[b]	0.075	0.210	34	58	5.1
Mn-MgAl hydrotalcite (Mg/Al = 4.57)[c]	0.070	0.214	31	117	2.7
Mn-MgAl hydrotalcite (Mg/Al = 4.80)[d]	0.035	0.109	37	115	2.9
Mn-MgAl hydrotalcite (Mg/Al = 4.88)[e]	0.018	0.056	44	116	3.0
Mn/MgAl hydrotalcite (Mg/Al = 5)[f]	0.065	–	90	104	3.0
Mn/calcined MgAl hydrotalcite (Mg/Al = 5)[f]	0.040	–	139	110	2.6
MnAl hydrotalcite (Mn/Al = 5.07, CO_3^{2-})[g]	0.847	–	67	61	5.0
MnAl hydrotalcite (Mn/Al = 5, NO_3^-)[h]	0.831	–	51	20	20.4
MnO_4^--exchanged MgAl hydrotalcite	–	–	38	129	2.1
MgAl hydrotalcite (Mg/Al = 5)	–	–	93	106	3.0

[a] Mn loading 1.14 mmol g^{-1} of solid.

[b] Mn loading 1.18 mmol g^{-1} of solid.

[c] Mn loading 1.19 mmol g^{-1} of solid.

[d] Mn loading 0.59 mmol g^{-1} of solid.

[e] Mn loading 0.28 mmol g^{-1} of solid.

[f] Mn loading 1.0 mmol g^{-1} of solid.

[g] Prepared in the presence of CO_3^{2-} as a guest inorganic anion.

[h] Prepared in the presence of NO_3^- as a guest inorganic anion.

[i] 0.15 g hydrotalcite, suspended in 2 ml phenolphthalein indicator solution, is titrated with 0.01 M benzoic acid.

[j] Time required for half H_2O_2 decomposition (half of 1 ml of 31 wt% H_2O_2 by 0.1 g catalyst) at 60 °C.

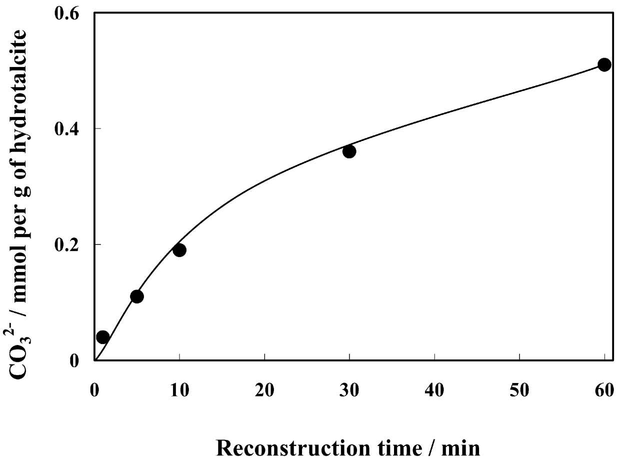


Fig. 4. Changes in the amount of CO_3^{2-} anion in Mn-MgAl hydrotalcite (prepared from MgAl hydrotalcite having Mg/Al molar ratio of 5.0 by providing Mn input of 1.0 mmol g^{-1} of hydrotalcite) as a function of reconstruction time during its preparation by adopting the 'memory effect.'

appreciable amounts of mixed-oxide material and suggests the formation of a thick layer of Mn-MgAl hydrotalcite over the magnesium–aluminum-type mixed oxides.

Based on the above findings, we propose that the formation of Mn-MgAl hydrotalcite by contacting magnesium–aluminum mixed oxide with aqueous Mn(II) cations proceeds through a dissolution–recrystallization mechanism. In the presence of aqueous acidic Mn(II) nitrate solution (pH about 4.5), Mg(II) cations in the mixed oxides tend to dissolve, while Mg(II) cations in the solution tend to form the hydrotalcite phase, probably due to self-organization as the motivating force, similar to that observed in the conventional coprecipitation method. The copresence of Mn(II) cation reasonably resulted in the incorporation of Mn(II) at the Mg(II) site. It is important here to note that in the initial course of reconstruction (particularly <5 min), the amount of Mn accumulated in the solid material was found to be slightly greater than the decrease in the amount of Mg, suggesting the presence of additional Mn(II) cations as absorbed or adsorbed species on the basic surfaces of MgAl hydrotalcite and/or hydrotalcite-derived solids (Fig. 3). This absorption or adsorption of acidic Mn (II) species on the basic material seems to occur in the early stage of dissolution. The slight decrease in the Al content observed during the preparation of Mn-MgAl hydrotalcite by the reconstruction process seems to be due to the partial dissolution of basic Al species in contact with aqueous acidic Mn(II) nitrate solution. Similar effects were observed for the incorporation of Mn into MgAl hydrotalcites with Mg/Al molar ratios of 2 and 3.

For various Mn-MgAl hydrotalcites with similar Mn loadings but different Mg/Al molar ratios, the number of basic sites, as measured by the nonaqueous benzoic acid titration method, is increased with an increasing Mg/Al ratio (Table 1). Similar effects of Mg/Al ratios in the Mn-MgAl hydrotalcites on the H_2O_2 decomposition activity (at 60 °C) are also observed. This is expected because the H_2O_2 decomposition activity of hydrotalcite is due mostly to its basicity. Thus, with increasing basic sites of Mn-MgAl hydrotalcite, the $t_{1/2}$ for H_2O_2 decomposition is decreased, or, in other words, the H_2O_2 decomposition activity is increased (Table 1). An increased Mn content in Mn-MgAl hydrotalcites (prepared from MgAl hydrotalcites with similar Mg/Al ratios) does not affect the basicity but does slightly increase the H_2O_2 decomposition activity.

3.2. Alkylaromatics oxidation by molecular O_2

To develop highly active Mn-containing hydrotalcite-based heterogeneous solids for the oxidation of ethylbenzene (which is difficult to oxidize due to the absence of an electron-donating aromatic ring-activating group), we studied ethylbenzene oxidation with molecular oxygen on hydrotalcite and hydrotalcite-derived catalysts (Table 2). Generally, acetophenone is the major product, along with minor quantities of benzaldehyde and 1-phenylethanol and traces of ethylbenzene hydroperoxide in the ethylbenzene oxidation over Mn-based solids.

Among the various Mn-containing hydrotalcite and hydrotalcite-derived catalysts used in the present study, the Mn-MgAl hydrotalcites are most efficient for the oxidation of ethylbenzene to acetophenone with atmospheric pressure of molecular oxygen even in the absence of any solvents and reducing reagents (entries 1–5). Mn-MgAl hydrotalcite with a Mg/Al molar ratio close to 5 shows the best performance. MnAl hydrotalcite prepared by the conventional co-precipitation method using CO_3^{2-} or NO_3^- as a guest inorganic anion is also active for ethylbenzene oxidation reaction; however, the TON over both of these catalysts is low compared with that of the Mn-MgAl hydrotalcites (entries 10 and 11). It is interesting to note that among the different Mn-containing hydrotalcite and hydrotalcite-derived catalysts, MnAl hydrotalcite prepared in the presence of NO_3^- as a guest inorganic anion shows lower acetophenone selectivity. This is due to the presence of ethylbenzene hydroperoxide in the reaction mixture, which apparently is related to the lower basicity of the catalyst (Table 1). The MnO_4^--exchanged MgAl hydrotalcite synthesized following a procedure similar to that reported by Choudhary et al. (entry 12) also exhibits lower catalytic activity compared with the Mn-MgAl hydrotalcite. The TON of Mn-MgAl hydrotalcite is about 4.5 times higher than that of the MnO_4^--exchanged MgAl hydrotalcite in the ethylbenzene oxidation under similar experimental conditions. Mn/MgAl hydrotalcite, Mn/calcined MgAl hydrotalcite, and MgAl hydrotalcite without Mn show very low ethylbenzene oxidation activity (entries 8, 9, and 13).

The ethylbenzene oxidation activity of Mn-MgAl hydrotalcites with similar Mn contents (i.e., close to 1.18 mmol per g of hydrotalcite solid) but different Mg/Al molar ratios ($Mg/Al = 1.75$ to 4.57 mol mol^{-1}) varies significantly depending on the Mg/Al ratio (entries 1–3). The higher the Mg/Al ratio (in other words, the higher the basicity), the higher the ethylbenzene oxidation activity. Choudhary et al. observed a similar effect for MnO_4^--exchanged MgAl hydrotalcite for ethylbenzene oxidation. The beneficial effect of basicity in the alkylaromatic oxidation reaction is quite well known; aqueous alkali has been widely used industrially for the transformation of alkylbenzene to alkylbenzene hydroperoxide by molecular oxygen [27]. It is important here to note that the catalytic activity of Mn-MgAl

Table 2
Results on ethylbenzene oxidation over various Mn-containing basic solid catalysts [reaction conditions: ethylbenzene = 100 mmol, catalyst = 0.4 mmol based on Mn, oxygen flow = 5 ml min^{-1}, temperature = 135 °C, and reaction time = 5 h]

Entry	Catalysts	Conversion (%)	Ketone selectivity (%)	TON (mol mol^{-1})[j]
1	Mn-MgAl hydrotalcite (Mg/Al = 1.75)[a]	37.4	96.3	93.5
2	Mn-MgAl hydrotalcite (Mg/Al = 2.69)[b]	41.1	96.0	102.7
3	Mn-MgAl hydrotalcite (Mg/Al = 4.57)[c]	47.3	96.5	118.2
4	Mn-MgAl hydrotalcite (Mg/Al = 4.80)[d]	49.1	96.9	122.7
5	Mn-MgAl hydrotalcite (Mg/Al = 4.88)[e]	50.3	96.7	125.6
6	Mn-MgAl hydrotalcite (Mg/Al = 4.88)[e,f]	51.0	96.5	127.5
7	Mn-MgAl hydrotalcite (Mg/Al = 4.88)[e,g]	0.9	98.6	–
8	Mn/MgAl hydrotalcite (Mg/Al = 5)[h]	0.7	95.2	–
9	Mn/calcined MgAl hydrotalcite (Mg/Al = 5)[h]	0.6	95.1	–
10	MnAl hydrotalcite (Mn/Al = 5.07, CO_3^{2-})[i]	26.1	94.7	2.8
11	MnAl hydrotalcite (Mn/Al = 5, NO_3^-)[i]	23.5	81.3	2.5
12	MnO_4^--exchanged MgAl hydrotalcite (Mg/Al = 5)	10.7	95.8	26.8
13	MgAl hydrotalcite (Mg/Al = 5)	0.4	100	100

[a] Mn loading 1.14 mmol g^{-1} of solid.
[b] Mn loading 1.18 mmol g^{-1} of solid.
[c] Mn loading 1.19 mmol g^{-1} of solid.
[d] Mn loading 0.59 mmol g^{-1} of solid.
[e] Mn loading 0.28 mmol g^{-1} of solid.
[f] Fourth reuse of the catalyst.
[g] Presence of 5.0 mmol of hydroquinone.
[h] Mn loading 1.0 mmol g^{-1} of solid.
[i] Amount of catalyst = 9.3 mmol Mn.
[j] TON is calculated based on total amount of Mn present in the catalyst.

hydrotalcite prepared with MgAl hydrotalcite with a Mg/Al molar ratio of ca. 5 increases slowly with decreasing Mn loading, even though the amount of Mn used for the reactions is kept constant at 0.4 mmol (entries 3–5). Comparing the physicochemical properties of the above catalysts suggest that the higher catalytic performance (based on TON) of the catalyst with lower Mn loading seems to be due in part to the larger portion of the surface-exposed catalytically active Mn species as a result of the formation of a relatively thin layer of Mn-MgAl hydrotalcite over the magnesium–aluminum mixed oxide. This is supported by the small decrease in the BET surface area of Mn-MgAl hydrotalcite with lower Mn loading compared with that with higher Mn loading (Table 1). Among the different Mn-MgAl hydrotalcites with Mg/Al molar ratios of 1.75–4.88 and Mn content of 0.28–1.19 mmol per g of hydrotalcite, the catalyst with the Mg/Al ratio of 4.88 mol mol^{-1} and Mn loading of 0.28 mmol per g of hydrotalcite shows the highest activity in the oxidation of ethylbenzene to acetophenone.

The foregoing findings demonstrate that among the various Mn-containing hydrotalcite and hydrotalcite-based solids, the Mn-MgAl hydrotalcites prepared by adopting the "memory effect" of hydrotalcite are highly efficient catalysts for the ethylbenzene oxidation reaction using atmospheric pressure of molecular oxygen as the sole oxidant. The catalytic activity order of different Mn-containing hydrotalcite-based solids used in the present study is as follows: Mn-MgAl hydrotalcite ≫ MnO_4^--exchanged MgAl hydrotalcite ≫ MnAl hydrotalcite ≫ Mn/MgAl hydrotalcite or Mn/calcined MgAl hydrotalcite.

The very low catalytic activity of Mn/MgAl hydrotalcite and Mn/calcined MgAl hydrotalcite (Table 2, entries 8 and 9) in comparison with the high activity of MnAl hydrotalcite or Mn-MgAl hydrotalcites (Table 2, entries 1–5 and 10–12) in the oxidation of ethylbenzene indicates that the Mn species not included in the brucite-like structure of hydrotalcite exhibit almost no activity for this reaction, because it is reasonable to suppose that Mn is not incorporated in the brucite structure in the supported catalysts. On the other hand, in MnAl hydrotalcite and Mn-MgAl hydrotalcite, Mn is present in association with Al in the brucite-like structure, which seems to be responsible for their high alkylaromatic oxidation activity. Meanwhile, the comparatively lower activity (based on TON) of MnAl hydrotalcite prepared by the coprecipitation method compared with Mn-MgAl hydrotalcite synthesized by adopting the "memory effect" for ethylbenzene oxidation seems to be due to the presence of smaller numbers of accessible catalytically active Mn species. Compared with the total amount of Mn present in the MnAl hydrotalcite, a very small fraction of Mn species available on the outer surfaces are accessible only for their catalytic activities. On the other hand, in Mn-MgAl hydrotalcite, most of the Mn species are present on the surface and thus are accessible to the reactants in the oxidation reaction. The participation of surface-exposed Mn species as the main catalytic active centers is supported by the high oxidation activity of Mn-MgAl hydrotalcite for various bulky alkylaromatics substrate (Table 4). The low catalytic performance of MnO_4^--exchanged MgAl hydrotalcite seems to be due mainly to its presence in the narrow interlayer space of hydrotalcite, resulting in its restricted accessibility to the reactant. Apart from this, the other possible reason for the different catalytic performance of Mn-MgAl hydrotalcite and MnO_4^--exchanged MgAl hydrotalcite could be the presence of different catalytically active species, that is, Mn in different oxidation states.

To compare the catalytic activity of Mn-MgAl hydrotalcite with other transition metals containing hydrotalcites for ethylbenzene oxidation, a number of layered double hydroxides containing various transition metals (e.g., Ni, Zn, Cu, Co, Fe, Cr) were prepared in a procedure similar to that used for the incorporation of Mn into the MgAl hydrotalcite material, and the activities were tested under similar experimental conditions (Table 3). Of the various transition metal-based hydrotalcite catalysts, Ni-MgAl hydrotalcite exhibits the best catalytic performance in ethylbenzene oxidation; however, the activity of Ni-MgAl hydrotalcite is be significantly lower than that of Mn-MgAl hydrotalcite. The other transition metals containing hydrotalcite catalysts show significantly lower activities. Note that the Mn-MgAl hydrotalcite exhibits slightly lower acetophenone selectivity compared with the other transition metal-containing MgAl hydrotalcite-based solid catalysts.

To rule out the possibility of homogeneous reaction caused by leaching of active catalytic components in the oxidation of ethylbenzene in the presence of Mn-MgAl hydrotalcite (with a Mg/Al ratio of 4.88 mol mol^{-1} and a Mn loading of 0.28 mmol per g of hydrotalcite), the solid catalyst was filtered off from the hot liquid reaction mixture after 1 h of reaction, and the oxidation was continued with the resulting filtrate for another 4 h. The ethylbenzene conversion and acetophenone selectivity of 10.3% and 98.1%, respectively, after 1 h of reaction are not changed significantly even after additional 4 h of reaction under the above conditions; indicating that the leached-out metal ions (if any) are not responsible for the observed activity and/or selectivity (results not shown). ICP analysis of the resulting filtrate obtained after 5 h of reaction indicates the presence of Mn in traces (at only the ppb level).

Table 3

Catalytic results on ethylbenzene oxidation over various transition metal-containing MgAl hydrotalcites [reaction conditions: ethylbenzene = 100 mmol, catalyst = 0.4 mmol based on transition metal, oxygen flow = 5 ml min^{-1}, temperature = 135 °C, and time = 5 h]

Catalyst	Conversion (%)	Ketone selectivity (%)
Mn-MgAl hydrotalcite	47.3	96.5
Ni-MgAl hydrotalcite	29.7	99.4
Zn-MgAl hydrotalcite	0.3	100
Cu-MgAl hydrotalcite	2.1	99.5
Co-MgAl hydrotalcite	3.2	99.6
Fe-MgAl hydrotalcite	0.5	100
Cr-MgAl hydrotalcite	1.1	99.5

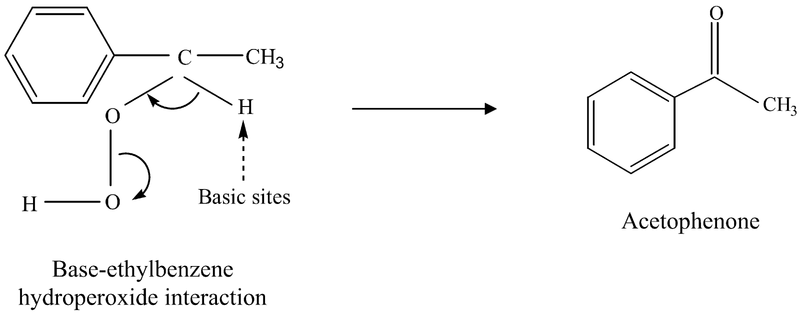
In addition, to confirm the advantage of the heterogeneous nature of Mn-MgAl hydrotalcite in liquid-phase oxidation process, we reused the Mn-MgAl hydrotalcite in ethylbenzene oxidation several times, after its separation from the hot liquid reaction mixture followed by washing with reactant ethylbenzene while avoiding the loss of catalyst fine particles. No significant changes in activity and acetophenone selectivity are observed even after the fourth successive reuse of the catalyst in the oxidation reaction (Table 2, entry 6). Inconsistent with the ICP analysis of the filtrate, the Mn content in the used catalyst is quite similar to that in the fresh catalyst. The XRD pattern of the fresh catalyst is not significantly changed after the oxidation reaction (results not shown). Moreover, the surface area of the used catalyst is also found to be similar, 41 $\text{m}^2\,\text{g}^{-1}$, compared with 44 $\text{m}^2\,\text{g}^{-1}$ for the fresh catalyst. The foregoing results indicate that Mn-MgAl hydrotalcite is quite stable and reusable in liquid-phase ethylbenzene oxidation under the present reaction conditions.

The Mn-MgAl hydrotalcite showing the best catalytic performance in the present study was also further evaluated for the oxidation of a wide range of alkylaromatics to their corresponding benzylic ketones using atmospheric pressure of molecular oxygen as a sole oxidant at 135 °C under solvent-free condition to investigate the scope and limitation of this oxidation process. As shown in Table 4, alkylbenzene conversion is high in most cases, even under solvent-free reaction conditions. In all cases, the $\text{–CH}_2\text{–}$ group of alkylaromatics is selectively converted to the –CO– group, indicating high chemoselectivity in the oxidation. Alkylbenzenes with different alkyl chain lengths of C_2 and C_4 are transformed into the corresponding benzylic ketones at moderate yield (about 50%) and conversion is not affected significantly with the chain length of substrate (entries 1, 2). The ethylbenzene derivatives possessing an electron donating substituent such as –CH_3 or –NH_2 at the 4-position afford the corresponding acetophenones in good yield (62–65%) (entries 3, 4). The amine function is intact under the present reaction conditions. The presence of the electron-withdrawing substituent –NO_2 group adversely affects the corresponding acetophenone yield (entry 5). Bulky alkylarenes, such as diphenylmethane and 4-ethylbiphenyl, are also oxidized to give the corresponding oxygenated products in very high yield (70–79%) (entries 6, 7). In all cases, only the benzylic C–H bonds of alkylaromatics are oxidized selectively to their corresponding ketones.

Table 4

Results on oxidation of various alkylaromatics catalyzed by Mn-MgAl hydrotalcite prepared from MgAl hydrotalcite having a Mg/Al molar ratio of 5 and Mn loading of 0.28 mmol per g of solid [reaction conditions: alkylaromatics = 100 mmol, catalyst = 0.4 mmol based on Mn, oxygen flow = 5 ml min^{-1}, temperature = 135 °C, and time = 5 h]

Entry	Alkylaromatics	Conversion (%)	Major product	Ketone selectivity (%)
1	Ethylbenzene	50.3	Acetophenone	96.7
2	Butylbenzene	49.7	Butyrophenone	94.1
3	4-Methylethylbenzene	62.8	4-Methylacotophenone	97.0
4	4-Aminoethylbenzene	65.1	4-Aminoacetophenone	95.1
5	4-Nitroethylbenzene	1.8	4-Nitroacetophenone	96.8
6	Diphenylmethane	70.1	Benzophenone	95.1
7	4-Phenylethylbenzene	78.5	4-Phenylacetophenone	92.7



Scheme 2.

Although the mechanism of oxygen activation and transfer by the Mn-containing hydrotalcite-based basic catalyst for alkylaromatic oxidation remains incompletely understood, the finding of traces of ethylbenzene hydroperoxide in the reaction mixture suggests that the reaction proceeds through the formation of ethylbenzene hydroperoxide as an active intermediate. The formation of ethylbenzene hydroperoxide through redox processes was confirmed by analyzing the presence of Mn species in two different oxidation states, +2 and +3 (as observed from XPS analysis), in the catalyst obtained after ethylbenzene oxidation. The transformation of ethylbenzene to ethylbenzene hydroperoxide by free-radical pathway is confirmed by the drastic decrease in ethylbenzene oxidation activity of Mn-MgAl hydrotalcite on addition of hydroquinone as a free-radical scavenger (Table 2, entry 7). Based on the four identified products in the ethylbenzene oxidation reaction we speculate that the ethylbenzene oxidation involves the following reactions over the Mn-based hydrotalcite catalysts:

$$C_6H_5\text{–}CH_2\text{–}CH_3 + O_2 \rightarrow C_6H_5\text{–}CH(OOH)\text{–}CH_3,$$
$$C_6H_5\text{–}CH(OOH)\text{–}CH_3 \rightarrow C_6H_5\text{–}CO\text{–}CH_3 + H_2O,$$
$$C_6H_5\text{–}CH(OOH)\text{–}CH_3 \rightarrow C_6H_5\text{–}CHO + CH_3OH,$$
$$C_6H_5\text{–}CH(OOH)\text{–}CH_3 \rightarrow C_6H_5\text{–}CH(OH)\text{–}CH_3 + 0.5O_2.$$

The above reaction scheme suggests that the intermediate ethylbenzene hydroperoxide can be converted into three different types of products: acetophenone, benzaldehyde and 1-phenylethanol. Because the basicity of Mn-containing hydrotalcite is responsible for exhibiting high acetophenone selectivity, we believe that the basic sites of the hydrotalcite catalyst can selectively transform the intermediate ethylbenzene hydroperoxide to yield acetophenone under the reaction conditions as shown in Scheme 2. This assumption is supported by the fact that MnAl hydrotalcite prepared using NO_3^- with lower basicity exhibited lower acetophenone selectivity compared with the MnAl hydrotalcite or Mn-MgAl hydrotalcite synthesized in the presence of CO_3^{2-} as a guest inorganic anion with higher basicity. Further investigations into the detailed reaction mechanism including the role of basic sites are in progress.

4. Conclusion

Mn was successfully incorporated onto the surface of MgAl hydrotalcite by the postsynthesis method in the presence of atmospheric CO_2 as a source of the CO_3^{2-} anion. The surface-enriched Mn in Mn-MgAl hydrotalcite showed very high catalytic activity in the oxidation of various alkylaromatics to their corresponding benzylic ketones with atmospheric pressure of molecular oxygen as the sole oxidant under solvent-free and mild reaction conditions. The catalytic performance of Mn-MgAl hydrotalcite postsynthesized by adopting the "memory effect" was found to be much higher than that of MnAl hydrotalcite prepared by a conventional coprecipitation technique or MnO_4^--exchanged MgAl hydrotalcite synthesized by adopting the "memory effect." We have confirmed that the Mn-MgAl hydrotalcite is stable and reusable in the reaction.

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