NiAl hydrotalcite as an efficient and environmentally friendly solid catalyst for solvent-free liquid-phase selective oxidation of ethylbenzene to acetophenone with 1 atm of molecular oxygen

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Abstract

NiAl hydrotalcites with Ni/Al molar ratios of 2–5 and prepared using CO_3^{2-}, Cl^-, NO_3^-, or SO_4^{2-} as a guest inorganic anion, were evaluated for the liquid-phase selective oxidation of a methylene group of ethylbenzene to carbonyl functionality with atmospheric pressure of oxygen as the sole oxidant under solvent-free and mild reaction conditions. Among the different NiAl hydrotalcites, the catalyst with a Ni/Al ratio of 5 $mol\,mol^{-1}$ prepared in the presence of CO_3^{2-} anion exhibited the greatest catalytic activity for the ethylbenzene oxidation reaction. NiAl hydrotalcite prepared with CO_3^{2-} as a guest inorganic anion also showed very high acetophenone selectivity ($>99\%$) compared with those prepared using Cl^-, NO_3^-, or SO_4^{2-} anions. Compared with other transition metal–containing hydrotalcite-like solid catalysts (e.g., CuAl-, ZnAl-, CoAl-, MgFe-, MgCr-), with similar molar compositions and prepared in the presence of the CO_3^{2-} anion, the catalytic activity of NiAl hydrotalcite was much higher in the above oxidation reaction. The active NiAl hydrotalcite also exhibited good catalytic performance for the oxidation of a wide range of alkylaromatics to their corresponding benzylic ketones under similar experimental conditions. The NiAl hydrotalcite can be easily prepared from cheap, commercially available reagents and is stable and reusable for the ethylbenzene oxidation even in the absence of solvents and reducing reagents.
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1. Introduction

Aromatic ketones are important chemical intermediates for the synthesis of a various perfumes, drugs, and pharmaceuticals. Production of these ketones by Friedel–Crafts acylation of aromatics by acyl halide or acid anhydride, using stoichiometric quantities of homogeneous acid, leads to the formation of a large volume of toxic and corrosive wastes [1]. Previously, efforts have been made to produce benzylic ketones by oxidizing the methylene group of alkylaromatics using stoichiometric quantities of $KMnO_4$ as an oxidizing agent [2]. However, in the above stoichiometric oxidation, the volume of waste pro-

duced is also very large, and separating reactants and products from the liquid reaction mixture is difficult. Recently, there has been increased interest in developing clean, economical catalytic processes for synthesizing value-added product ketones by benzylic oxidation of alkylaromatics [3–20]. The current industrial production of benzylic ketones is based on the oxidation of alkylbenzenes with molecular oxygen using cobalt cycloalkanecarboxylate or cobalt acetate as a catalyst in acetic acid [5]. But this method suffers from the corrosive nature of the solvent and homogeneous characteristics of the catalyst. Hence, the use of heterogeneous catalysts in 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. So far, a few transition metal-
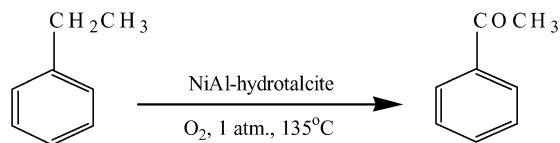
Scheme 1.

containing heterogeneous solids based on Ru, Cu, Fe, Co, and Mn have been reported for the liquid-phase oxidation of alkylaromatics to ketones by molecular O_2 [13–20]. To the best of our knowledge, however, no report is available in the literature on the oxidation of alkylaromatics by a nickel catalyst with molecular oxygen. Layered double hydroxides (hydrotalcites) have received much attention because of their potential for shape recognition of guest materials, catalysts, catalyst supports, and ion exchangers [21–23]. Various kinds of transition metal cations as potential catalytic active centers can be readily incorporated into the hydrotalcite framework via their isomorphic substitution for Mg^{II} or Al^{III} cations at the octahedral sites of the Brucite-like layers. In addition, the surface basicities can be tuned by changing the anionic species in the interlayer.

This paper reports for the first time the activation of molecular oxygen by a Ni-containing basic hydrotalcite catalyst for the selective oxidation of benzylic C–H bonds of ethylbenzene (which is difficult to oxidize due to the absence of an electron-donating aromatic ring-activating group) to acetophenone (Scheme 1) in the absence of any solvents and reducing reagents. In addition, the effect of the amount of Ni and the presence of different guest inorganic anions (e.g., CO_3^{2-}, Cl^-, NO_3^-, SO_4^{2-}) in the Ni-containing hydrotalcite on their oxidation activity and/or acetophenone selectivity is thoroughly investigated. The catalytic activity of NiAl hydrotalcite is compared with that of other transition metal-containing hydrotalcite-like solids for ethylbenzene oxidation under similar experimental conditions. Moreover, the oxidation of a series of alkylaromatics over the best NiAl hydrotalcite catalyst is studied to explore the scope and limitations of this oxidation process. The reusability and stability of NiAl hydrotalcite for the ethylbenzene oxidation is also investigated.

2. Experimental

NiAl hydrotalcites were prepared by a modified version of the coprecipitation procedure reported previously [24]. In a typical procedure, a mixed aqueous solution of Ni^{2+} and Al^{3+} nitrates (with Ni/Al molar ratios ranging from 2.0 to 5.0) were added dropwise to an aqueous solution of a guest inorganic anion (e.g., NaCl, Na_2CO_3, $NaNO_3$, Na_2SO_4) under vigorous stirring. The solution pH was adjusted to 10.5 ± 0.1 by adding aqueous NaOH, and the resulting gel-like material was aged at $40\,^\circ$C for 1 h. The resultant slurry was then cooled to room temperature and separated by filtration, washed with distilled water several times, and dried at $100\,^\circ$C for 20 h. Ni-containing MgAl hydrotalcites with Mg/Al molar ratios ranging from 2.0 to 5.0 but with similar Ni content (ca. 1.0 mmol per g of hydrotalcite) were synthesized by adopting the "memory effect" of hydrotalcite. In a typical procedure, a thermally decomposed

hydrotalcite mass (calcined at $500\,^\circ$C for 5 h) was reconstructed into the hydrotalcite structure along with Ni cations by allowing it to contact aqueous Ni^{II} nitrate solution. Ni/γ-Al_2O_3 catalysts were prepared by the incipient-wetness impregnation technique using aqueous $Ni(NO_3)_2$ solution. Before catalytic use, all of the materials were further heated at $200\,^\circ$C for 12 h. The hydrotalcite structure of the catalysts was confirmed by X-ray diffraction (XRD) (using a Mac Science M3X model 1030 instrument equipped with a Cu-K_α radiation source), surface area was measured by the N_2 adsorption–desorption method at $-196\,^\circ$C (using a Bell Japan Belsorp 28SA sorptometer), elemental analysis was performed on a Perkin–Elmer 240C elemental analyzer, surface composition was determined by an Shimadzu ESCA-3200 electron spectrometer, and the crystal size was obtained by a Hitachi S-5200 scanning electron microscope. The basicity of the hydrotalcite materials was examined by titrating them with nonaqueous benzoic acid using phenolphthalein ($pK_a = 9.3$) as an indicator and/or measuring the pH of their suspension in water (0.30 g of catalyst in 20 mL of deionized water at $27\,^\circ$C).

The catalytic oxidation of alkylbenzenes in the absence of solvent over different solid catalysts 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 the vigorously stirred reaction mixture, containing 122.5 mmol of alkylbenzene and a required amount of solid catalyst, in the form of fine powder, at $135\,^\circ$C for up to 5 h. The reaction products (identified by comparison with authentic samples) and unconverted alkylbenzene present in the reaction mixture were quantified with a gas chromatograph equipped with a flame ionization detector using the internal standard method; the selectivity was calculated based on alkylbenzene. Turnover number (TON) was calculated based on the mol of alkylaromatics converted per mol of Ni. The amount of ethylbenzene hydroperoxide in the reaction mixture was estimated by the standard iodometric titration method.

The H_2O_2 decomposition over the different hydrotalcite catalysts was studied in a magnetically stirred glass reactor (capacity, 50 mL) at $60\,^\circ$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 ($H_2O_2 = H_2O + (1/2)O_2$) as a function of reaction time.

3. Results and discussion

3.1. Catalyst characterization

Data on the characterization of different NiAl hydrotalcites for Ni/Al ratios in the product and their surface areas are given in Table 1. The formation of the hydrotalcite phase was confirmed by XRD. The XRD patterns for NiAl hydrotalcites with a Ni/Al molar ratio of 5.0 prepared in the presence of four different guest inorganic anions (CO_3^{2-}, Cl^-, NO_3^-, or SO_4^{2-}) are presented in Fig. 1. Hydrotalcite catalysts were also characterized for their basicity and H_2O_2 decomposition activity; the results are given in Table 2.

Table 1

Physico-chemical characteristics of the NiAl-hydrotalcites having different Ni/Al molar ratios prepared using four different guest inorganic anions

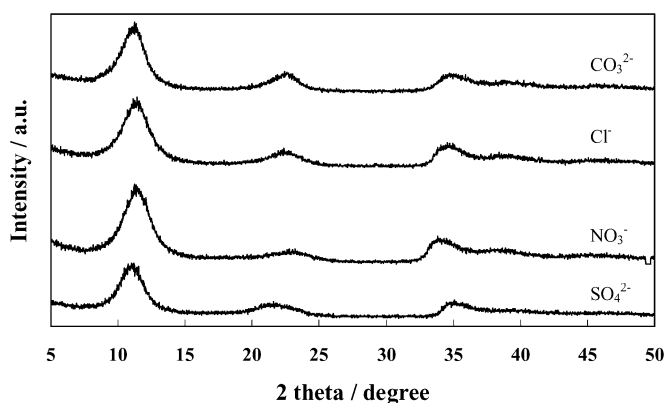| Guest inorganic anion	Ni/Al molar ratio		Surface area $(m^2\,g^{-1})$
	In the gel	In the product	
CO_3^{2-}	2.0	1.85	86
CO_3^{2-}	3.0	2.83	91
CO_3^{2-}	4.0	3.80	90
CO_3^{2-}	5.0	4.82	92
Cl^-	5.0	5.02	71
NO_3^-	5.0	5.05	53
SO_4^{2-}	5.0	4.98	61

Fig. 1. Representative X-ray diffraction patterns of NiAl-hydrotalcite having a Ni/Al molar ratio of 5.0 prepared in the presence of CO_3^{2-}, Cl^-, NO_3^- or SO_4^{2-} as a guest inorganic anion.

Table 2

Basicity and H_2O_2 decomposition activity of NiAl-hydrotalcites having different Ni/Al molar ratios prepared using four different guest inorganic anions

Ni/Al molar ratio in the gel	Inorganic anion	pH of suspension in water[a]	µmol basic sites per g of hydrotalcite[b]	$t_{1/2}$ for H_2O_2 decomposition (min)[c]
2	CO_3^{2-}	8.1	16	27.8
3	CO_3^{2-}	8.3	20	22.3
4	CO_3^{2-}	8.7	27	16.6
5	CO_3^{2-}	9.4	48	5.1
5	Cl^-	8.0	–	39.5
5	NO_3^-	7.8	–	43.2
5	SO_4^{2-}	7.1	–	65.3

[a] Suspension of 0.3 g hydrotalcite in 20 mL deionized water.
[b] 0.15 g hydrotalcite, suspended in 2 mL phenolphthalein indicator solution, is titrated with 0.01 M benzoic acid.
[c] Time required for half H_2O_2 decomposition (half of 1 mL of 31% H_2O_2 by 0.1 g catalyst) at 60 °C.

The surface and bulk properties of NiAl hydrotalcites vary depending on the Ni/Al molar ratios and/or the presence of guest inorganic anions (Table 1). No significant differences and/or trends are observed in surface areas of the NiAl hydrotalcite with different Ni/Al ratios prepared with CO_3^{2-} anions. However, the surface areas vary markedly for the NiAl hydrotalcite with a Ni/Al molar ratio of 5.0 prepared in the presence of different guest inorganic anions; the catalyst prepared with CO_3^{2-} has the highest surface area, and that prepared with NO_3^- has the lowest surface area.

The effect of Ni/Al ratios and the presence of guest inorganic anions on the basicity (measured in terms of pH of hydrotalcite–water slurry) and the number of basic sites (obtained by non-aqueous benzoic acid titration) of NiAl hydrotalcites suggest that both basicity and number of basic sites of the hydrotalcite increase with increasing Ni/Al ratio for the hydrotalcite prepared with CO_3^{2-} as a guest inorganic anion. The basicity and the number of basic sites of NiAl hydrotalcite with a Ni/Al ratio of 5.0 mol mol^{-1} prepared in the presence of different guest inorganic anions is $CO_3^{2-} > Cl^- > NO_3^- > SO_4^{2-}$ (Table 2). Similar effects of Ni/Al ratios and the presence of guest inorganic anions in NiAl hydrotalcites on H_2O_2 decomposition activity (at 60 °C) are also observed. This is expected because the H_2O_2 decomposition activity of hydrotalcite is mostly responsible for its basicity. Hence with increasing basicity and/or basic sites of NiAl hydrotalcites, the half-life, $t_{1/2}$, for H_2O_2 decomposition is decreased; in other words, H_2O_2 decomposition activity is increased.

The FE-SEM images in Fig. 2 show that all of the NiAl hydrotalcite materials with Ni/Al molar ratio of 5.0 prepared with four different guest inorganic anions form plate-like agglomerated crystals. However, the size of the plates depends on the guest inorganic anion. NiAl hydrotalcite prepared with CO_3^{2-} shows a smaller plate size compared with those prepared with NO_3^-, Cl^-, or SO_4^{2-} as a guest inorganic anion.

3.2. Catalytic reaction

To identify and develop the suitable Ni-containing heterogeneous solids for the oxidation of ethylbenzene (which is difficult to oxidize due to the absence of electron-donating aromatic ring activating group), a study of hydrotalcite and supported nickel catalyst with different Ni contents was undertaken using molecular oxygen as an oxidant (Table 3). Generally, acetophenone was found to be the main product, along with minor quantities of benzaldehyde and traces of ethylbenzene hydroperoxide.

Based on the catalytic results, the following important observations can be made:

– NiAl hydrotalcite was found to be the active catalyst for the oxidation of ethylbenzene to acetophenone with atmospheric pressure of molecular oxygen even in the absence of solvents and reducing reagents (entries 1–7). However, Ni supported on γ-Al_2O_3 with different compositions showed no ethylbenzene oxidation activity under similar experimental conditions (entries 8 and 9).
– Ethylbenzene oxidation activity of NiAl hydrotalcites (with Ni/Al molar ratio of 5) prepared with four different guest inorganic anions (CO_3^{2-}, Cl^-, NO_3^-, or SO_4^{2-}) varied significantly depending on their presence in the hydrotalcite material (entries 4–7). Among these, the catalyst prepared with CO_3^{2-} showed the best performance; the activity order for different anions was $CO_3^{2-} > Cl^- > NO_3^- > SO_4^{2-}$. The NiAl hydrotalcite prepared using Cl^-, NO_3^-, or SO_4^{2-} also showed much lower acetophenone selectiv-
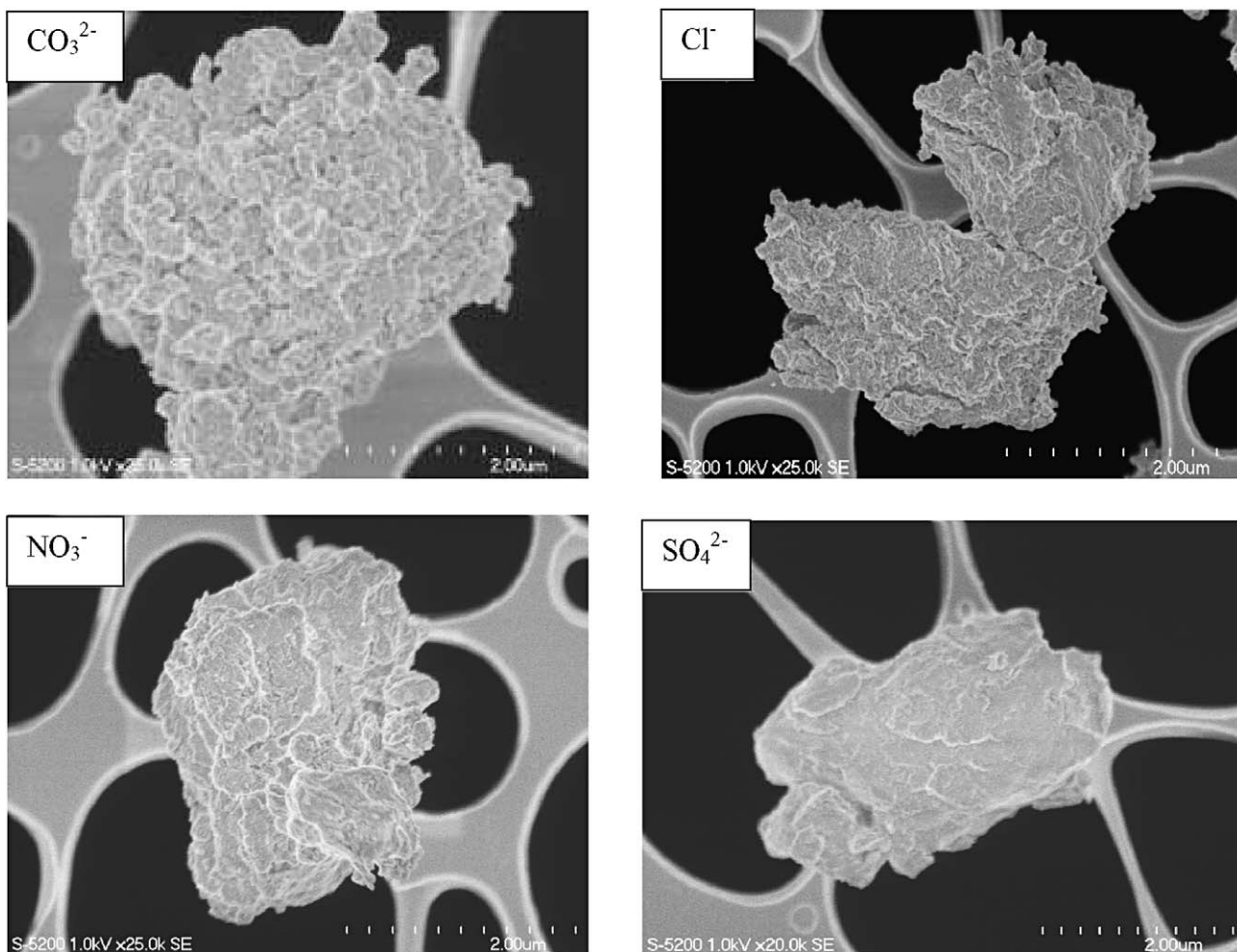
Fig. 2. FE-SEM images of NiAl-hydrotalcite having a Ni/Al molar ratio of 5.0 prepared by using CO_3^{2-}, Cl^-, NO_3^- or SO_4^{2-} as a guest inorganic anion.

Table 3
Results on ethylbenzene oxidation over different Ni-containing catalysts [Reaction conditions: ethylbenzene = 122.5 mmol, catalyst/aromatic substrate = 0.02 g mmol^{-1}, oxygen flow = 5 mL min^{-1} and temperature = 135 °C]

Entry	Catalysts	Guest inorganic anion	Conversion (%)	Selectivity (%)	TON (mol mol^{-1})
1	NiAl-hydrotalcite (2:1)	CO_3^{2-}	28	99.5	1.2
2	NiAl-hydrotalcite (3:1)	CO_3^{2-}	31	99.8	1.3
3	NiAl-hydrotalcite (4:1)	CO_3^{2-}	32	99.4	1.4
4	NiAl-hydrotalcite (5:1)	CO_3^{2-}	47	99.3	2.0
5	NiAl-hydrotalcite (5:1)	Cl^-	28	79.5	1.2
6	NiAl-hydrotalcite (5:1)	NO_3^-	24	74.2	1.1
7	NiAl-hydrotalcite (5:1)	SO_4^{2-}	23	64.0	1.0
8	Ni/γ-Al$_2$O$_3$ (2 wt%)	–	no reaction	–	–
9	Ni/γ-Al$_2$O$_3$ (5 wt%)	–	no reaction	–	–
10	NiAl-hydrotalcite (5:1)[a]	CO_3^{2-}	<1	99.1	–
11	MgAl-hydrotalcite	CO_3^{2-}	<1	100	–
12	No	–	<1	100	–

[a] Presence of hydroquinone (5 mmol).

ity compared with that synthesized with CO_3^{2-} as a guest inorganic anion.

– The catalytic activity of NiAl hydrotalcite was increased with increasing Ni content (entries 1–4). Among the different NiAl hydrotalcites with Ni/Al molar ratios ranging from 2.0 to 5.0, the catalyst with Ni/Al ratio of 5.0 mol mol^{-1} prepared with CO_3^{2-} as a guest inorganic anion showed the highest activity, as well as very high selectivity in the oxidation of ethylbenzene to acetophenone.
– MgAl hydrotalcite without Ni showed very low ethylbenzene oxidation activity (entry 11).
– Ethylbenzene oxidation occurred in the absence of catalyst, albeit very slowly (entry 12).

These observations reveal that NiAl hydrotalcites can efficiently catalyze the liquid-phase oxidation of ethylbenzene to acetophenone by molecular oxygen under solvent-free and mild reaction conditions. However, both Ni/γ-Al$_2$O$_3$ and MgAl hydrotalcites without Ni are quite inactive for this oxidation. The presence of guest inorganic anions in the interlayer space of NiAl hydrotalcites greatly affects both catalytic activity and selectivity in ethylbenzene oxidation. Among the various NiAl hydrotalcites, the catalyst with a Ni/Al ratio of 5 mol mol^{-1} prepared with CO_3^{2-} as a guest anion showed the highest catalytic activity as well as very high acetophenone selectivity in the above oxidation reaction. The comparatively lower catalytic activity of NiAl hydrotalcites prepared using NO_3^-, Cl^-, or SO_4^{2-} as a guest inorganic anion seems to be due in part
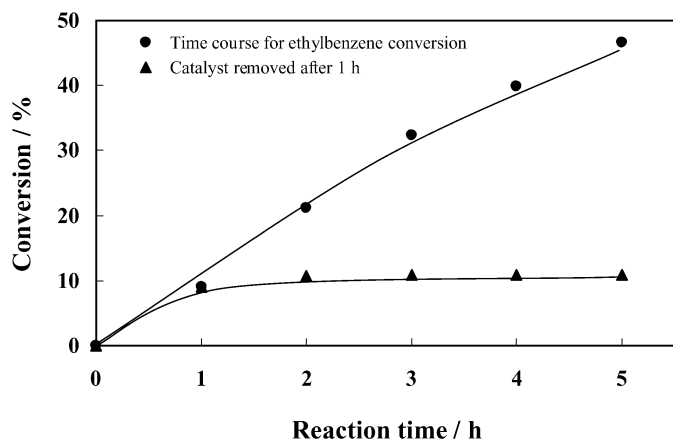
Fig. 3. Time course of ethylbenzene oxidation over NiAl-hydrotalcite having Ni/Al molar ratio of 5.0 prepared with CO_3^{2-} as a guest inorganic anion [Reaction conditions: ethylbenzene = 122.5 mmol, catalyst/aromatic substrate = 0.02 g mmol^{-1}, oxygen flow = 5 mL min^{-1} and temperature = 135 °C].

to their lower BET surface areas as a consequence of larger particle sizes as observed on the FE-SEM and N_2 adsorption–desorption studies (Fig. 2; Table 1). However, a significant contribution of basicity to catalytic activity is still a possibility, as we discuss below. The low acetophenone selectivity obtained for NiAl hydrotalcites prepared with NO_3^-, Cl^-, or SO_4^{2-} is due to the large amount of ethylbenzene hydroperoxide in the reaction mixture, which is apparently related to their lower basicity. The role of basic sites in the selective conversion of intermediate ethylbenzene hydroperoxide to acetophenone is discussed later.

The time course analysis of ethylbenzene oxidation over NiAl-hydrotalcites showing the highest catalytic activity in Fig. 3 reveals that with increasing reaction time, ethylbenzene conversion increased gradually without significantly affecting acetophenone selectivity. In addition, the reaction proceeded at a negligibly slow rate once the solid catalyst was removed (while hot) from the liquid reaction mixture after 1 h of reaction. The foregoing observations indicate that the oxidation reaction catalyzed by solid NiAl hydrotalcites is mostly heterogeneous. To confirm the true heterogeneous nature of NiAl hydrotalcites in alkylaromatic oxidation reactions, the catalyst with a Ni/Al molar ratio of 5.0 prepared with CO_3^{2-} as a guest inorganic anion was reused in the ethylbenzene oxidation several times. This catalyst was reused after the solid was separated from the liquid reaction mixture by centrifugation, followed by several washings with reactant ethylbenzene while avoiding the loss of catalyst fine particles. After the fourth catalyst reuse, the selectivity of acetophenone was close to 100% in all cases, and the conversion hardly changed. Comparing the Ni/Al molar ratio of the fresh and used catalysts by inductively coupled plasma (ICP) analysis confirmed that Ni was not leached during the reaction; the used and fresh catalysts had similar Ni content. A negligibly small amount of Ni was observed in the liquid reaction mixture after its separation by hot filtration from the solid catalyst. It is interesting to note that the catalytic activity increased slightly after its first use in the oxidation process,

Table 4
Physico-chemical properties and catalytic results on ethylbenzene oxidation over various transition metal containing hydrotalcites [Reaction conditions: ethylbenzene = 122.5 mmol, catalyst/aromatic substrate = 0.02 g mmol^{-1}, oxygen flow = 5 mL min^{-1} and temperature = 135 °C]

Catalyst	XRD phases	Surface area ($m^2 g^{-1}$)	Conversion (%)	Selectivity (%)
Zn–Al-HT	Hydrotalcite	53	0.5	99.5
Cu–Al-HT	Hydrotalcite, $Cu(OH)_2$, $Al(OH)_3$	42	3.8	99.1
Co–Al-HT	Hydrotalcite	62	6.7	99.2
Mg–Fe-HT	Hydrotalcite	60	0.7	99.3
Mg–Cr-HT	Hydrotalcite	71	1.8	99.4

whereas selectivity was not significantly altered. The increase in activity may be due to the removal of strongly adsorbed water from the catalyst during the first use and subsequent uses. XRD and N_2 adsorption–desorption analysis of the used catalysts also confirm that the structural features of the hydrotalcite did not changed during the oxidation reaction; XRD patterns and surface areas were similar in the used and fresh catalysts (results not shown).

Although NiAl hydrotalcite was found to be an effective catalyst for the ethylbenzene oxidation reaction, Ni/γ-Al_2O_3 with varying compositions and MgAl hydrotalcite without Ni exhibited almost no ethylbenzene oxidation activity. These findings strongly suggest that Ni present in the hydrotalcite structure was responsible for the activity in the oxidation process. To compare the catalytic activity of other transition metal-containing hydrotalcites for ethylbenzene oxidation, a number of double-layered hydroxides containing various transition metals, such as CoAl, CuAl, ZnAl, MgFe, and MgCr hydrotalcites with M^{II}/M^{III} molar ratios of 5.0, prepared using CO_3^{2-} as a guest inorganic anion, were tested. However, these exhibited significantly lower activity (<7.0% conversion in 5 h under similar experimental conditions) compared with the NiAl hydrotalcite samples (Tables 3 and 4). It is important to note here that the earlier-reported solid catalysts based on Ru, Cu, Fe, Co, and Mn have limitations in the ethylbenzene oxidation reaction. The catalytic activity of Ru- and Cu-based heterogeneous solids is restricted to doubly activated alkylaromatics; these catalysts are unable to oxidize ethylbenzene [13,15]. Although Fe- and Co-containing solids are active for ethylbenzene oxidation, Fe porphyrin has low acetophenone selectivity and inferior catalytic stability [16], and Co-based catalysts suffer from poor reusability [17,18]. Moreover, the Mn-containing catalyst has high activity in ethylbenzene oxidation only after a long reaction period or at high oxygen pressures [19,20]. Therefore, NiAl hydrotalcites seem to be unique in their efficient ethylbenzene oxidation at 1 atm of molecular O_2.

NiAl hydrotalcite with a Ni/Al ratio of 5 mol mol^{-1} proved to be the best catalyst in the present study. Thus, it was further evaluated for the oxidation of various types of alkylbenzenes to their corresponding benzylic ketones using atmospheric pressure of molecular oxygen as a sole oxidant under solvent-free conditions, to investigate the scope and limitation of this oxidation process. Table 5 gives the results of alkylbenzene conversion and ketone selectivity in the oxidation of different alkyl-

Table 5
Results on oxidation of various alkylaromatics catalyzed by NiAl-hydrotalcite having Ni/Al molar ratio of 5.0 prepared with CO_3^{2-} as a guest inorganic anion [Reaction conditions: alkylbenzene = 122.5 mmol, catalyst/aromatic substrate = 0.02 g mmol^{-1}, oxygen flow = 5 mL min^{-1} and temperature = 135 °C]

Entry	Alkylaromatics	Conversion (%)	Major product	Selectivity (%)
1	Ethylbenzene	47	Acetophenone	99.3
2	Propylbenzene	44	Propiophenone	95.7
3	Butylbenzene	45	Butyrophenone	93.7
4	4-Methylehtylbenzene	59	4-Methylacetophenone	99.5
5	4-Aminoethylbenzene	60	4-Aminoacetophenone	94.3
6	Diphenylmethane	62	Benzophenone	96.9
7	Fluorene	63	9-Fluorenone	91.7
8	Xanthane	62	Xanthaone	92.4
9	4-Phenylethylbenzene	73	4-Phenylacetophenone	93.6
10	4-Nitroethylbenzene	2	4-Nitroacetophenone	99.3

benzenes with molecular oxygen at 135 °C over the NiAl hydrotalcite catalyst. Alkylbenzene conversion was quite high in most cases, indicating the high oxidation activity of this catalyst even under solvent-free reaction conditions. In all cases, the –CH$_2$– group of alkylbenzene was converted to a –CO– group with very high selectivity, indicating high chemoselectivity in oxidation. Alkylbenzenes with varying alkyl chain lengths (from C$_2$ to C$_4$) formed corresponding phenones in moderate yields (44–47%) and were not significantly affected by the chain length of alkylbenzene substrates (entries 1–3). The ethylbenzene derivatives with an electron-donating substituent, such as –CH$_3$ or –NH$_2$, at the 4-position afforded the corresponding acetophenones in good yields (58–60%) (entries 4–5). Moreover, the amine function was not oxidized under the present reaction conditions. However, the presence of the electron-withdrawing –NO$_2$ group in the ethylbenzene derivative adversely affected the corresponding acetophenone derivative yield (entry 10). A number of alkylarenes, including diphenylmethane, fluorene, xanthane, and 4-ethylbiphenyl, were oxidized to give the corresponding oxygenated products in high yields (62–74%) (entries 6–9). It is important here to note that in all cases, only the benzylic C–H bonds of alkylaromatics were oxidized selectively to their corresponding ketones.

The observed inert nature of Ni/γ-Al$_2$O$_3$ catalysts (Table 3, entries 8 and 9) compared with the high activity of NiAl hydrotalcites (Table 3, entries 1–7) in the oxidation of ethylbenzene indicates that the free Ni species is inactive for this reaction. It seems that in the NiAl hydrotalcites, Ni is present in association with Al, which apparently is responsible for the high ethylbenzene oxidation activity of this catalyst. Similar phenomena have been observed for alcohol oxidation with molecular oxygen over Ni-containing hydrotalcite catalysts [24]. The remarkably high activity of NiAl hydrotalcites for various bulky alkylarenes (Table 5, entries 6–9) suggests that the small interlayer space of layered hydrotalcite probably makes no significant contribution to the above oxidation process; only the Ni species exposed to the external surfaces seems to be responsible for this catalytic reaction. It is expected that, compared with the total amount of Ni incorporated into the hydrotalcite structure, a very small

Table 6
Physico-chemical properties and ethylbenzene oxidation activities of various Ni-containing MgAl-hydrotalcites [Reaction conditions: ethylbenzene = 122.5 mmol, catalyst = 0.49 mmol Ni, oxygen flow = 5 mL min^{-1} and temperature = 135 °C].

Mg/Al molar ratio	Surface area (m^2 g^{-1})	pH of suspension in water[a]	µmol basic sites per g of hydrotalcite[b]	Conversion (%)	Selectivity (%)	TON (mol mol^{-1})
2	8.5	9.1	46.5	22	99.1	53
3	8.2	9.6	61.3	25	99.4	62
5	8.5	9.9	125.4	30	99.3	75

[a] Suspension of 0.3 g hydrotalcite in 20 mL deionized water.
[b] 0.15 g hydrotalcite, suspended in 2 mL phenolphthalein indicator solution, is titrated with 0.01 M benzoic acid.
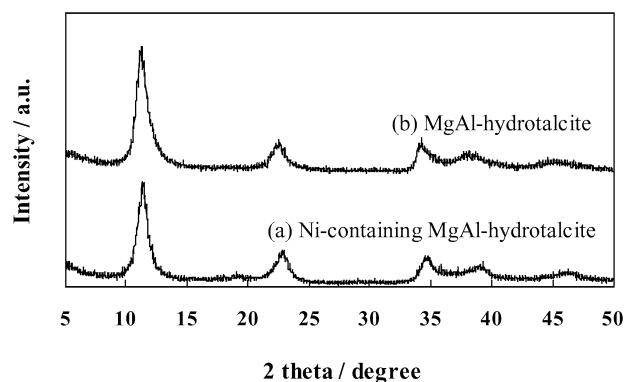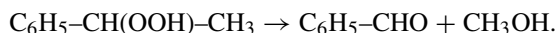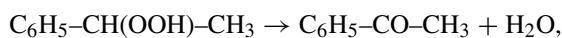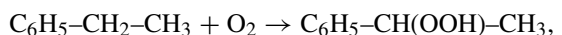

Fig. 4. X-ray diffraction patterns of MgAl-hydrotalcite (having a Ni/Al molar ratio of 5.0) with (a) or without (b) Ni.

fraction of Ni species is available on the outer surfaces for their catalytic action, which may be the reason for the low TON of NiAl hydrotalcites for the ethylbenzene oxidation reaction (Table 3).

By changing the method of incorporating Ni into the hydrotalcite material, we have succeeded in dramatically increasing the TON of Ni-containing hydrotalcites in the ethylbenzene oxidation reaction. Ni-containing MgAl hydrotalcites (with different Mg/Al ratios but similar Ni contents) prepared by adopting the "memory effect" of MgAl hydrotalcite showed a marked increase in TON for ethylbenzene oxidation (Table 6). After 5 h of reaction, the TON of Ni-containing MgAl hydrotalcite (with a Mg/Al ratio of 5 mol mol^{-1}) reached 74.7, which is about 38 times higher as that observed for NiAl hydrotalcite prepared by the conventional coprecipitation method (Table 3, entry 4). Although XRD patterns did not change, a drastic decrease in surface area was observed after Ni was incorporated into the MgAl hydrotalcite material compared with that of the parent MgAl hydrotalcite precursor (Fig. 4; Table 6). The ICP and XPS analyses of bulk and surface Ni compositions clearly show that during the above reconstruction process, some of the Mg sites present mostly on the surface layer of hydrotalcite was replaced by Ni, resulting in the Ni-containing MgAl hydrotalcite (not shown). The formation of surface-enriched Ni in the Ni-containing hydrotalcite seems to be the main reason for its high catalytic performance in the alkylbenzene oxidation process. Interestingly, the activity of the Ni-containing MgAl hydrotalcite catalyst showed a dependence on its Mg/Al ratio.

For the different MgAl hydrotalcites with similar Ni content, the higher the Mg/Al ratio (or, in other words, the higher the basicity), the greater the ethylbenzene oxidation activity (Table 6). These results support our earlier observations (Table 3, entries 4–7) and indicate a significant contribution of basicity to the catalytic activity of Ni-containing hydrotalcite for the ethylbenzene oxidation reaction. The precise reason for this behavior is not clear at present; however, note that aqueous alkali has been used industrially for the transformation of alkylbenzene to alkylbenzene hydroperoxide by molecular oxygen [26].

Although oxygen activation by Ni-containing hydrotalcite for alcohol oxidation is well known [25], the mechanism of this oxygen activation and transfer by the hydrotalcite catalyst for alkylaromatics oxidation remains unclearly understood. Nonetheless, the following observations narrow the possibilities. A drastic decrease in ethylbenzene oxidation activity (Table 3, entry 10) of NiAl hydrotalcite by the addition of a free-radical scavenger (i.e., hydroquinone) and, moreover, the presence of ethylbenzene hydroperoxide in the reaction mixture indicate the involvement of a free-radical mechanism in the present case. The formation of acetophenone and ethylbenzene hydroperoxide indicates that ethylbenzene oxidation involves the following reactions over all of the catalysts or even in the absence of any catalyst:

$$C_6H_5-CH_2-CH_3 + O_2 \rightarrow C_6H_5-CH(OOH)-CH_3,$$

$$C_6H_5-CH(OOH)-CH_3 \rightarrow C_6H_5-CO-CH_3 + H_2O,$$

$$C_6H_5-CH(OOH)-CH_3 \rightarrow C_6H_5-CHO + CH_3OH.$$

As shown in the above reaction schemes, the intermediate ethylbenzene hydroperoxide can react in two different ways to form two different products, acetophenone and benzaldehyde. However, the possibility of benzaldehyde formation from the oxidative dehydrogenation of ethylbenzene to styrene, followed by its subsequent oxidation over the hydrotalcite-based catalyst, cannot be excluded. Based on our catalytic results, we believe that the basic site of the hydrotalcite catalyst is responsible for the conversion of intermediate ethylbenzene hydroperoxide to afford the selective formation of acetophenone under the reaction conditions. This assumption is supported by the fact that NiAl hydrotalcite prepared using Cl^-, NO_3^-, or SO_4^{2-} and with lower basicities exhibited lower acetophenone selectivity compared with that synthesized with CO_3^{2-} (which has a higher basicity). Further investigations of the detailed reaction mechanism, including the role of Ni and particularly the basic sites, are currently under way.

4. Conclusion

In this paper, we have demonstrated for the first time the NiAl hydrotalcite-promoted selective oxidation of alkylaromatics to the corresponding benzylic ketones with molecular oxygen as a sole oxidant under solvent-free and mild reaction conditions. We have shown that the presence of guest inorganic anions in NiAl hydrotalcite significantly affects acetophenone selectivity in the ethylbenzene oxidation process. In addition, ethylbenzene oxidation activity is increased with increasing Ni content in the NiAl hydrotalcite prepared by the conventional coprecipitation technique; however, the catalytic activity of Ni-containing hydrotalcite is increased drastically by simply changing the method of incorporating Ni into the MgAl hydrotalcite material. Moreover, preactivation of hydrotalcite catalyst is not necessary, and the NiAl hydrotalcite is reusable after the reaction. Our proposed method is also advantageous from the standpoint of low cost, environmental friendliness, and operational simplicity, and it may be applicable to large-scale reactions.

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