# Catalysis by Calcined $Zn^{2+}/Al^{3+}$ Layered Double Hydroxides in Friedel–Crafts Alkylation of Benzene with Benzyl Chloride

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Amorphous oxides formed upon the calcination of $Zn_2Al$ layered double hydroxide chloride or carbonate intercalates showed high catalytic efficiency in the benzylation of benzene with benzyl chloride. The IR spectra of pyridine adsorbed on amorphous oxides suggest that the benzylation activity is due to the formation of zinc chloride on the surface.

Layered double hydroxides (LDHs) are non-stoichiometric compounds composed of positively charged brucite-like layers of divalent and trivalent metal hydroxides with intercalated anions and water molecules. LDHs are expressed by the general formula $[M(II)_{(1-x)}M(III)_x(OH)_2]^{x+}[A^{m-}{}_{x/m}]nH_2O$, where M(II) is a divalent metal ion, M(III) is a trivalent metal ion, $A^{m-}$ is an anion with valency $m$, and $x$ is a constant, generally between 0.21 and 0.33.

Mixed oxides obtained by the thermal decomposition of LDH carbonate intercalates have high basicity, and act as catalysts for base-catalyzed reactions, especially for the $Mg^{2+}/Al^{3+}$ system.[1] The nature of the anions in the interlayer, which decomposes during a thermal treatment, plays an important role in the acid–base properties of the oxides derived from LDHs. For instance, the oxides obtained from the thermal decomposition of $Mg^{2+}/Al^{3+}$ LDH chloride intercalates possess acidic sites in addition to basic sites.[2,3] However, the function of thermally decomposed materials as acid catalysts in liquid-phase organic reactions is still not completely understood. In this paper, we report that the amorphous mixed oxide formed by the thermal decomposition of $Zn_2Al$ LDH is exceedingly active in the benzylation of benzene with benzyl chloride at room temperature.

The present work aims to clarify the function of the amorphous mixed oxide as a solid acid catalyst in liquid-phase Friedel–Crafts alkylation. To this end, calcination was performed for both chloride and carbonate intercalates, and the catalytic properties of these materials were then examined in the benzylation of benzene to diphenylmethane at room temperature.

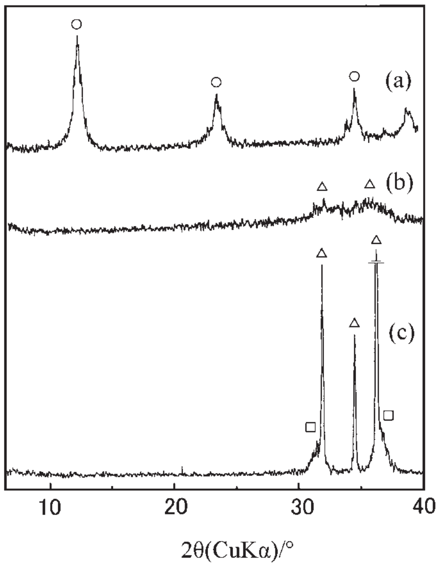

Fig. 1. XRD patterns of $Zn_2Al$ LDH chloride intercalates calcined at (a) 150 °C, (b) 350 °C, and (c) 500 °C for 1 h in air. ○: LDH; △: ZnO; □: $ZnAl_2O_4$.

Table 1. Benzylation of Benzene with Benzyl Chloride at Room Temperature over Mixed Oxides Formed by the Thermal Decomposition of $Zn_2Al$ LDH Chloride and Carbonate Intercalates[a)]

| LDH | Calcination temp.[b)]/°C | Phases detected by XRD | $Ph_2CH_2$ yield/% Reaction time/min 15 | 30 | 60 |
|---|---|---|---|---|---|
| Chloride | 150 | LDH | 2 | 17 | 17 |
| | 350 | Amorphous ZnO | 67 | 73 | 83 |
| | 500 | ZnO + $ZnAl_2O_4$ | 12 | 14 | 17 |
| Carbonate | 300 | Amorphous ZnO | 64 | 85 | 85 |

a) Reaction condition: catalyst 0.5 g, benzyl chloride 20 mmol, benzene 60 $cm^3$. b) Calcination was carried out in air for 1 h.

The XRD patterns of $Zn_2Al$ LDH chloride intercalates calcined at 150 °C, 350 °C, and 500 °C for 1 h in air are shown in Fig. 1. The XRD pattern of the 150 °C sample indicates that the layered structure survives up to this temperature. The XRD pattern of the 350 °C sample reveals that the layered structure has collapsed, and that a highly amorphous mixed oxide phase with a ZnO-type structure has been produced.[4] The XRD pattern of the 500 °C sample indicates the appearance of crystalline ZnO and $ZnAl_2O_4$ spinel phases. The XRD patterns of samples obtained by the calcination of carbonate intercalates indicated that calcination at 300 °C produced amorphous ZnO-type mixed oxides, and that above 600 °C, the amorphous oxide transformed to crystalline ZnO and $ZnAl_2O_4$ spinel phases (data not shown).

Table 1 gives the results of the benzylation of benzene with benzyl chloride at room temperature over mixed oxides formed by the thermal decomposition of $Zn_2Al$ LDH chloride and carbonate intercalates. The crystalline LDH chloride intercalates and crystalline mixed oxides obtained by calcining at 500 °C showed low activity, but the activity was drastically increased for calcination at 350 °C to give an amorphous oxide. Benzylation using the amorphous oxide yielded diphenylmethane in 83% after 60 min. The amorphous oxide obtained by calcining the LDH carbonate intercalates showed a similar-

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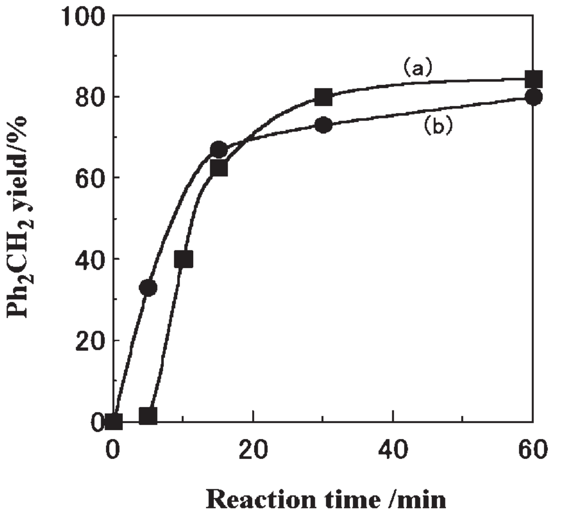

Fig. 2. Diphenylmethane yield vs reaction time plots for the benzylation at room temperature over (a) $Zn_2Al$ LDH carbonate calcined at 300 °C, (b) LDH chloride calcined at 350 °C.

ly high activity to those obtained from the chloride intercalates. However, in the case of a reaction using carbonate derived amorphous oxide, an induction period was observed for the formation of the diphenylmethane (Fig. 2). The induction period indicates that the catalysts are activated during the initial reaction period.

The nature of the acid sites for the oxides obtained by calcining $Zn_2Al$ LDH chlorides or carbonate intercalates was characterized by the FT-IR spectra of the adsorbed probe molecule pyridine. The FT-IR spectrum of pyridine adsorbed on an amorphous ZnO-type mixed oxide obtained from an LDH chloride intercalates exhibited sharp bands at 1448 and 1608 $cm^{-1}$ (Fig. 3(b)). These bands result from the vibrational modes of pyridine coordinatively bound to Lewis acid sites.[5] Pinnavaia and co-workers[2] assumed that, upon calcination, the interlayer chloride replaces the hydroxy groups in the brucite-like layers. The generation of Lewis acidity in the amorphous mixed oxide derived from the chloride likely originates from the formation of a zinc chloride phase. On the other hand, an amorphous oxide derived from LDH carbonate does not indicate the presence of coordinatively bound pyridine (Fig. 3(a)). Thus, the amorphous oxide derived from the carbonate essentially did not include Lewis acid sites. However, high activity was observed in benzylation. It is presumed that the Lewis acid sites of the oxide derived from LDH carbonate were created by substitution of the oxygen on the surface of the amorphous oxide with chloride, which probably originated from HCl produced by hydrolysis from the small amount of water contained in the benzyl chloride system. To confirm this, we also investigated the FT-IR spectra of the adsorbed pyridine on amorphous oxide after a treatment with benzyl chloride. The benzyl chloride treatment was performed at room temperature by suspending 0.5 g of amorphous oxide in cyclohexane (20 $cm^3$) containing benzyl chloride (1 mmol). The FT-IR spectrum obtained after the benzyl chloride treatment of amorphous oxide from the LDH carbonate intercalate exhibited sharp peaks at 1448 $cm^{-1}$ and 1608 $cm^{-1}$ consistent with pyridine coordinated to Lewis acid sites (Fig. 3(c)).

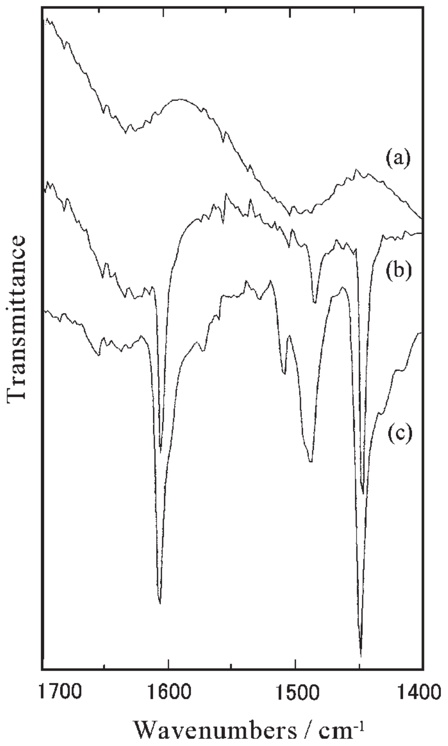

Fig. 3. IR spectra of pyridine adsorbed on (a) $Zn_2Al$ LDH carbonate calcined at 300 °C, (b) LDH chloride calcined at 350 °C, and (c) benzyl chloride treated LDH carbonate calcined at 300 °C.

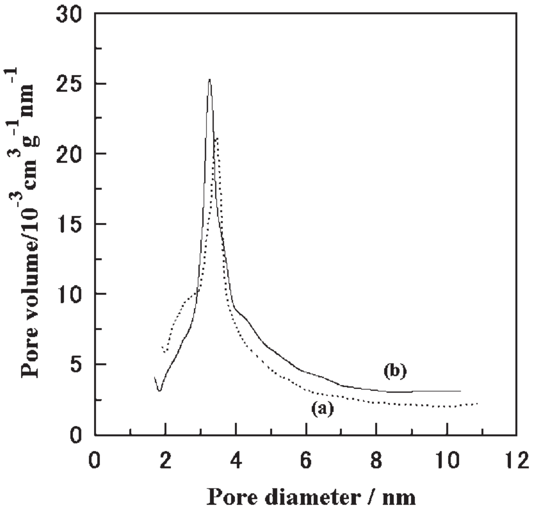

Fig. 4. Pore-size distribution of the (a) $Zn_2Al$ LDH carbonate calcined at 300 °C, (b) chloride calcined at 350 °C.

Amorphous mixed oxides with the ZnO-type structure, obtained by calcining $Zn_2Al$ LDH chloride or carbonate, efficiently catalyzed benzylation, possibly due to the formation of zinc chloride. Clark and co-workers[6,7] have reported the use of a montmorillonite supported zinc chloride, "clayzic", in Friedel–Crafts alkylation. They concluded that clayzic owes its remarkable Friedel–Crafts activity to the presence of high local concentrations of zinc ions in structural mesopores. Figure 4 shows pore-size distribution curves for the BJH desorption ($dV/dD$) of pore volumes for the $Zn_2Al$ LDH chloride and carbonate derived amorphous mixed oxides. The pore-size distribution curves show that $Zn_2Al$ LDH derived mixed oxides possess porosity, principally in the mesopore range. We believe that, as with "clayzic", the Friedel–Crafts activity in our system is closely related to the presence of mesopores.

In benzylation using the $Zn_2Al$ LDH derived amorphous oxide, dissolved zinc ions were not detected in the reaction mixture. Thus, the amorphous oxides were proven to catalyze the benzylation as insoluble heterogeneous catalysts.

## Experimental

**Synthesis of LDH.** $Zn^{2+}/Al^{3+}$ LDHs ($Zn^{2+}/Al^{3+}$ atomic ratio $= 2$) containing $Cl^-$ or $CO_3{}^{2-}$ as interlayer anions, were prepared at room temperature by coprecipitation according to a procedure of Ramkumar and co-workers.[4]

**Reaction.** Benzyl chloride (20 mmol), benzene (60 $cm^3$), and LDH (0.5 g), which was heat-treated at 150–500 °C in air for 1 h, were mixed together and stirred at room temperature for a specified time. The reaction products were determined by gas chromatography.

**FT-IR Measurement of Adsorbed Pyridine.** The adsorption of pyridine was performed by exposing the sample to saturated pyridine vapor at room temperature, which was then outgassed at room temperature under 0.13 Pa. FT-IR was performed at room temperature using a KBr pellet.

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