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Hydrotalcite-Derived Mg/Al Mixed Oxides as Support Materials for the Friedel–Crafts Catalyst $ZnCl_2$

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$ZnCl_2$ supported on Mg/Al mixed oxides obtained through the thermal decomposition of hydrotalcite showed high catalytic activity in the benzylation of benzene with benzyl chloride at room temperature. The surface properties of hydrotalcite-derived mixed oxides suggested that they increased the catalytic activities of $ZnCl_2$ owing to their high mesoporosity, with pore sizes in the vicinity of 10 nm.

Solid-supported zinc chloride catalysts (Clayzic-type catalysts) have been extensively studied as Friedel–Crafts catalyst alternatives to replace the conventional toxic homogeneous reagent aluminum chloride. Clark and co-workers[1,2] showed that zinc chloride supported on acid-treated montmorillonite K10 (Clayzic) exhibits remarkable activity in the alkylation of benzene with benzyl chloride to give a high yield of diphenylmethane. Rhodes and co-worker[3] showed that high-porosity silica is a more active support than the acid-treated clays. Recently, a new class of more efficient support materials has been employed, including hydroxyapatite,[4] sol–gel-derived silica[5] and alumina,[6] fluoride-modified sol–gel-derived aluminosilicates,[7] and MCM-41,[8] for Friedel–Crafts catalyst $ZnCl_2$.

Layered double hydroxides (LDHs), also known as hydrotalcite-like anionic clays, are non-stoichiometric compounds composed of positively charged brucite-like layers of divalent and trivalent metal hydroxides with intercalated anions and water molecules. Calcination of LDHs at high temperature leads to mixed-metal oxides. The mixed oxides obtained by thermal decomposition of LDHs exhibit several desirable properties as heterogeneous catalysts or catalyst supports, such as ultrafine particle size, high specific surface area, high basicity, and good thermal stability: especially hydrotalcite (HT), in which Mg^{2+} and Al^{3+} are found in the brucite-like layers and carbonate species in the interlayer.[9] In addition to the above properties, it has recently been reported that HT-derived mixed oxides possess significant mesoporosity.[10] However, there are essentially no known instances in which HT-derived mixed oxides are used as supports on the basis of their mesoporosity.

In the present paper, we demonstrate that HT-derived Mg/Al mixed oxide supports are effective in increasing the activity of the Friedel–Crafts alkylation catalyst $ZnCl_2$. To this end, $ZnCl_2$ catalysts supported on HT-derived mixed oxides are prepared and tested for the room temperature benzylation of benzene to diphenylmethane using benzyl chloride. The mixed oxide supports are further characterized in terms of their surface areas, pore volumes, and pore-size distributions.

Figure 1 shows the XRD patterns of HT (Mg/Al = 2) calcined between 100 and 1100 °C in air for 1 h. The XRD pattern of the sample calcined at 300 °C indicates that the layered structure persisted up to this temperature. Upon calcination at 500 °C, the layered structure collapsed and formed a highly amorphous Mg/Al mixed oxide phase with a MgO-like structure (periclasse), which agrees with the results of Constantino and co-worker.[11] The XRD pattern of the sample calcined at 1100 °C indicates the appearance of $MgAl_2O_4$ spinel phases and crystalline MgO.

The surface areas and pore volumes of the thermal decomposition products were measured. The results are summarized in Table 1. Also shown are the results of the room temperature benzylation of benzene with benzyl chloride using $ZnCl_2$ supported on each of these materials at a loading of $2\,mmol\,g^{-1}$. The supported catalysts were activated at 250 °C for 1 h under vacuum, and their catalytic activities were measured. The $ZnCl_2$ supported on HT calcined at 400 °C to give the HT phase showed low activity. However, when an Mg/Al mixed oxide formed by calcination at 500–900 °C was used as the support, catalytic activity increased drastically. For instance, $ZnCl_2$ catalysts supported on mixed oxides obtained through calcination at 700 and 900 °C gave diphenylmethane in 98% yield over 0.5 h. This yield is identical to that obtained with the same reaction using a high-porosity silica EP12 supported $ZnCl_2$ catalyst, which has particularly high activity among Clayzic-type catalysts.[3] $ZnCl_2$ supported on HT calcined at 1100 °C also showed low activity. In this case, XRD data indicated the formation of crystalline MgO and $MgAl_2O_4$. We have also performed the benzylation in the presence of $ZnCl_2$

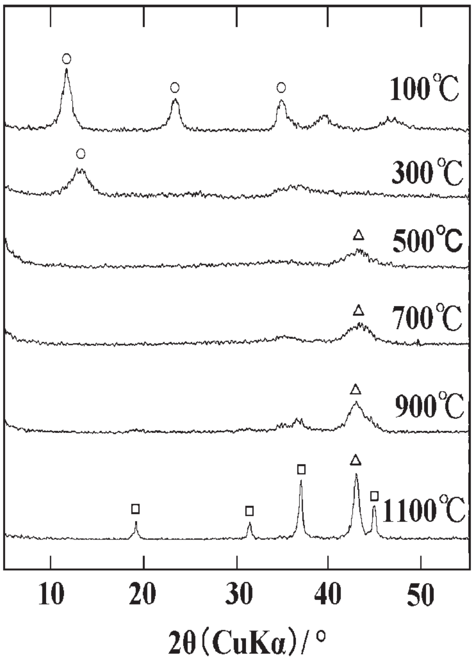

Fig. 1. XRD patterns of hydrotalcite calcined at various temperatures. ○: HT; △: MgO; □: $MgAl_2O_4$.

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Table 1. Surface Properties of Thermal Decomposition Products of Hydrotalcite, and the Catalytic Activity of $ZnCl_2$ Supported on These Materials at a Loading of 2 mmol g^{-1} for Room Temperature Benzylation of Benzene[a)]

HT calcination temp[b)]/°C	Phases detected by XRD	Surface area/$m^2 g^{-1}$	Pore volume /$cm^3 g^{-1}$	Ph_2CH_2 yield /%
300	HT	118	0.61	25
500	MgO	318	0.94	90
700	MgO	238	0.97	98
900	MgO	177	0.93	98
1100	MgO + $MgAl_2O_4$	51	0.32	25

a) Benzylation conditions: catalyst 0.5 g, benzyl chloride 20 mmol, benzene 100 cm^3, 0.5 h. b) Calcination was carried out in air for 1 h.

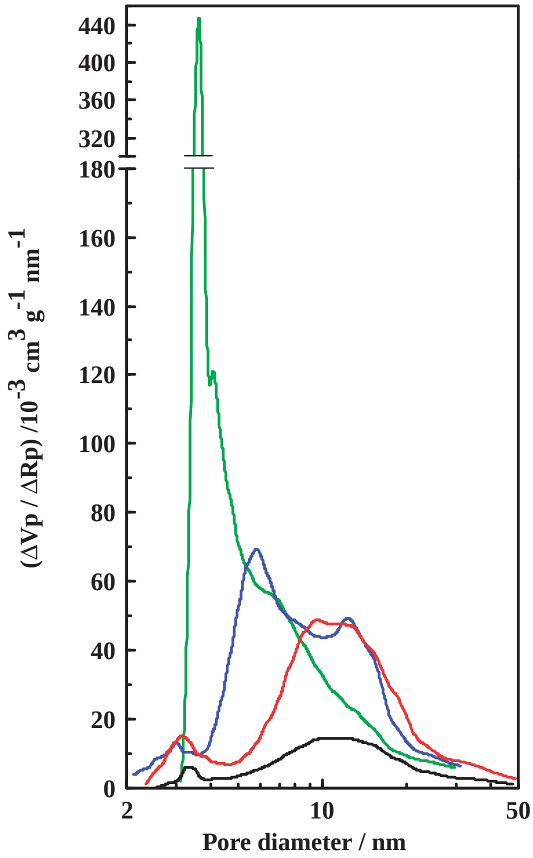

Fig. 2. Pore-size distributions of mixed oxides formed by calcination of hydrotalcite at 500 (green), 700 (blue), 900 (red), and 1100 °C (black).

alone and mixed oxides alone using the same quantity contained in 0.5 g of $ZnCl_2$-supported catalysts. Both reactions used $ZnCl_2$ and HT calcined at 500–900 °C; no diphenylmethane formation was detected under the same reaction conditions as those used in the case of the $ZnCl_2$-supported catalysts (0.5 h at room temperature). Thus, it was confirmed that Mg/Al mixed oxides with the MgO structure formed by calcination at 700–900 °C function to increase the activity of Friedel–Crafts catalysts of $ZnCl_2$.

It is particularly noteworthy that the surface area of HT decreased sharply from 318 to 238 to 177 $m^2 g^{-1}$ as the calcination temperature increased 500 to 700 to 900 °C, whereas the activity of $ZnCl_2$ supported on HT calcined at 700–900 °C was slightly higher than that of $ZnCl_2$ supported on HT calcined at 500 °C. However, pore volume had a different dependence on calcination temperature than surface area did. The pore volume remained nearly constant (0.93–0.97 $cm^3 g^{-1}$) up to a calcination temperature of 900 °C. These results suggest that the effectiveness of HT-derived mixed oxides as supports for $ZnCl_2$ catalysts may be due to their high pore volume rather than high surface area.

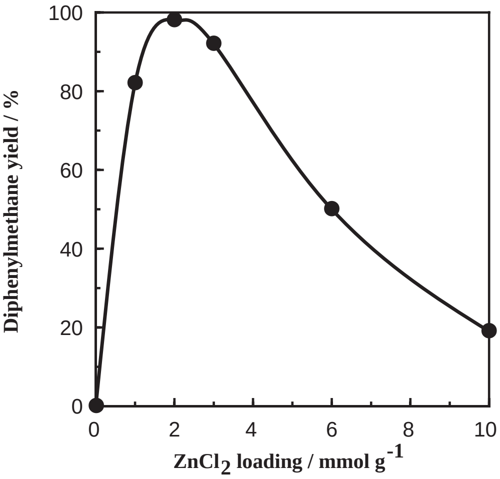

Fig. 3. Effect of $ZnCl_2$ loading in the $ZnCl_2$/HT-derived mixed-oxide catalyst on benzylation activity.

It is concluded that Clayzic owes its remarkable Friedel–Crafts activity to the presence of high local concentrations of zinc ions in structural mesopores.[2] Rhodes and co-worker[12] have shown that the highest alkylation catalytic activities of Clayzic-type catalysts are associated with supports with significant mesoporosity (pore of diameter: 10–12 nm). Figure 2 shows pore-size distribution curves for the HT-derived oxides. The mixed oxides obtained by calcination at 700 and 900 °C, which were the most effective supports, exhibited maximum pore volumes at a diameter of around 10 nm. This suggested that the effectiveness of HT-derived mixed oxides as supports for $ZnCl_2$ catalysts was due to the presence of a significant proportion of mesopores with a diameter of around 10 nm.

The catalytic activity of $ZnCl_2$ supported on HT-derived mixed oxides was highly dependent on the $ZnCl_2$-loading. The activity reached its maximum value at 2.0 mmol g^{-1}, decreasing rapidly at loadings above 4.0 mmol g^{-1} (Fig. 3). A similar loading dependence of catalytic activity has been observed for $ZnCl_2$ supported on acid-treated montmorillonite and silica EP12, and is explained through the state of $ZnCl_2$.[2,3] That is, most of the $ZnCl_2$ at optimal loading is present in the form of isolated moieties on the mesoporous surface of the mixed oxide. At higher loadings, a crystalline $ZnCl_2$ is formed that is inactive in the Friedel–Crafts reaction.

In conclusion, HT-derived amorphous mixed oxides were demonstrated to be effective catalyst supports, increasing the catalytic activity of $ZnCl_2$ in Friedel–Crafts alkylation owing to their mesoporous structure.

Experimental

Synthesis of Hydrotalcite. Hydrotalcite (Mg^{2+}/Al^{3+} molar ratio = 2) was prepared at room temperature by coprecipitation according to the procedure of Miyata.[13]

Preparation of $ZnCl_2$/Calcined HT. 10 mmol of $ZnCl_2$ and 10 g of calcined HT were mixed in 100 mL of methanol and evaporated to dryness.

Reaction. Benzyl chloride (20 mmol), benzene (100 cm^3), and the catalyst (0.5 g) were mixed by stirring at room temperature for 0.5 h. The reaction products were determined by gas chromatography.

Surface Properties. The nitrogen adsorption–desorption isotherms were measured at liquid-nitrogen temperatures with a Micromeritics instrument (ASAP). Surface areas were determined using the BET adsorption method. Pore-size distributions were calculated using the BJH method on the desorption branch of the isotherm.

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