New hydrotalcite-like anionic clays containing Zr^{4+} in the layers

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New hydrotalcite-like anionic clays containing Zr^{4+} in the brucite-like layers are synthesised by a simple coprecipitation technique; these materials show very interesting properties as catalysts for liquid-phase hydroxylation of phenol with H_2O_2.

Hydrotalcite (HT)-like anionic clays are a new family of interesting materials with applications as catalysts, catalyst supports, ion exchangers and composite materials.[1–3] The structure of these compounds can be visualised as being made of brucite $[Mg(OH)_2]$-like octahedral layers in which a part of Mg^{2+} is isomorphously substituted by trivalent cations. The excess positive charge of the layer is compensated by hydrated anions, such as CO_3^{2-}, present in the interlayer. The materials are represented generally by the formula: $[M^{II}_{1-x},M^{III}_{x},\text{-}(OH)_2]^{x+}[(A^{n-})_{x/n}\cdot yH_2O]^{x-}$, where M^{II} = Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}; M^{III}[4,5] = Al^{3+}, Fe^{3+}, Cr^{3+}, Ga^{3+}, V^{3+}, and more recently,[6] Ru^{3+} and Rh^{3+}. A large number of HT-like compounds with a wide variety of cation pairs including a Co–Ti^{IV} layered double hydroxide[7] have been reported in recent years. We now report the synthesis of a Zr^{4+} containing HT-like material using a simple coprecipitation technique. The importance of Zr or Ti containing HT-like compounds stems from the fact that, similar to zeolites containing Zr (Zr-silicalites) or Ti (Ti-silicalites), they can be used as catalysts for liquid-phase hydroxylation/oxidation of various organic substrates.[8–11] In the present investigation, we report our preliminary studies on the synthesis of new Zr-containing anionic clays and their catalytic performance in the liquid-phase hydroxylation of phenol.

Zr-containing hydrotalcites with various Mg : Al : Zr atomic ratios were synthesized by a coprecipitation method at room temperature by reacting aqueous solutions containing a mixture of $Mg(NO_3)_2$, $Al(NO_3)_3$ and $ZrO(NO_3)_2$ and a mixture of NaOH and Na_2CO_3 at a constant pH (*ca.* 10). The resulting precipitate was filtered, washed with distilled water several times until the pH of the filtrate was 7 and then dried at 373 K overnight. The incorporation of Zr in the brucite-like layers was confirmed by powder X-ray diffraction (PXRD/Rigaku, D-MAX III VC model, with Ni-filtered Cu-Kα radiation), UV–VIS diffuse reflectance spectroscopy (UV–VIS DRS; Shimadzu, UV–VIS Spectrophotometer 2101 PC model) and catalytic hydroxylation of phenol using hydrogen peroxide (H_2O_2) as the oxidant.

Fig. 1 shows the PXRD patterns of Mg : Al : Zr-HT with Mg : Al : Zr atomic ratio ranging from 3 : 1 : 0 to 3 : 0 : 1. A single phase corresponding to HT is obtained for all the samples although the crystallinity of the samples decreases with increasing Zr content (Table 1). A binary Zr containing HT without Al forms a poorly crystalline ZrO_2 phase [Fig. 1(*k*)] rather than a HT phase, indicating that the presence of Al favours the formation of a pure HT-like phase. The crystallographic parameters were evaluated employing least-squares refinement assuming a hexagonal crystal system for samples Zr0.0-HT–Zr0.6-HT whose PXRD peaks were intense and sharp enough for accurate determination. The increase in lattice parameters *a* and *c* with a concomitant increase in the unit cell volume *U* (Table 1) with increasing Zr content clearly demonstrates the effective incorporation of Zr^{4+} in the HT framework. The increase in *a* can be attributed to the isomorphous substitution of Al^{3+} (Shannon ionic radius 0.53 Å)[12] in the octahedral coordination by Zr^{4+} (Shannon ionic radius 0.72 Å) in the HT matrix. The increase in *c* may be due to the weakening of the interaction between the brucite-like layer and the interlayer anions or due to the larger number of anions. Furthermore, since a part of the trivalent cation Al^{3+} is being substituted by the tetravalent cation Zr^{4+}, the interlayer should accommodate more CO_3^{2-} anions for charge compensation. This is supported by an increase in carbon content from 2.44% for Zr0.0-HT to 3.55% for Zr0.6-HT (Table 1). Hence, based on the chemical composition presented in Table 1, the Zr containing HT-like compounds with Mg/Al + Zr = 3 can be represented by the following general formula: $Mg_6Al_{2-x}Zr_x(OH)_{16}\cdot[(x + 2)/2]CO_3\cdot yH_2O$, where *x* can vary from 0 to at least 1.2.

Thermal calcination of these samples at 723 K results in the formation of an MgO phase whose *d*(200) value increases from 2.0934 Å for Zr0.0-HT to 2.1174 Å for Zr0.5-HT, indicating the dissolution of Zr^{4+} in the MgO lattice. However, a poorly crystalline ZrO_2 phase, in addition to an MgO phase is noticed in the PXRD of the samples above Zr0.5-HT.

The dispersion of Zr in the HT framework was studied by UV–VIS DRS (Fig. 2). All these samples, including that

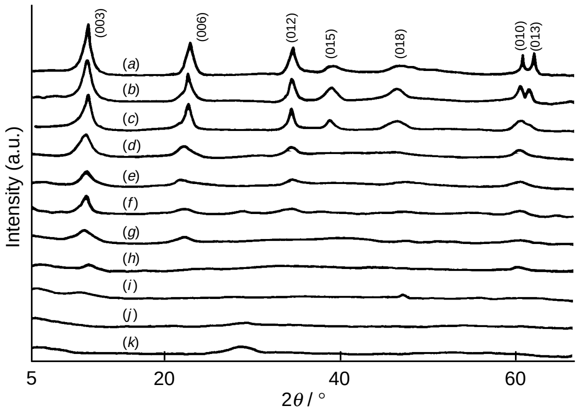

Fig. 1 PXRD patterns of MgAlZr-HT: (*a*) Zr0.0-HT, (*b*) Zr0.1-HT, (*c*) Zr0.2-HT, (*d*) Zr0.3-HT, (*e*) Zr0.4-HT, (*f*) Zr0.5-HT, (*g*) Zr0.6-HT, (*h*) Zr0.7-HT, (*i*) Zr0.8-HT, (*j*) Zr0.9-HT, (*k*) Zr1.0-HT

Table 1 Chemical compositions and lattice parameters of MgAlZr-HT

Sample	Mg : Al : Zr atomic ratio[a]	Carbon content[b] (%)	Lattice parameters[c] *a*/Å		
			a/Å	*c*/Å	*U*/Å^3
Zr0.0-HT	3 : 0.96 : 0.00	2.44	3.0584	23.1811	187.8
Zr0.1-HT	3 : 0.85 : 0.07	—	3.0643	23.4570	190.8
Zr0.2-HT	3 : 0.78 : 0.14	2.71	3.0688	23.5305	191.9
Zr0.3-HT	3 : 0.68 : 0.21	2.91	3.0687	23.7243	193.5
Zr0.4-HT	3 : 0.67 : 0.33	3.01	3.0732	23.7681	194.4
Zr0.5-HT	3 : 0.57 : 0.37	—	3.0773	23.9383	196.3
Zr0.6-HT	3 : 0.52 : 0.50	3.51	3.0780	24.1184	197.9

[a] Determined by X-ray fluorescence spectroscopy. [b] Determined by CHN microanalysis. [c] Refined using least square fitting method for hexagonal crystal system.

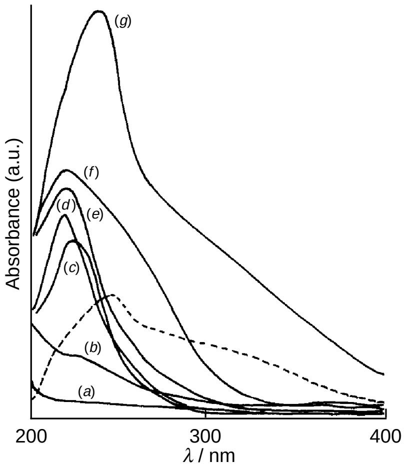

Fig. 2 UV–VIS diffuse reflectance spectra of MgAlZr-HT: (*a*) Zr0.0-HT, (*b*) Zr0.1-HT, (*c*) Zr0.3-HT, (*d*) Zr0.3-CHT, (*e*) Zr0.5-HT, (*f*) Zr0.8-HT, (*g*) pure ZrO_2, (---) Zr0.0-HT + pure ZrO_2 (physical mixture)

calcined at 723 K [Fig. 2(*d*)], exhibited a single narrow band around 210 nm. This absorption band is attributed to charge transfer involving isolated Zr^{IV} species.[9,10] Both pure ZrO_2 and a physical mixture of Zr0.0-HT and ZrO_2 exhibited bands around 240 and 320 nm. These results clearly demonstrate the absence of any ZrO_2 species within the sample and indicate that the Zr^{4+} cations are well dispersed in the HT matrix, similar to that in Zr-silicates.[9–11]

Some of the Zr containing hydrotalcites have been tested as catalysts in the hydroxylation of phenol using H_2O_2 as the oxidant. Preliminary studies with H_2O_2/phenol ratios from 0.5 to 8 using solvents such as water, CCl_4 or MeOH did not show any catalytic activity. However, appreciable activity (up to around 10% conversion of phenol) was observed when light petroleum (bp 60–80 °C) was used as the solvent. Table 2 summarizes the results of hydroxylation of phenol over various Zr containing hydrotalcites. It is interesting to note from the Table that the turnover number (TON; moles of phenol converted per mole of Zr atom) increases four-fold (1.0 to 3.8) when H_2O_2 is added dropwise using a syringe pump. Similarly, a two-fold increase (1.0 to 1.9) in catalytic activity is noticed if the sample is calcined at 723 K for 5 h. In all these cases, catechol is obtained as a unique product (100% selectivity). Upon increasing the H_2O_2/phenol ratio, the TON also increases considerably, but the selectivity of catechol decreases at the expense of hydroquinone. The absence of catalytic activity in the case of pure MgAl-HT without Zr (Zr0.0-HT) or pure ZrO_2 clearly indicates that the Zr incorporated in the HT framework plays a pivotal role in catalytic activity. Surprisingly, under similar experimental conditions, the Zr-containing silicalite (ZrS-1) which showed appreciable conversion in aqueous medium,[8] is found to be inactive in the hydroxylation of phenol. Further work is in progress in order to investigate the above differences and also to compare the catalytic performance with new Ti-containing hydrotalcites.

Table 2 Hydroxylation of phenol with H_2O_2 over MgAlZr-HT

Catalyst	H_2O_2/phenol molar ratio	TON[a]	Product selectivity (mass%) Catechol	Hydroquinone
Zr0.0-HT	5.0	—	—	—
Zr0.1-HT	5.0	1.4	100	—
Zr0.3-HT	5.0	1.0	100	—
Zr0.3-HT[b]	5.0	3.8	100	—
Zr0.3-CHT[c]	5.0	1.9	100	—
Zr0.3-HT	7.0	29.1	73.8	26.2
Zr0.3-HT	10.0	40.5	65.1	34.9
ZrS-1	5.0	—	—	—
ZrO_2	5.0	—	—	—

[a] TON = Turnover number (mole of phenol converted per mole of Zr atom). [b] H_2O_2 was added dropwise using a syringe pump at a rate of 0.5 ml h^{-1}. [c] Sample calcined at 723 K for 5 h. *Reaction conditions*: solvent light petroleum (bp 60–80 °C) 30 ml; phenol, 1 g; catalyst, 100 mg; temperature 353 K; time 8 h.

Based on the above experimental evidence, we report that pure and crystalline Zr containing HT-like compounds can be easily synthesized by a simple coprecipitation method. The Zr atoms are highly dispersed in the HT matrix and the resulting Zr-HT-like compounds are active in the catalytic hydroxylation of phenol to catechol.

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Footnote and References

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