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Catalysis Today 114 (2006) 397–402

CATALYSIS TODAY

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Studies of the effects of synthetic procedure on base catalysis using hydroxide-intercalated layer double hydroxides

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Available online 3 April 2006

Abstract

Layer double hydroxides (LDHs) based on the hydrotalcite structure ($Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$) have been synthesized by coprecipitation, sol–gel and urea hydrolysis methods and with Mg:Al ratios of 2:1 and 5:1. Scanning electron microscopy shows the coprecipitated phases present the smallest individual crystallite sizes (ca. 150 nm) with the largest crystallites (2–4 μm) for urea hydrolysis. Sol–gel samples show crystallites (150–450 nm) fused together into much larger particles. The samples have been calcined at 723 K in flowing air to produce metal oxide phases which have then been rehydrated in the presence of hydroxide ions to produce meixnerite-like LDH phases ($Mg_6Al_2(OH)_{20}{\cdot}4H_2O$). The base catalytic activity of these rehydrated samples has been measured by GC for the aldol self-condensation of acetone. Activity data has been correlated with sample characteristics to gain insight into the active sites and mode of action of these catalysts.

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Keywords: Base catalysis; Layer double hydroxides; Hydrotalcite; Aldol condensation

1. Introduction

Green chemistry can be described as the development of chemical technology causing minimum environmental impact [1]. Catalysis is a technology which can deliver green chemistry; ideally reactants are efficiently and selectively converted into the desired product with no side reactions and using less energy and the catalyst facilitating this process is endlessly recycled, thus creating no waste.

In this context, the replacement of liquid bases (e.g. $NaOH_{(aq.)}$) with solid base catalysts is a matter of increasing urgency because liquid bases are not catalytic. Thus, stoichiometric quantities (plus an excess) of highly corrosive liquid base are added to reactions creating stoichiometric quantities of by-product along with salts created by neutralisation of excess base, all needing separation and disposal. By comparison, solid base catalysts are less corrosive, easy to separate from the reaction and truly catalytic, so smaller quantities can be used. There is also no excess base to neutralise and the catalysts can be recycled, significantly reducing waste by-products. By comparison with solid base catalysts, solid acid catalysts have received more attention because of their more widespread use in industrial reactions. For instance, Tanabe and Hölderich have carried out a recent survey of industrial processes using solid acid–base catalysts finding 103 solid acid-classified processes compared to only 14 for solid bases [2]. There is, therefore an urgent need to carry out a fundamental study of new base catalyst materials using industrially relevant reactions if base catalysts are to parallel the success of their solid acid counterparts.

Materials previously studied as solid base catalysts include alkaline earth oxides, alkali metals or alkali metal compounds supported on metal oxides, zeolites and mixed metal oxides produced by the thermal decomposition of layer double hydroxides (LDHs) [3]. However, these catalysts can require high temperature pre-treatment after which they are easily poisoned by CO_2 and/or H_2O (except zeolites but these are generally only weakly basic) and, secondly, they can require specialised equipment to prepare (e.g. in $NH_{3(l)}$).

In 1998, Figueras and co-workers, reported aldol condensation activity for LDHs prepared by rehydration of calcined LDHs (prepared by precipitation) linking activity to hydroxide

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doi:10.1016/j.cattod.2006.02.035

anions [4] and Figueras has recently reviewed LDH base catalysis [5]. Synthetic LDHs are isostructural analogues of natural occurring hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$) with positively charged brucite-like layers containing Mg^{2+} and either Al^{3+} hydroxide edge-sharing octahedra with CO_3^{2-}, or other anions, and H_2O molecules between these layers [6]. Choudary and co-workers reported acetone/substituted-benzaldehyde aldol condensation activity for rehydrated LDHs showing catalyst versatility [7]. Tichit and co-workers have compared the acid–base properties of precipitated and sol–gel synthesized LDHs showing the latter to be more basic [8] and also compared MgAl and NiAl LDHs [9], whilst de Jong and co-workers have studied basic sites on precipitated [10] and hydrothermally treated [11] LDHs.

Hydroxide-intercalated MgAl LDH catalysts (Mg:Al = 2:1 and 5:1) have been prepared by rehydration of MgAl oxides produced by calcination of the corresponding carbonate-intercalated LDHs. These precursor LDHs have been prepared by coprecipitation, sol–gel methods and urea hydrolysis to investigate the influence of preparative method on catalyst characteristics and base catalytic activity for aldol condensation.

2. Experimental

2.1. Catalyst preparation

Coprecipitated LDHs were prepared using two solutions: 300 ml, 1 mol dm^{-3} aqueous solution of $Mg(NO_3)_2$ and $Al(NO_3)_3$ with the required Mg:Al ratio and 300 ml, 2.5 mol dm^{-3} aqueous $NaHCO_3$ solution (chemicals from Aldrich). Both solutions were heated to 343 K and combined together through a Pyrex glass T-piece (flow rate ca. 40 ml min^{-1}) feeding into 200 ml of vigorously stirred distilled water at 343 K. The pH was held between 6.8 and 7 by adjusting the flow rate of the $NaHCO_3$ solution. After the solutions were added, the mixture was aged in the mother liquor at 343 K for 30 min and filtered.

Sol–gel LDHs were prepared using a similar method to coprecipitated LDHs using a method adapted from the literature [12]. Variations from the coprecipitation method were that base solution was 300 ml of 2.25 mol dm^{-3} NaOH and 0.25 mol dm^{-3} $NaHCO_3$, the pH was held between 11.4 and 11.6 and here the mixture was aged in the mother liquor at 353 K for 3 h before washing with copious amounts of distilled water and filtering.

LDHs were prepared by urea hydrolysis using a method adapted from the literature [13]. A 500 ml solution containing $Mg(NO_3)_2$, $Al(NO_3)_3$ and urea was prepared with the required Mg:Al ratio to a total metal ion concentration of 0.06 mol dm^{-3} and with a urea concentration of 2 mol dm^{-3}. The solution was stirred and heated to 363 K for 42 h. After cooling, the resulting slurry was filtered, washed with distilled water and dried at 343 K.

Dry LDH powders were calcined to temperatures ranging at 723 K in a carbolite MTF tube furnace under flowing air (space velocity 30,000 h^{-1}). The final catalysts were prepared by suspending the calcined LDHs (0.4 g) in a 60 ml solution of ultra high quality water (Elgastat 18 MΩ cm^{-1}) containing 0.5 g NaOH (99.99%, Aldrich) under nitrogen for 48 h.

Initial LDH samples are labelled as follows: C = coprecipitated; SG = sol–gel; and U = urea hydrolysis followed by the Mg:Al ratio (thus, C2:1 is the Mg:Al 2:1 coprecipitated sample). Calcined samples are denoted C2:1C, SG2:1C, etc. and rehydrated samples are labelled C2:1_OH, SG2:1_OH, etc.

2.2. Characterisation techniques

X-ray powder diffraction was carried out using Ni-filtered Cu Kα1 radiation (λ = 1.54051 Å) on a X'Pert PRO theta–theta diffractometer (PANalytical Ltd.) at 45 kV and 35 mA. Data was collected using X'Pert Industry and analysed using Highscore software packages (PANalytical Ltd.). Samples were analysed in continuous scan mode (counting 10 s per 0.010° 2θ) between 5 and 75° 2θ.

Scanning electron microscopy was measured at 11 kV on a Hitachi S-520 SEM. EDAX was measured on the same instrument at 14 kV with an Oxford Instruments 7497 EDAX with Link ISIS computer software. Prior to analysis, samples were placed on conductive carbon tape on an aluminium stub and gold sputtered using an E5000 plasma coater (Polaron Equipment Ltd.) in a nitrogen plasma (0.1 Torr, 1 kV, 8 mA) for 5 min.

Thermal gravimetric analysis and differential scanning calorimetry were measured using a SDTQ600 TGA/DSC (TA Instruments Ltd.). Samples (typically 10 mg) were analysed in an alumina holder running at 10 K min^{-1} between room temperature and 1273 K.

Infrared spectroscopy was measured using KBr discs on a Tensor 27 FT-IR with OPUS software (Bruker Ltd.) typically with 32 scans and 4 cm^{-1} resolution.

3. Activity tests

Tests were carried out at 273 K and at 298 K using acetone (25 ml) and LDH catalyst (0.05 g). A blank (acetone only) and a reference catalyst (0.1 g NaOH to 25 ml acetone) were also tested. Aliquots (50 μl) were removed using an Eppendorf micropipette before reaction and at 1 and 3 h and diluted to 1 ml in acetone (HPLC grade). Products were analysed using a Varian CP3800 GC with FID detector on a ZB-wax column (30 m, 0.25 mm i.d., 0.5 μm phase), calibrated using in-house standards. The heating programme was 6 min at 313 K, then 20 K min^{-1} to 433 K, then 10 K min^{-1} to 473 K and a 6 min dwell at 473 K.

4. Results and discussion

Comparing the powder XRD data for the initial phases, the characteristic hydrotalcite LDH phase [14] was observed for all the MgAl 2:1 preparative methods. The $d_{0\,0\,3}$ spacing has been highlighted in Fig. 1A to emphasise the consistent interlayer spacing between samples. For MgAl 5:1, the sol–gel and urea hydrolysis samples showed only the hydrotalcite phase but the coprecipitated sample (Fig. 1B) showed a second

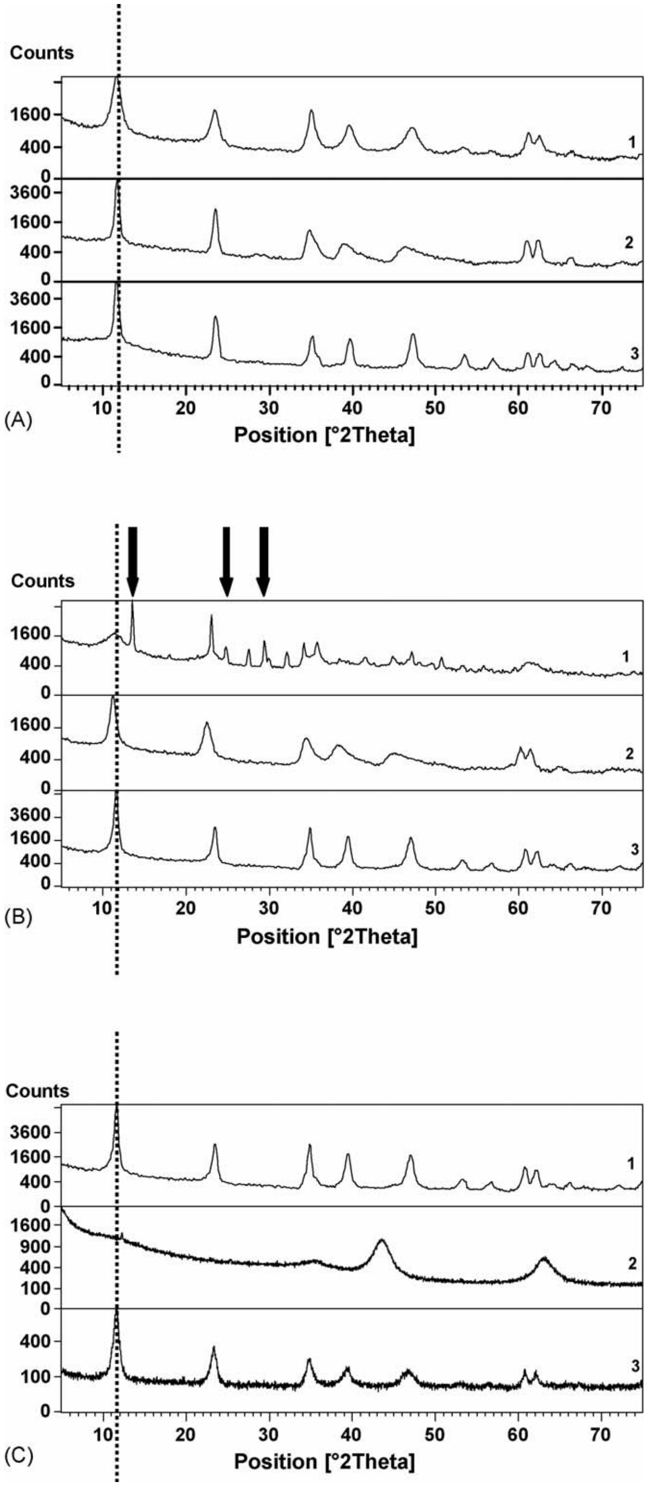

Fig. 1. (A) XRD analysis of (1) C2:1, (2) SG2:1 and (3) U2:1 precursors. (B) XRD analysis of (1) C5:1, (2) SG5:1 and (3) U5:1 precursors; arrows indicate nesquehonite phase. (C) XRD analysis of (1) U5:1, (2) U5:1C and (3) U5:1_OH. Dashed lines indicate LDH $d_{0\,0\,3}$ spacing.

phase isostructural with nesquehonite, a magnesium carbonate hydrate ($MgCO_3\cdot 3H_2O$) [15]. Fig. 1A and B show more reflections (e.g. at ca. 55° and above 64° 2θ) in the urea hydrolysis samples compared to others but these can all be indexed to a hydrotalcite phase [14]. The additional reflections are of low intensity and are too weak and broad to be observed in the less crystalline sol–gel and coprecipitated samples. There was also an increase in intensity and a narrowing of the diffracted peaks for sol–gel and urea hydrolysis samples compared to coprecipitated (Fig. 1A and B). This has been ascribed to increasing particle size and improved crystallinity; both of which were confirmed by SEM studies. For instance, for a Mg:Al ratio of 2:1 the coprecipitated particle sizes were <150 nm, the sol–gel particles ranged from 150 to 450 nm and the urea samples exhibiting well defined platelets of 2–4 μm size (Fig. 2).

TGA data for the precursor samples was in line with published data for MgAl LDHs with initial loss of interlayer water between 298 and ca. 510 K and then loss of interlayer carbonate and hydroxyls from the metal hydroxide layers from 510 to 773 K [6]. The total weight loss (up to 1273 K) was ca. 43% for all samples in line with the calculated values (43.2% for Mg:Al 2:1 and 42.9% for 5:1) except for C5:1 where the weight loss was ca. 55% by 1273 K reflecting the presence of nesquehonite as a second phase ($MgCO_3\dot{}\,3H_2O$ to MgO gives 71% weight loss). A calcination temperature of 723 K was used to ensure maximal carbonate loss at the lowest possible temperature because an excessive calcination temperature would inhibit rehydration to the LDH phase. At 723 K the TGA data, run at 10 K min^{-1}, confirmed that >90% conversion to metal oxide should have occurred in all samples although, during catalyst preparation, the 4 h dwell at 723 K would have been expected to increase the degree of conversion to the oxide. XRD data for all calcined samples showed broad, low intensity peaks corresponding to an MgO phase [16]. Scanning electron microscopy (e.g. Fig. 2c and d) showed that the varying crystallite sizes observed in the precursors across the series, coprecipitated to sol–gel to urea hydrolysis, remained in the calcined samples. The broad diffraction peaks observed by XRPD may be due to crystallites not being single diffraction domains or due to low crystallinity which was, in turn, related to the low calcination temperature (723 K). All the rehydrated samples showed only the characteristic hydrotalcite structure (Fig. 1C shows the XRD data for U5:1, U5:1C and U5:1_OH for comparison). Interestingly, this included C5:1_OH for which the initial precursor contained the additional nesquehonite phase. However, these data did not differentiate between carbonate or hydroxide interlayer anions as the same interlayer *d*-spacing would be expected for both (ca. 7.7 Å). Instead, the absence of carbonate and presence of interlayer hydroxide ions was confirmed by infrared spectroscopy by the absence of the strong carbonate peak at ca. 1400 cm^{-1} and the emergence of a sharp peak at ca. 3700 cm^{-1} (indicative of discreet hydroxide) as a shoulder on the broad 3600–3000 cm^{-1} OH stretching mode ascribed to the metal hydroxide layers and H-bonded interlayer water [6]. EDAX analysis also confirmed the absence of carbon in the rehydrated samples. It should be noted here that successful production of hydroxide-intercalated samples was only possible when using high purity sodium hydroxide (99.99%) as reagent grade NaOH (>98%) contains sodium carbonate as an impurity. Such is the preference of LDH phases for carbonate that this small impurity was sufficient to produce

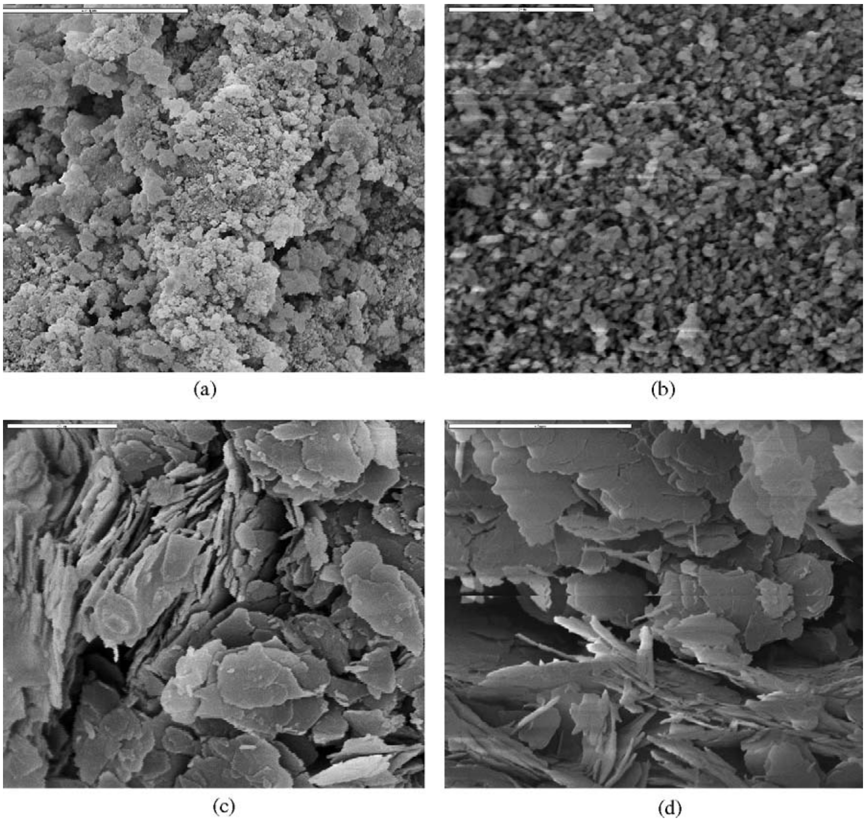

Fig. 2. Scanning electron micrographs of (a) C2:1—scale bar is 20 μm, (b) SG2:1—scale bar is 2 μm, (c) U2:1—scale bar is 2 μm and (d) U2:1C—scale bar is 5 μm.

carbonate-intercalated LDHs on rehydration (again confirmed by IR spectroscopy).

Fig. 3 shows scanning electron micrographs of each of the catalysts prior to reaction. The urea hydrolysis samples can be seen to be made up of individual platelet particles in line with the typical morphology for hydrotalcite-like materials. These samples show smaller platelet particles (100–400 nm across) on the surface of groups of much larger platelet particles (ca. 2–5 μm). The smaller particles were not apparent in the original (U2:1 and U5:1) or the corresponding calcined samples and so must be produced during the rehydration process. There is also evidence for platelet morphology in the coprecipitated samples. However, the particles are smaller (ca. 200 nm long) and less well defined compared with U2:1_OH and U5:1_OH. The morphology of the sol–gel samples is different again and it appears that smaller particles (ca. 500 nm across) have fused together (with some evidence of layering) to form very much larger particles.

The data for the activity tests (Table 1) show % yield by weight of 4-methyl-4-hydroxy-2-pentanone or diacetone alcohol (DAA) from the aldol self-condensation of acetone after 1 and 3 h. Blank tests (no catalyst) showed no DAA yield and NaOH (0.1 g compared to 0.05 g of LDH catalyst) showed yields comparable to the least active LDH materials (from the sol–gel preparation). For the LDH catalysts, we have used this test reaction to study the effects of catalyst preparation, composition and also the effect of reaction temperature (273 and 298 K). As expected, all the catalysts show higher activities at 298 K compared to 273 K and higher yields of DAA after 3 h compared to 1 h. It is possible for diacetone alcohol to undergo dehydroxylation to produce 4-methyl-3-pentene-2-one (mesityl oxide) as a by-product. In addition, for more basic, alkali metal doped MgO it has been reported that mesityl oxide can undergo further reaction with another acetone molecule to produce isophorone [17]. However, in all our activity tests, diacetone alcohol was the only product observed regardless of catalyst, reaction temperature or time.

Firstly, comparing the preparative methods, the urea hydrolysis samples show the highest activity followed by the coprecipitated catalysts with the sol–gel samples showing the lowest yields of diacetone alcohol. Catalysts with greater basicity might be expected to give rise to dehydrated products of diacetone alcohol (e.g. mesityl oxide). The absence of any by-products suggests that the different preparative routes do not give rise to large differences in basicities between the catalysts. One reason for the enhanced activity in the urea samples may be that these samples show better crystallinity in the XRD and SEM data and the loss of the lamellar structure has previously been linked to poor activity [9]. It is not possible, at this stage, to differentiate whether the need for a lamellar structure arises from active sites in the interlayer region or on the surfaces of the crystallites. However, it should be noted that, if crystallinity was the only reason for enhanced activity for the urea hydrolysis catalysts, then the sol–gel samples show better crystallinity than the coprecipitated samples and so should be more active which is not the case. Instead, our data suggest that crystallite shape may also be important as the urea hydrolysis crystallites are larger and

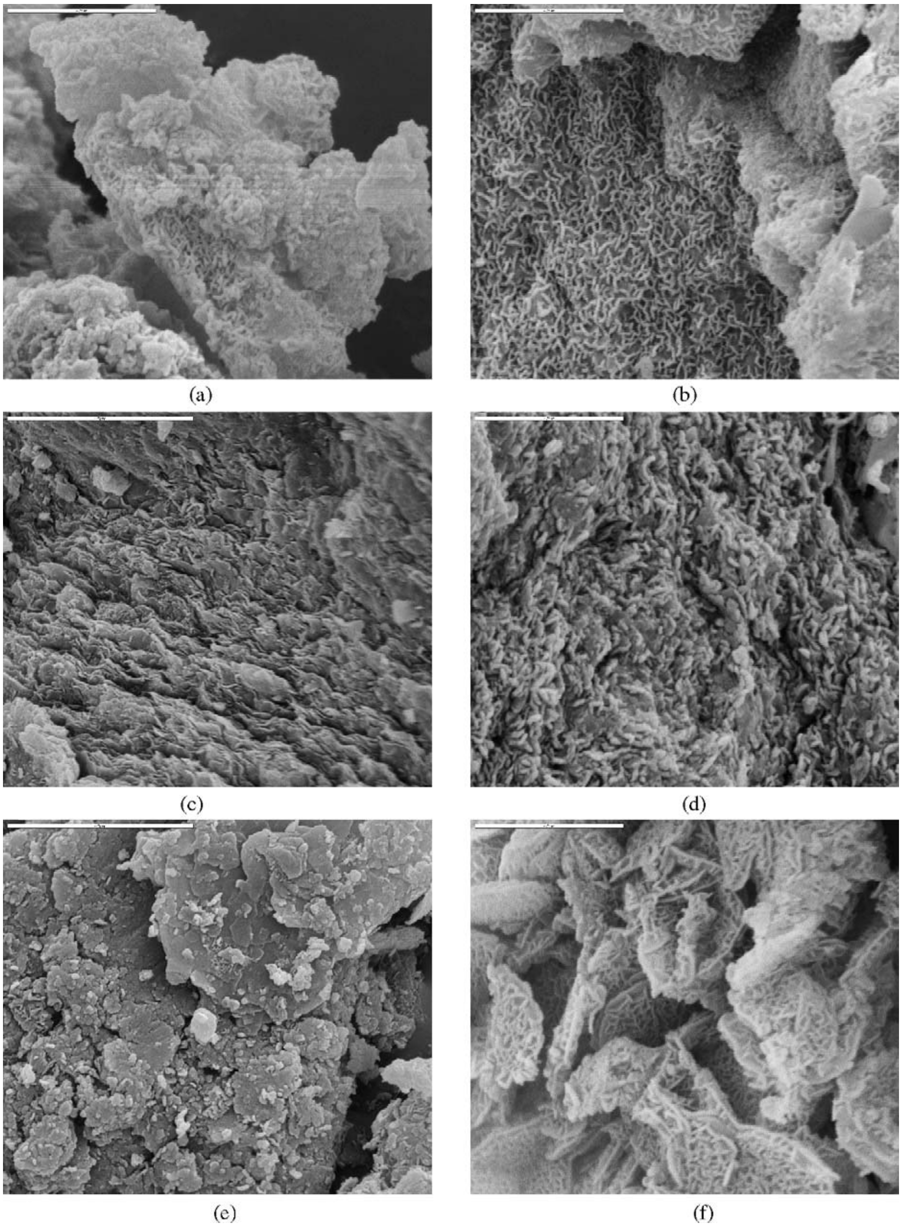

Fig. 3. Scanning electron micrographs of catalysts produced by rehydration of calcined LDH samples: (a) C2:1_OH; (b) C5:1_OH; (c) SG2:1_OH; (d) SG5:1_OH; (e) U2:1_OH; and (f) U5:1_OH. Scale bars are 2 μm except for (c) and (e) where it is 5 μm.

have higher aspect ratios than the other catalysts. This is interesting as previous workers have suggested that LDH basic sites are most likely situated at crystallite edges [10,11] but, if this was the case, then the coprecipitated and sol–gel catalysts would be expected to present the highest activities because their smaller particle size would result in a greater proportion of ‘‘crystallite-edge’’ sites.

Looking at the effect of Mg:Al ratio, there are not great differences in activity between the Mg:Al 2:1 and Mg:Al 5:1 catalysts for the sol–gel and urea samples, whilst there is some

Table 1
% yield of diacetone alcohol from acetone self-condensation after 1 and 3 h

Temperature (K)	Time (h)	C2:1_OH	C5:1_OH	SG2:1_OH	SG5:1_OH	U2:1_OH	U5:1_OH	NaOH
273	1	7.1	5.2	1.8	1.7	11.2	12.9	3.0
	3	10.7	8.8	3.6	3.0	15.2	13.7	4.4
298	1	11.6	9.1	4.5	3.7	16.2	17.1	5.7
	3	13.7	12.0	6.0	6.0	17.7	18.0	7.7

limited evidence for slightly higher DAA yields for C2:1_OH compared to C5:1_OH. This is interesting as a lower Mg:Al ratio would reflect a higher proportion of Al^{3+} ions in the metal hydroxide layers of the LDH structure. This, in turn, would need to be balanced by a higher proportion of hydroxide anions which would be expected to lead to an increased number of basic sites. In the samples tested here, there should be 2.5 times as many Al^{3+} in the Mg:Al 5:1 samples compared to Mg:Al 2:1, so in theory there should be 2.5 times the number of OH^- active sites. The absence of a significant influence of Mg:Al ratio on activity may indicate that either there are basic sites other than OH^- active in the reaction or that only a small proportion of the basic sites are active and this proportion is similar regardless of Mg:Al ratio. Previous data reported for the citral/acetone condensation using coprecipitated catalysts suggested that only 5% of the basic active sites available are active in this reaction which supports the latter [10,11].

5. Conclusions

This work has shown that hydroxide-intercalated layer double hydroxides can be produced by the rehydration of calcined oxides producing catalysts with similar composition and structure within Mg:Al ratio or initial preparative method. Activity data for acetone self-condensation shows that the initial mode of LDH preparation does influence activity but there was no evidence that it affects basicity for this reaction as only one product was measured throughout. Our data also suggest that it is less likely that basic active sites are situated only at crystallite edges because there of the greater activity for catalysts produced from urea hydrolysis methods and these exhibit larger crystallites with higher aspect ratios and improved crystallinity compared to coprecipitated or sol–gel samples. Instead, the enhanced lamellar structure in these samples is also believed to be important.

Acknowledgements

We gratefully acknowledge EU-ESF funding for BV, and the technical assistance of Mr. Stephen Jones (XRPD), Mr. Kevin Spencer (TGA/DSC), Mr. Andrew Davies (SEM/EDAX) and Mr. Denis Williams (GC).

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