

SYNTHESIS AND CATALYTIC PROPERTIES OF SILICATE-INTERCALATED LAYERED DOUBLE HYDROXIDES FORMED BY INTRAGALLERY HYDROLYSIS OF TETRAETHYLORTHOSILICATE

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Abstract—Layered double hydroxides (LDH's) interlayered with silicate anions were prepared by reaction of tetraethylorthosilicate (TEOS) with synthetic meixnerite-like precursors of the type $[Mg_{1-x}Al_x(OH)_2][OH^-]_x \cdot zH_2O$, where $(1-x)/x \approx 2, 3$, or 4. TEOS hydrolysis at ambient temperature occurred readily in the galleries of the hydroxide precursors with $(1-x)/x \approx 3$ or 4, but a temperature of $\sim 100^\circ C$ was required to achieve silicate intercalation for the LDH composition with $(1-x)/x \approx 2$. On the basis of the observed gallery heights ($\sim 7.0\text{--}7.2 \text{ \AA}$) and ^{29}Si MAS NMR spectra that indicated the presence of Q^2 , Q^3 , and Q^4 SiO_4 sites, the intercalated silicate anions, which are formed by condensation reactions of silanol groups and partial neutralization of SiOH groups with gallery hydroxide ions, are assigned short chain structures. Also, some O_3SiOH groups become grafted to the LDH layers by condensation with MOH groups on the gallery surfaces. The LDH-silicates exhibited comparable non-microporous N_2 BET surface areas in the range 59–85 m^2/g , but they differed substantially in acid/base reactivities, as judged by their relative activities for the catalytic dehydration/disproportionation of 2-methyl-3-buten-2-ol (MBOH). Under reaction conditions where the LDH structure is retained ($150^\circ C$), all the silicate intercalates showed mainly basic reactivities for the disproportionation of MBOH to acetone and acetylene. However, all the LDH silicates were less reactive than the corresponding LDH carbonates. Conversion of the LDH silicates to metal oxides at $450^\circ C$ introduced acidic activity for MBOH dehydration, whereas the metal oxides formed by LDH carbonate decomposition were exclusively basic under analogous conditions.

Key Words—2-methyl-3-buten-2-ol conversion, Acidic and basic properties, Intragallery hydrolysis, Layered double hydroxides, Silicate intercalation, Tetraethylorthosilicate.

INTRODUCTION

There has been considerable interest in layered double hydroxide (LDH) compounds of the type $[M^{II}_{1-x}M^{III}_x(OH)_2][A^{n-}]_{x/n} \cdot zH_2O$. In these structures the brucite ($Mg(OH)_2$)-like layers have M^{II} substituted by M^{III} and the layers are charge balanced by the hydrated A^n gallery anions. Significant efforts have been made to utilize LDH compositions as heterogeneous catalysts or catalyst precursors, ion exchangers and adsorbers, and other new materials (Cavani *et al* 1991). Recent developments in the pillaring of LDH's by robust polyoxometalate (POM) intercalants have introduced another important aspect of the catalytic applications of this class of materials by providing access to the microporous gallery space (Kwon *et al* 1988, Drezdson 1988, Chibwe and Jones 1989, Dimotakis and Pinnaivaia 1990, Wang *et al* 1992, Naria *et al* 1993, Tatsumi *et al* 1992). Shape selectivity for the epoxidation of alkenes, for example, has been demonstrated for LDH-POM intercalates of different gallery height (Tatsumi *et al* 1992).

Recent studies of ion exchange reactions of silicate

anions with simple LDH precursors have afforded silicate derivatives with potentially interesting catalytic properties (Schutz and Biloen 1987, Fyfe *et al* 1994). Polymerization of interlayer silicate anions was observed by Schutz and Biloen (1987) upon reaction of Mg_3Al - and $LiAl_2$ -LDH chlorides with basic silicate anions. In efforts to achieve a strong basic catalytic activity, as well as pillared access to the gallery surfaces Fyfe *et al* (1994) have investigated the reactions of LDH chlorides and the octasilicate ion $Si_8O_{20}^{8-}$.

Here we report a new approach to LDH-silicate intercalates based on the reaction of synthetic meixnerite-like LDH precursors of the type $[Mg_{1-x}Al_x(OH)_2][OH^-]_x$ ($x = 0.312, 0.231$ and 0.196) with tetraethylorthosilicate (TEOS). Our interest in TEOS as a silicate precursor was stimulated in part by the possibility that the monomeric $Si(OH)_4$ formed upon TEOS hydrolysis might undergo topotactic condensation with the hydroxyl groups of the LDH layers. One possible topotactic product is a 2:1 layered silicate. The conversion of an LDH to a 2:1 layered silicate structure would afford a novel material with the reversed charge polarity of a smectite or vermiculite. Such materials might be exceptionally basic when interlayered with silicate or hydroxide ions and potentially well suited for en-

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vironmentally relevant catalytic conversions, such as dechlorinations of chlorinated alkanes at ambient temperature. As will be demonstrated by the results of the present work, however, the base catalyzed hydrolytic condensation reactions of TEOS in LDH hydroxides resulted instead in simple LDH-silicate intercalates. The structural and textural properties of the LDH-silicates were studied, and their catalytic acidic and basic properties were investigated using the dehydration and disproportionation of 2-methyl-3-butyn-2-ol as probe reactions. The catalytic results were compared with those for LDH carbonate analogues.

EXPERIMENTAL

Materials preparation

Layered double hydroxides (LDHs) of the type $[Mg_{1-x}Al_x(OH)_2](CO_3)_{x/2} \cdot zH_2O$ ($(1-x)/x \approx 2, 3, \text{ or } 4$) were prepared by coprecipitation at constant pH. A 500-ml quantity of H_2O was placed in a reaction vessel at $40^\circ C$, and the pH was adjusted to 10.0 by the addition of several drops of a mixed base solution containing equal volumes of Na_2CO_3 (1.0 M) and NaOH (2.0 M). The mixed base solution and a mixed nitrate solution (2.0 M, 250 ml) of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ with a Mg/Al ratio of 2.0, 3.0, or 4.0 were then added to the H_2O at rates that maintained the pH at 10.0. The amount of mixed base solution was sufficient to make the overall CO_3^{2-}/Al^{3+} ratio equal to 1.5. Once all the mixed base solution was consumed, NaOH (2.0 M) was added to keep reaction pH at 10.0 for the rest of the precipitation. After complete delivery of the mixed nitrate solution, the reaction mixture was stirred vigorously for 4 h at $40^\circ C$ and then aged for 40 h at $70^\circ C$ with good stirring. Upon completion of the digestion period, the product suspension was cooled to room temperature and centrifuged. The resulting white product was then filtered and washed free of carbonate ion with water (as observed by $AgNO_3$ test). All products were air-dried on glass plates.

Aqueous suspensions (1.0 wt. %) of meixnerite-like Mg_3Al -, Mg_2Al - or Mg_4Al -LDH hydroxides were prepared from their corresponding LDH- CO_3 analogues by a thermal decomposition and reconstruction process (Sato *et al* 1988). The $Mg_{1-x}Al_x$ LDH carbonate (1.0 g) was first calcined in a quartz furnace for 5 h at $500^\circ C$ under a N_2 flow to form a mixed metal oxide solid solution. The calcined solid oxide was then placed in a sealed flask containing 100 ml of degassed H_2O under N_2 at room temperature for 5 days to form the $Mg_{1-x}Al_x$ LDH hydroxide.

For the preparation of LDH-silicates from Mg_4Al - and Mg_3Al -LDH hydroxides, neat $Si(OC_2H_5)_4$ was slowly added in excess to 100 ml H_2O of a LDH hydroxide suspension at room temperature under N_2 . The molar ratio of $Si/(Mg+Al)$ was 10.0. The reaction mixture was stirred for 24 h and then 200 ml of an-

hydrous ethanol was added to the suspension under N_2 at room temperature. The white product was centrifuged and washed with 200 ml of ethanol, a mixed solution of 100 ml ethanol and 100 ml water, and finally two times with 200 ml water. The product was dried in air at room temperature.

The intercalation reaction of the Mg_2Al -LDH hydroxide with $Si(OC_2H_5)_4$ was performed at refluxing conditions ($100^\circ C$) under N_2 for 24 h. The suspension was cooled to room temperature before the addition of 200 ml ethanol. All other operations were the same as described above for the Mg_3Al - and Mg_4Al -LDH silicate products.

Catalytic studies

2-Methyl-3-butyn-2-ol (MBOH) (Aldrich Chemical Company) was used without further purification. Chromatographic analysis confirmed the high purity of the reagent. The retention time and the response factor of the products formed from the acidic or basic catalytic reactions of MBOH (Lauron-Pernot *et al* 1991) were evaluated using reference compounds. The response factor of acetylene was determined by disproportionation of MBOH over MgO assuming that the molar ratio of the acetone/acetylene reaction products was one (Lauron-Pernot *et al* 1991). MBOH conversion was carried out in a micro reactor equipped with an Omega Programmable Temperature Controller Model CN2011K and an on-line Perkin-Elmer 8500 gas chromatograph. The liquid reactant was placed in a saturator at $24^\circ C$ and the vapor was introduced into the reactor by means of a He flow of 11.3 ml/min. A 150-mg quantity of the LDH-silicate with a particle size between $150 \mu m$ and $75 \mu m$ was placed in the reactor and activated at $150^\circ C$ or $450^\circ C$ under a He flow for 2 h. The reactor was equilibrated at the desired temperature and the MBOH stream was introduced at a flow rate of approximately 0.65 mmol/h (Conner *et al* 1950). The products were analyzed by gas chromatography after intervals of 1 h reaction time. The chromatograph was equipped with a FID detector and a $6'' \times \frac{1}{8}''$ O.D. stainless steel column packed with 3% SP-1500 on Carbopack B (80/120 mesh). Sample weight loss at constant temperature was determined by TGA using a ramp rate of $3^\circ C/min$ and then holding the temperature at $150^\circ C$ or $450^\circ C$ for 2 h.

Physical measurements

X-ray diffraction patterns of powdered samples were obtained at room temperature with a Rigaku X-ray diffractometer equipped with DMAXB software and curved graphite monochromator attachment for $Cu K_\alpha$ x-ray radiation. Quartz was used as a standard.

Fourier transformed infrared (FTIR) spectra of samples dispersed in KBr disks (1–2% w/w) were recorded with an IBM model IR 40S spectrometer.

Thermogravimetric analyses (TGA) were carried out

under N₂ on a Cahn 121TG System for solid samples (~50 mg) with a heating rate of 5°C/min. For the determination of weight loss at constant temperature (150°C and 450°C) the heating procedure approximated the conditions used for catalyst activation by utilizing a ramp rate of 3°C/min, followed by isothermal heating at the temperature for two hours.

Nitrogen adsorption/desorption isotherms at liquid nitrogen temperature were obtained on a Coulter Omnisorb (TM) 360CX sorptometer using ultrahigh purity nitrogen as the adsorbate and helium as the carrier gas. Samples of about 100 mg were outgassed overnight at 130°C under a vacuum of 10⁻⁵ torr. Surface areas were obtained by the BET method (Brunauer *et al* 1938). For the surface areas of LDH carbonates and silicates, the BET equation was applied over the partial pressure range of 0.05 < P/P₀ < 0.2 where the correlation coefficients were near one. Mesopore volumes in the pore radius range 10 Å to 200 Å were obtained from N₂ desorption branches (0.19 < P/P₀ < 0.95).

Transmission electron micrographs (TEM) were obtained with a JEOL 100CX TEM at the Center for Electron Optics at MSU. Samples were prepared by dipping copper grids coated with holey carbon films into a water suspension of the LDH and allowing the grid to dry in air.

²⁹Si MAS NMR experiments were performed on a Varian 400 VXR solid-state NMR spectrometer operated at 79.5 MHz. A Bruker multinuclear MAS probe equipped with zirconia rotors was used for all measurements. The ²⁹Si spin lattice relaxation times were determined experimentally by inversion recovery experiments. ²⁹Si MAS spectra were obtained using a 90° pulse of duration of 9 μs. The spinning rate was approximately 4 kHz. Delay times approximately 5 times as large as T₁ were allowed for full relaxation of the Si nucleus. The ²⁹Si chemical shifts relative to tetramethylsilane were determined using talc with a chemical shift of -98.1 ppm as an external reference. Deconvolution of overlapping spectral lines was carried out using Varian software VNMR (version 4.3) assuming Lorentzian line shapes.

Elemental analyses were performed by ICP emission spectroscopy at the Toxicology Laboratory at MSU. About 20 mg of the samples was dissolved in 100 ml HNO₃ solution (20% by vol.) for each analysis.

RESULTS AND DISCUSSION

In general, large gallery counter ions are the most promising pillaring agents for layered silicates (Yamanaka and Hattori 1991), layered metal oxides (Hou *et al* 1993) and layered double hydroxides (Kwon *et al* 1988, Drezdzone 1988, Chibwe and Jones 1989, Dimotakis and Pinnavaia 1990, Wang *et al* 1992, Narita *et al* 1993, Tatsumi *et al* 1992) and related ionic solids. In the case of positively charged LDH structures, several anionic species have been intercalated into the

gallery region of layers, including anionic surfactants, metallophthalocyanine tetrasulfonates (Meyn *et al* 1990, Chibwe and Pinnavaia 1993, Carrado *et al* 1993) and large polyoxometalates such as Mo₇O₂₄⁶⁻, H₂W₁₂O₄₀⁶⁻ and BVW₁₁O₄₀⁷⁻ (Kwon *et al* 1988, Drezdzone 1988, Chibwe and Jones 1989, Dimotakis and Pinnavaia 1990, Wang *et al* 1992, Narita *et al* 1993, Tatsumi *et al* 1992). However, relatively little work has been reported concerning the intercalation of silicate anions in LDH structures.

Two different approaches have been used to intercalate silicates into the gallery region of LDH hosts. Silicic acid in basic NaOH solution has been used by Schutz and Biloen (1987) as the silicate anion source for anion exchange reaction with an LDH chloride precursor. The intercalated silicate anions were assigned puckered two-dimensional silicate layers of [HSi₂O₅]_nⁿ⁻ with a hexagonal unit cell of a = b = 5.2 Å on the basis of ²⁹Si MAS NMR and selected area electron diffraction studies. Fyfe *et al* (1994) recently reported poly-silicate-intercalated LDH compounds prepared by ion exchange reactions of LDH chlorides and Si₈O₂₀⁸⁻. Access to the gallery micropores was claimed for the LDH-Si₈O₂₀⁸⁻ intercalates with gallery heights of ~7 Å. A related approach to mixed layered silicate metal (II) hydroxide compounds was reported by Ohtsuka *et al* (1990). The addition of a base to an aqueous suspension of sodium tetrasilic mica exchanged with M(II) (Mg, Ca, Mn, Ni, Zn and Co, etc.) resulted in chlorite-like intercalates with continuous 2:1 silicate layers and hydroxide interlayers with a cadmium iodide type structure and compositions of the type [M^{II}_x(OH)_{2x-1}(H₂O)]⁺ [Mg_{2.5}Si₄O₁₀F₂]⁻ (0.5 ≤ x ≤ 3).

In the present study we describe a complementary approach to the interlamellar silicate chemistry of LDH compounds using TEOS as the silicate reagent. A series of synthetic meixnerite-like LDH hydroxide analogs derived from [Mg_{1-x}Al_x(OH)₂][CO₃]_{x/2} ((1 - x)/x = 2.22, 3.33 and 4.12) were allowed to react with excess TEOS under N₂. The differences in the LDH charge densities afforded different intragallery concentrations of OH⁻ as a reactant. Thus, different structural types of intragallery silicate anions might form and become grafted to the LDH layers by condensation reaction with the hydroxide groups of the layer.

The reaction of TEOS with Mg₃Al- and Mg₄Al-LDH hydroxides at room temperature readily afforded silicate-intercalated derivatives. In contrast, the Mg₂Al-hydroxide showed no intercalation under the same reaction conditions, even in the presence of a large excess of TEOS. Since the Mg₂Al-LDH hydroxide has the highest layer charge density in the Mg_{1-x}Al_x hydroxide series, it is expected to have the strongest electrostatic H-bonding interactions between the LDH layers and gallery hydroxyl groups. The stronger H-bonding then may inhibit penetration of the TEOS molecules into the gallery regions. However, reaction under reflux

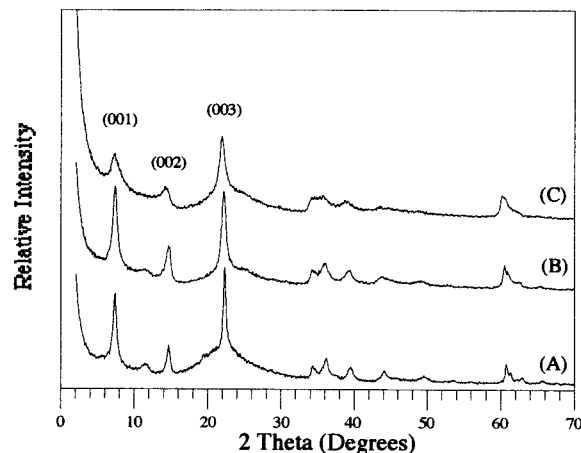


Figure 1. Powder XRD patterns of (A) Mg_2Al -, (B) Mg_3Al - and (C) Mg_4Al -LDH silicate intercalates.

conditions proved to be effective in obtaining the Mg_2Al -silicate intercalate. Neutral TEOS molecules migrate into the LDH gallery region and then react with interlayer water molecules and hydroxide ions to form a silicate structure via condensation of SiOH groups. The pH at room temperature dropped from ~ 11.5 for the initial meixnerite suspension to ~ 7.5 after reaction with TEOS, indicating that the gallery OH^- ions in the meixnerite-like intercalate indeed were consumed in the hydrolysis reaction with TEOS molecules. On the basis of a recent study of base-catalyzed hydrolysis and condensation reaction of TEOS (Harris *et al* 1990), we expect the intercalated TEOS first to be attacked by the gallery OH^- ions by a nucleophilic reaction mechanism, followed by further hydrolysis and condensation to form silicate anions between the host layers.

Our LDH-silicate products exhibited XRD patterns similar to the LDH-silicate intercalates prepared in other studies (Schutz and Biloen 1987, Fyfe *et al* 1994). Each of our $Mg_{1-x}Al_x$ -LDH silicates has a basal spacing of 12.0–12.2 Å as shown by the diffraction patterns in Figure 1. Since the LDH layer thickness is 4.8 Å, gallery heights of 7.0–7.2 Å were formed in the silicate intercalation reactions. In addition to $(00l)$ and $(hk0)$ reflections due to the LDH-silicate, two additional XRD reflections at about 11.5° (7.7 Å) and 22° – 24° (4.0–3.7 Å) also were observed in our samples. These same “extra” reflections also were reported for the products prepared by Schutz and Biloen (1987). Small quantities of unreacted LDH hydroxide might be responsible for the phase reflecting at 11.5° (7.7 Å). The broad reflections at 18° – 28° (4.9 to 3.2 Å) are due to amorphous silica by-products formed during the reaction. This latter assignment was confirmed by the XRD pattern for a commercial silica gel.

TEM images of our LDH silicate intercalates showed

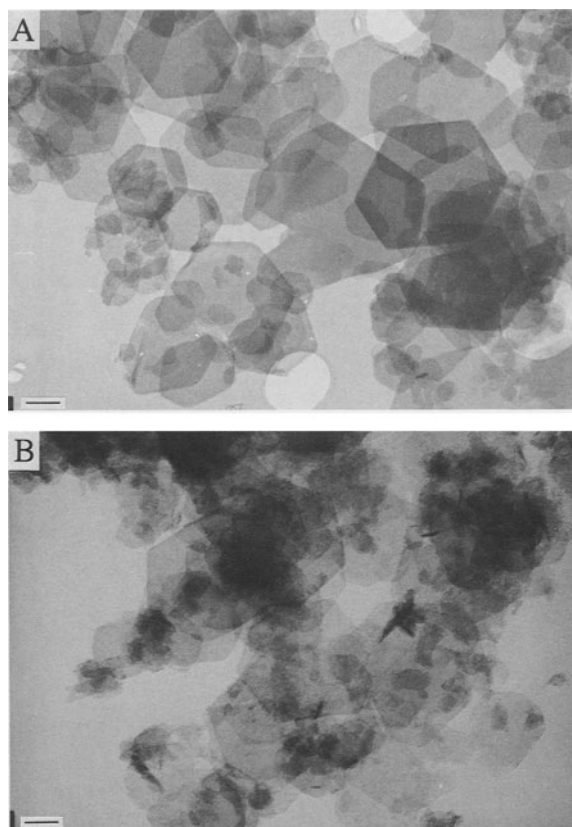


Figure 2. TEM images of Mg_3Al -LDH silicates: (A) hexagonal crystals with smooth, silica-free surfaces and (B) less commonly observed crystals containing a coating of amorphous silica. The scale bar is 1000 Å. Mg_2Al - and Mg_4Al -LDH silicates gave similar TEM images.

that the crystal morphologies of the meixnerite-like precursors were retained upon reaction with TEOS. As shown by the micrograph in Figure 2a for the Mg_3Al LDH silicate, most of the crystals exhibited hexagonal shapes (~ 500 – 2500 Å diameter) and smooth surfaces. However, some crystals were coated with a precipitate which we attribute to extragallery silica. This amorphous silica phase most likely forms by hydrolytic condensation of TEOS external to the LDH gallery and probably is responsible for the broad x-ray reflections observed at 22 – 24° .

Insights concerning the interlayer silicate structure was obtained by FTIR and ^{29}Si MAS NMR studies. All three silicate-intercalated Mg-Al LDHs showed strong vibrations at 950 – 1200 cm^{-1} in their FTIR spectra (Figure 3). These bands are quite similar to the LDH-silicate of Schutz and Biloen (1987), except that in our materials the bands are broader. According to Groenen *et al* (1987) broad absorption bands at 950 – 1200 cm^{-1} , indicate the presence of silicates in various polymeric forms.

As shown in Figure 4, the ^{29}Si MAS NMR spectra

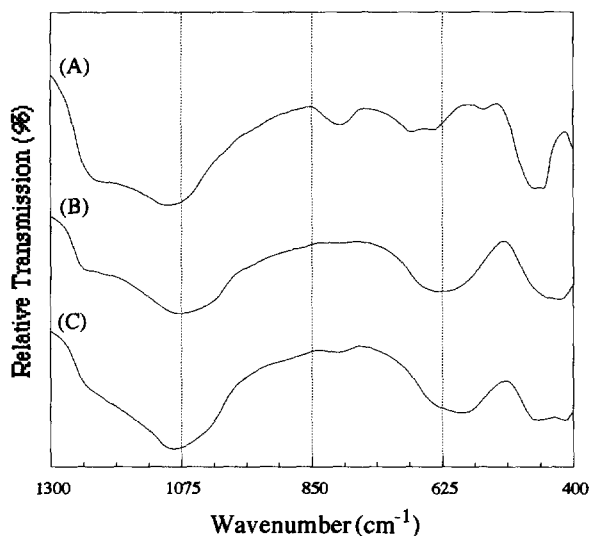


Figure 3. FTIR spectra for (A) Mg_2Al -, (B) Mg_3Al - and (C) Mg_4Al -LDH silicate intercalates.

of the LDH-silicates contained three ^{29}Si resonances at approximately -113 , -102 and -92 ppm, which are assigned to Q^4 , Q^3 and Q^2 SiO_4 sites, respectively. In contrast, previously reported LDH silicates exhibit a single Q^3 resonance (Schutz and Biloen 1987, Fyfe *et al* 1994). Table 1 provides the chemical shifts and relative intensities for our intercalates. Although the presence of some extragallery silica limits the interpretation of the NMR data, the analytical data shown in Table 2 indicate the molar $Si/(Mg + Al)$ ratios to be relatively low, in the range 0.33–0.54. Thus, it is unlikely that the Q^2 and Q^4 resonances are due exclusively to extragallery silica, because this would require the intercalated Si to octahedral $Mg + Al$ molar ratios to be unreasonably low (i.e., 0.10–0.18) and incompatible with the observed gallery heights of ~ 7.0 Å. Also, it is noteworthy that the possibility of a 2:1 layered silicate structure is precluded by the NMR results and the analytical data. A 2:1 layered silicate should exhibit only a Q^3 resonance and a Si to octahedral metal ion ratio of 1.33. We propose on the basis of the XRD gallery heights and the NMR and analytical data that short chain silicate structures, rather than a layered structures are formed in the LDH galleries and that some coupling O_3SiOH groups to the LDH layers and adjacent silicate chains occurs to give Q^4 sites. Formation of the intragallery polymeric silicate anions in meixnerite-like LDHs can be thought of as occurring in three distinct steps, namely, (i) the hydrolysis of TEOS to form $Si(OC_2H_5)_{4-y}(OH)_y$ precursors, (ii) condensation of silanol groups to form $SiOSi$ linkages, and (iii) neutralization of some $SiOH$ groups by hydroxide exchange ions of the LDH to form the interlayer polysilicate anions.

Based on a ^{29}Si NMR spectrum that contained only

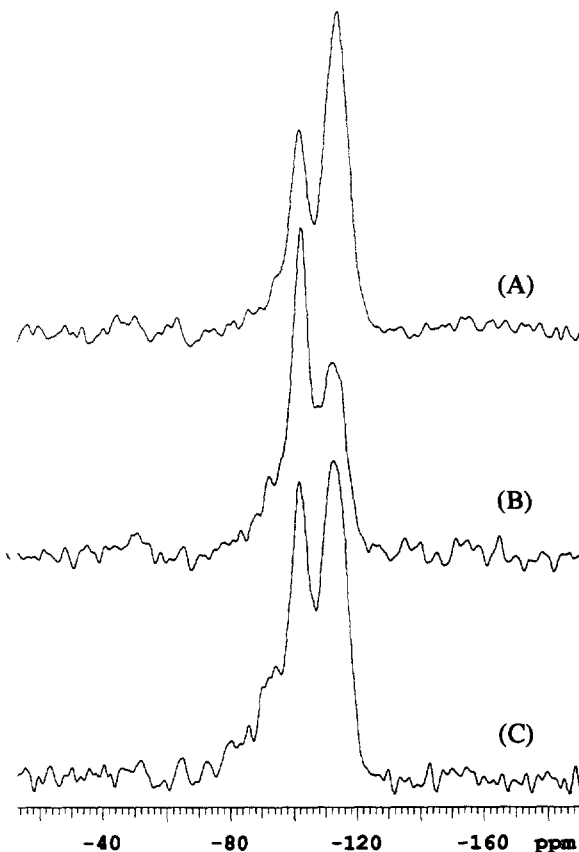


Figure 4. ^{29}Si MAS NMR spectra of (A) Mg_2Al -, (B) Mg_3Al - and (C) Mg_4Al -silicates. Q^2 , Q^3 and Q^4 ^{29}Si resonances were observed at -92 , $\sim(-102)$ and $\sim(-113)$ ppm, respectively, for all three compositions.

a single Q^3 resonance at -110 ppm, Schutz and Biloen (1987) proposed that their LDH-silicate had a polymeric $[HSi_2O_5]_n^-$ structure with different degrees of protonation in order to compensate the layer charge of the host LDH. According to a study of $(H_2Si_2O_5)_x$ silicates by Heidemann *et al* (1985) there are two types of structures that conform to this formulation, one de-

Table 1. ^{29}Si NMR data for the $Mg_{1-x}Al_x$ LDH silicate intercalates.

LDH-silicate	Peak position (ppm)	Relative intensity, %* (Q^2)	Line width (ppm)
Mg^2Al -silicate	-113.6 (Q^4)	67.6 (Q^4)	7.7 (Q^4)
	-101.4 (Q^3)	32.4 (Q^3)	6.9 (Q^3)
Mg^3Al -silicate	-112.9 (Q^4)	39.7 (Q^4)	8.1 (Q^4)
	-102.0 (Q^3)	48.4 (Q^3)	6.1 (Q^3)
	-92.0 (Q^2)	11.9 (Q^2)	10.5 (Q^2)
Mg_4Al -silicate	-112.9 (Q^4)	52.3 (Q^4)	8.3 (Q^4)
	-101.8 (Q^3)	29.9 (Q^3)	6.3 (Q^3)
	-92.0 (Q^2)	17.8 (Q^2)	13.0 (Q^2)

* Relative intensities were obtained by spectral deconvolution.

Table 2. Chemical compositions and textural properties of LDH intercalates.

LDH intercalate	Mg	Al	Si/ (Mg + Al)	S _{BET} ^a m ² /g	Mesopore volume ^b cm ³ /g
Mg ₂ Al-CO ₃	2.21	1.00		58	0.42
Mg ₃ Al-CO ₃	3.33	1.00		65	0.51
Mg ₄ Al-CO ₃	4.12	1.00		73	0.54
Mg ₂ Al-silicate	2.08	1.00	0.54	59	0.16
Mg ₃ Al-silicate	3.10	1.00	0.33	84	0.26
Mg ₄ Al-silicate	4.09	1.00	0.35	85	0.27

^a BET surface areas (S_{BET}) were obtained from N₂ adsorption isotherm in the range 0.05 < P/P₀ < 0.2.

^b Mesopore volumes were obtained from N₂ desorption isotherm in pore radius 10 Å to 200 Å.

noted α and the other δ . The α form is layered and consists of all Q³ sites for the SiO₄ groups, whereas in the δ form has the layers partially crosslinked, giving rise to both Q³ and Q⁴ sites. Thus, the NMR of the α form has only one Q³ ²⁹Si resonance at -101.8 ppm similar to Schutz and Biloen's compound (-104 ppm). But, the δ form shows three ²⁹Si resonances: one Q⁴ at -110 ppm and two Q³ sites at -101.8 and -98.4 ppm. Formation of a layered δ -type silicate structure in our LDH derivatives is precluded by the 7.0–7.2 Å gallery heights and the α silicate structure is eliminated by the NMR and analytical data.

The textural properties of our LDH silicates, as judged by N₂ adsorption/desorption experiments, are similar to those normally observed for nonmicroporous LDH intercalates. As shown by the results in Table 2, the BET N₂ surface areas for the LDH silicates (59–85 m²/g) are comparable to those observed for the corresponding carbonates. Both classes of LDH intercalates showed no microporosity, as determined by the t-plot method (De Boer *et al* 1966). Our LDH-silicate intercalates, therefore, do not possess gallery space accessible to guest molecules with a kinetic diameter greater than nitrogen (~4.6 Å), despite the 7.0–7.2 Å gallery heights. The inaccessibility of the gallery surfaces may

Table 3. Reactivity of LDH intercalates for MBOH conversion^a.

LDH intercalates	Reaction temp. (°C)	% Conversion	% Basic pathway	% Acid pathway	Activity (mmol h ⁻¹ /g)
Mg ₂ Al-CO ₃ ²⁻	80	29.0	~100	tr ^b	1.4
	110	95.5	~100	tr	4.6
Mg ₂ Al-silicate	110	4.39	43	57	0.24
	80	36.9	~100	tr	1.9
Mg ₃ Al-CO ₃ ²⁻	110	99.7	100	—	>5.1
	110	51.0	98	2	2.5
Mg ₃ Al-silicate	80	45.0	~100	tr	2.3
	110	99.9	~100	tr	>5.2
Mg ₄ Al-CO ₃ ²⁻	80	45.0	~100	tr	2.3
	110	99.9	~100	tr	>5.2
Mg ₄ Al-silicate	110	56.2	~100	tr	2.7

^a Activation temperature = 150°C (for 2h).

^b tr = insignificant trace amount of reaction product (Mbyne).

Table 4. MBOH reactivity of amorphous metal oxides derived from LDH intercalates.^a

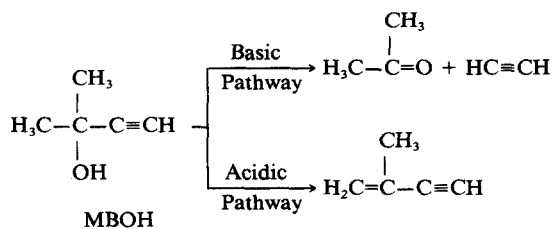
LDH precursor	Reaction temp. (°C)	% Conversion	% Basic pathway	% Acid pathway	Activity (mmol h ⁻¹ /g)
Mg ₂ Al-CO ₃ ²⁻	110	24.4	~100	tr ^b	1.8
Mg ₂ Al-silicate	150	33.5	79	21	1.7
Mg ₃ Al-CO ₃ ²⁻	110	37.0	~100	tr	2.8
Mg ₃ Al-silicate	150	9.8	67	33	0.58
Mg ₄ Al-CO ₃ ²⁻	110	12.0	~100	tr	0.90
Mg ₄ Al-silicate	150	14.3	78	22	0.82

^a Activation temperature = 450°C (for 2h).

^b tr = insignificant trace amounts of reaction product (Mbyne).

be due to the blocking effects caused by the deposition of silica at the crystallite edges. Some indirect evidence for such blocking is provided by the adsorption data. Note that the LDH-silicate intercalates exhibit substantially smaller mesopore volumes than the LDH carbonates. This suggests some changes in interparticle texture occurred during the TEOS reaction, probably due to the deposition of the extragallery silica.

The catalytic reactivities of our Mg_{1-x}Al_x LDH silicates were examined using the dehydration / disproportionation of 2-methyl-3-butyn-2-ol (MBOH) as a probe reaction. This latter substrate is very efficient in characterizing the surface acidic and basic properties of solid catalysts (Lauron-Pernot *et al* 1991). MBOH undergoes disproportionation over a basic catalyst and dehydration over an acidic catalyst, as shown in the following scheme:



For comparison with the catalytic performance of LDH silicates, the MBOH test also was carried out for the corresponding LDH carbonates. Both the LDH carbonate and silicate intercalates after activation at 150°C retained their layered structures as judged by XRD and TGA studies. As shown by the results in Table 3 the catalytic activities for MBOH conversion decreased in the order of Mg₄Al > Mg₃Al > Mg₂Al for both classes of LDH intercalates. The LDH carbonates showed exclusively basic selectivities, producing acetylene and acetone disproportionation products. The higher magnesium content of the layers seemed to improve the basic reactivity of the LDH carbonates. The reactivity pattern of the carbonate derivatives also could be related to their surface areas that increase in the same order (see Table 2). For the LDH-silicates, the Mg₂Al

intercalate with the highest silicate content showed relatively low overall reactivity. Owing to the low conversion observed for the Mg_2Al silicate, the relative acid-base selectivity in this case is not chemically significant. However, both the Mg_3Al and Mg_4Al silicates showed high reactivities and high basic selectivities. On the basis of the relative MBOH reactivities, the LDH carbonate compounds are more active than the LDH silicates, indicating that the intragallery silicate anions are not as basic as the carbonate anions.

Table 4 summarizes the MBOH test results obtained for mixed metal oxide catalysts formed by thermal decomposition of LDH intercalates after activation at 450°C. TGA and XRD studies showed that both the silicate and carbonate intercalates decomposed and became X-ray amorphous after thermal treatment at 450°C. The oxides derived from LDH carbonates show higher MBOH activity than those derived from the LDH silicate compounds. The mixed metal oxides obtained from the carbonate precursors decreased in MBOH reactivity in the order $Mg_3Al > Mg_2Al > Mg_4Al$. The reactivities of the oxides derived from LDH-silicates paralleled the silicate content of the initial intercalate with the catalytic activity decreasing in the order $Mg_2Al > Mg_4Al > Mg_3Al$ silicate. Acidic as well as basic activity was observed for the oxides obtained from LDH-silicate precursors, while only basic selectivity was observed for the oxides derived from LDH carbonate precursors. Condensation reaction of the interlayer Si-OH groups and the Al-OH groups of the LDH layer during the thermal treatment at 450°C might afford the acidic sites.

CONCLUSIONS

$Si(OC_2H_5)_{4-y}(OH)_y$ precursors formed by the hydrolysis of tetraethylorthosilicate (TEOS) react with the exchangeable hydroxide ions in the galleries of meixnerite-like $Mg_{1-x}Al_x$ layered double hydroxides to afford non-microporous derivatives intercalated by polymeric silicate anions. Even for the intercalated products formed at ambient temperatures, the interlayer silicate anions are partially grafted to the host layers, but there is no structural resemblance to 2:1 layered silicates. The reactivities of the LDH-silicates for the base-catalyzed dehydration of 2-methyl-3-butyn-2-ol (MBOH) increases with increasing magnesium content of the host layers. However, the catalytic reactivities of the LDH silicates are lower than those observed for the corresponding LDH carbonates, indicating that the intragallery silicate anions are not as basic as the carbonate anions. Also, the metal oxides derived from the LDH carbonates are more active basic catalysts than those formed from the LDH silicates. However, the oxides obtained from LDH silicates exhibit an unusual combination mixed acidic and basic properties that may find future use in catalytic chemistry.

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