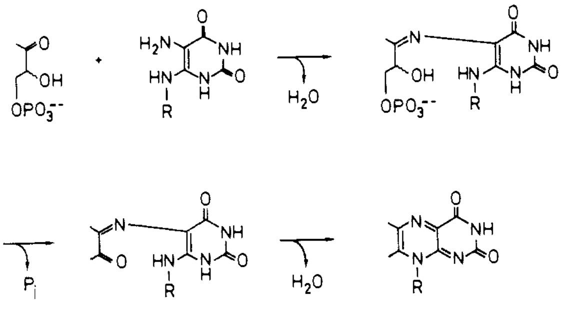
Scheme III. Hypothetical Mechanism for the Enzymatic Formation of 6,7-Dimethyl-8-ribityllumazine (3)



introduction of deuterium from D_2O to positions 1 and 3 of **2** (Figure 2, bottom).

The available evidence is consistent with a hypothetical reaction mechanism starting with the generation of a methyl group by Lobry de Bryn–van Ekenstein reaction (Scheme II). Subsequent migration of C-5 to C-3 as anion followed by elimination of formate could complete the reaction.

The condensation of [1-^{13}C]-**2** with the pyrimidine **3** catalyzed by the β subunit of heavy riboflavin synthase from *Bacillus subtilis* yielded **4** predominantly labeled at the 6α methyl group in agreement with earlier studies.[2] A hypothetical mechanism for this reaction is summarized in Scheme III.

Acknowledgment. This work was supported by grants from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Astrid König and Angelika Kohnle for expert technical and secretarial assistance.

Registry No. 1, 551-85-9; **2**, 114155-98-5; **3**, 17014-74-3; **4**, 2535-20-8; riboflavin, 83-88-5; riboflavin synthase, 9075-82-5.

Pillaring of Layered Double Hydroxides (LDH's) by Polyoxometalate Anions

Taehyun Kwon, George A. Tsigdinos, and
Thomas J. Pinnavaia*

*Department of Chemistry and Center for Fundamental
Materials Research, Michigan State University
East Lansing, Michigan 48824*

Received December 29, 1987

Layered silicate clays (LSC's) intercalated by pillaring polyoxocations are precursors to an important class of microporous catalysts[1] for a large number of reactions,[2] including shape selective petroleum cracking.[1,3] To date, smectite clays are the only host structures known to be pillarable by purely inorganic oxo ions. In the present work we report the oxo ion pillaring of a new family of lamellar ionic compounds, namely the layered double hydroxides (LDH's).

In LDH's, the structural polarity is the reverse of LSC's, i.e., the layers are two-dimensional hydroxo cations and the gallery species are anions. Typical compositions are $[M_{1-x}^{II}M_x^{III}(OH)_2][A^{n-}]_{x/n}\cdot yH_2O$, where M^{II} and M^{III} occupy octahedral positions in the hydroxide sheets, A is the gallery anion, and $x = 0.17$–0.33. Although many different oxo anions have been encapsulated in LDH's by topotactic ion exchange reactions,[4] the oxo ions have been small (CO_3^{2-}, SO_4^{2-}) and the interlayer gallery heights have been limited to values corresponding to one or two layers of space-filling oxygen.

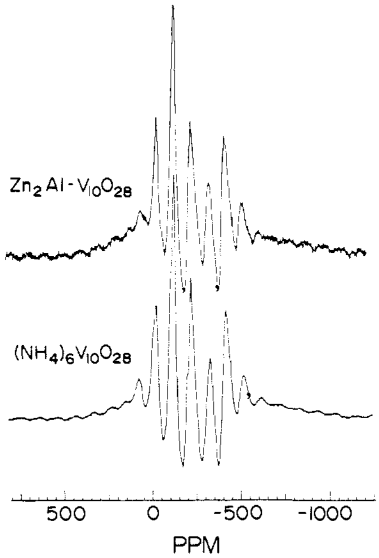


Figure 1. ^{51}V MAS NMR spectra for the Zn_2Al–$V_{10}O_{28}$ intercalate and for $(NH_4)_6V_{10}O_{28}\cdot 6H_2O$ obtained at 47.32 MHz and a spinning rate (4.8 KHz).

Polyoxometalates (POM's) should be ideal pillaring agents for LDH's. These anions generally possess structures consisting of multiple layers of space-filling oxygens as well as a wide range of charge densities.[5] Robust POM's should impart large gallery heights, and those with suitably high charge densities should give rise to large lateral anion spacings, thereby providing access to the intracrystalline gallery surfaces.

The decavanadate anion, $V_{10}O_{28}^{6-}$, was selected as our initial pillaring agent. LDH's with idealized formulas of $[Zn_2Al(OH)_6]Cl\cdot 2H_2O$, $[Zn_2Cr(OH)_6]Cl\cdot 2H_2O$, and $[Ni_3Al(OH)_8]Cl\cdot 2.3H_2O$ were prepared by previously reported coprecipitation methods.[6] Chemical analyses and X-ray basal spacings (d_{001} = 7.62 Å) were compatible with the indicated formulas. Pillaring was achieved by ion exchange of the chloride LDH with $[NH_4]_6[V_{10}O_{28}]\cdot 6H_2O$ at pH 4.5 and 25 °C.[7,8] For each product, chemical analysis indicated the absence of chloride and the presence of 0.17 mol $V_{10}O_{28}^{6-}$ per LDH equivalent, as expected for complete exchange. The basal spacings (d_{001} = 11.9 Å) corresponded to gallery heights of 7.1 Å (three oxygen planes) and to a $V_{10}O_{28}^{6-}$ orientation in which the C_2 axis is parallel to the host layers.

Further verification of intercalated $V_{10}O_{28}^{6-}$ was obtained from the ^{51}V MAS-NMR spectrum of the pillared Zn_2Al intercalate in comparison to the spectrum for the ammonium salt (Figure 1). Although the spectra were obtained at the spectrometer frequency (47.32 MHz) and spinning rate (4.8 KHz) which does not lead to isotropic averaging of chemical shifts, the spectra are qualitatively similar and indicative of the anion retaining its

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(7) The pH during the exchange reaction was carefully monitored and controlled by the addition of dilute HCl in order to minimize the hydrolysis of $V_{10}O_{28}^{6-}$.[8] At pH values in the range of 5.5–10.0, formation of a LDH–$V_4O_{12}^{4-}$ phase was observed as a coproduct with d_{001} = 9.51 Å.

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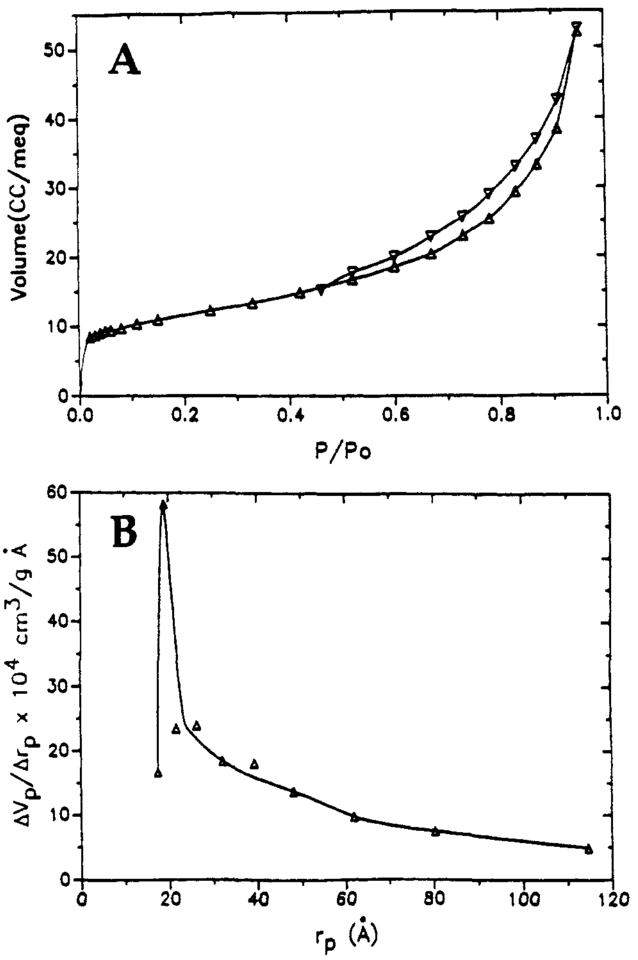

Figure 2. (A) N_2 adsorption (△) and desorption (▽) isotherms at 196 °C for the $Zn_2Cr-V_{10}O_{28}$ intercalate. (B) Mesopore distribution derived from the hysteresis loop beginning at $P/P_0 = 0.42$.

integrity in the intercalated state.

On the basis of the estimated size of $V_{10}O_{28}{}^{6-}$[9] and the unit cell sizes of the LDH hosts,[10] the surface areas should be between 25 and 60 m^2/mequiv. We observe N_2 BET surface areas in the range 35–41 m^2/mequiv indicating that the intracrystalline gallery surfaces indeed have been made accessible by pillaring.[11]

The N_2 adsorption/desorption isotherms for the $Zn_2Cr-V_{10}O_{28}$ systems are shown in Figure 2A. The substantial adsorption in the low P/P_0 region indicates the presence of micropores (<20 Å),[13] whereas the hysteresis starting at $P/P_0 = 0.42$ is indicative of the presence of some mesopores with a maximum near 20 Å (cf. Figure 2B). Analogous features were absent in the N_2 adsorption isotherm of the unpillared Zn_2Cr-Cl system.

Layered double hydroxides typically decompose at relatively low temperatures (<350 °C).[12] Nevertheless, there is considerable promise for the use of pillared LDH's for intracrystalline catalytic reactions. Certain POM's, including decavanadate, exhibit photocatalytic properties at ambient temperatures.[14] To illustrate the potential utility of LDH–POM intercalates, we carried out the photooxidation of isopropyl alcohol to acetone. A suspension of the $Zn_2Al-V_{10}O_{28}$ intercalate (0.0506 g, 0.0164 mmol) in isopropyl alcohol (11.0 mL) was irradiated in 48 h by a 450-W Hg vapor lamp equipped with a water filter and a 295-nm long pass filter. For the reaction under an argon atmosphere, only a stoichiometric amount of acetone was produced, and the intercalated decavanadate was converted to the blue reduced form. However, under oxygen, the decavanadate was partially reoxidized, and the reaction became catalytic, producing 6 mol of acetone per mol of decavanadate. Under equivalent oxygenated reaction conditions in homogeneous solution, the acetone yield was only 2.0 mmol/mequiv. Thus, the LDH intercalated catalyst is substantially more active than the homogeneous catalyst, despite scattering by the host particles.

The results reported here demonstrate for the first time that high-charge density LDH's can be pillared by POM anions, providing that the pillaring anion has a relatively high charge density. Preliminary studies indicate that LDH's can be pillared by other POM anions. For instance, we have observed that Keggin ions such as $H_2W_{12}O_{40}{}^{6-}$ and $BVW_{11}O_{40}{}^{7-}$ can be successfully intercalated in LDH's, affording derivatives with gallery heights of 9.6 Å. Future studies will focus on the possibility of shape selective catalysis for these new microporous solids.

Acknowledgment. The support of this research by the Michigan State University Center for Fundamental Materials Research and by the National Science Foundation through the Division of Materials Research Grant no. 85-14154 is gratefully acknowledged.

Registry No. ^{51}V, 7440-62-2; N_2, 7727-37-9.

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(11) LDH's with small gallery cations can have appreciable external surface areas if the coprecipitated crystals are small and thin.[12] However, the surface areas observed here for the $V_{10}O_{28}{}^{6-}$ derivatives are at least four times as large as those for the parent starting materials containing intercalated chloride ions. Surface areas are reported here in m^2/mequiv rather than on a more conventional mass basis in order to compensate for differences in equivalent weights.

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η^1-Coordination versus η^2-Coordination in Transition-Metal Phosphinomethanide Complexes: Synthesis and X-ray Structure of $Cp_2Zr(Cl)[C(PMe_2)(SiMe_3)_2]$

Hans H. Karsch,* Brigitte Deubelly, Josef Hofmann,
Ursula Pieper, and Gerhard Müller

Anorganisch-chemisches Institut
Technische Universität München, Lichtenbergstr. 4
D-8046 Garching, Federal Republic of Germany

Received December 2, 1987

Phosphinomethanides $[R_2PCH_2]^-$ (R = Ph, Me) have been shown to exhibit powerful coordinative ability to transition-metal centers. Frequently, the ligand is formed at the metal center via intramolecular C–H activation of coordinated methylphosphines,[1] but, in other cases, the latter have to be metalated by addition of a strong base.[2] A more general method involves the reaction of lithium phosphinomethanides with metal halides (eq 1).[3,4]

$$M\text{-}Cl + LiCH_2PR_2 \rightarrow M\text{-}CH_2PR_2 \qquad (1)$$

At coordinatively unsaturated metal centers η^2-coordination of the ligands via their P and carbanionic C atoms occurs spontaneously in most cases, thereby leading to the formation of three-membered rings $\overline{M\text{-}C\text{-}P}$. This requirement is also met by

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