JOURNAL OF CATALYSIS 112, 126–134 (1988)

Hydrogen Reduction of $Pt(NH_3)_4^{2+}$ Supported on Montmorillonite

JEFFREY B. HARRISON,[1] VAUGHN E. BERKHEISER, AND GREGORY W. ERDOS

Agriculture Experimental Station and Soil Science Department, University of Florida, Gainesville, Florida 32611

Received February 17, 1987; revised February 1, 1988

The addition of molecular hydrogen at 140°C to $Pt(NH_3)_4^{2+}$ complexes exchanged on Wyoming montmorillonites, at varying metal weight to support weight ratios, results in metal reduction according to the reaction $Pt(NH_3)_4^{2+} + H_2 \rightarrow Pt + 2NH_4^+ + 2NH_3$. In a parallel reaction the concurrent reduction of structural iron(III) occurs, producing an increase in the layer charge of the mineral. Charge balance is maintained by the additional formation of ammonium cations by ammine protonation. Metal reduction is accompanied by the collective migration of atoms and/or crystallites from the internal surface of the mineral to sites of low negative charge on the external surface and edges. At high metal concentrations, large clusters of 100 Å are easily visible by transmission electron microscopy. Also apparent is a high proportion of the metal crystallites formed in diameters of 50 Å or less. As the metal concentration decreases, mean metal diameters decrease and the particle size distributions become narrower. © 1988 Academic Press, Inc.

INTRODUCTION

A number of studies have documented the influence of the interlamellar surface on the formation of organometallic species on clay minerals and adsorbed transition metal–metal complexes (*1–7*). Pinnavaia and Welty (*7*) demonstrated that rhodium complexes supported on hectorite had a higher activity toward hex-1-ene hydrogenation in solution phase than the same complexes supported on a Dowex 50 resin or a Rh_2^{4+} homogeneous solution. They concluded that the interlamellar surface enhanced the reactivity of Rh_2^{4+} toward metal hydride formation.

To evaluate the utility of smectite minerals for supported noble metal catalysts, a study was undertaken to determine the suitability of a Wyoming montmorillonite mineral as a support for various loadings of platinum. A description of the ion exchange of the platinum tetrammine cation and its subsequent reduction is given. In addition, the location and electronic environment of the metal center before and after reduction are discussed.

METHODS

Wyoming montmorillonite was obtained from the Clay Minerals Repository, University of Missouri, Columbia, Missouri. The clay was washed with 1 *N* NaOAc (pH 5.0) at 80°C to remove carbonates and treated with Na citrate dithionite to remove free iron oxides. The mineral was further washed five times with NH_4Cl, followed by repeated washings with deionized H_2O until chloride was undetectable with $AgNO_3$. The <2-μm fraction was separated by centrifugation. The approximate unit cell formula of the anhydrous product is

$$(NH_4^+)_{0.90}(Al_{3.07}Fe^{3+}_{0.23}Fe^{2+}_{0.18}Mg_{0.31})(Si_{7.69}Al_{0.31})O_{20}(OH)_4$$

based upon published analysis (*8*).

A fully loaded platinum catalyst was prepared by washing the <2-μm fraction five times with a 0.1 *M* solution of tetrammine nitrate salt (from Alfa Chemicals). The excess salt was removed by washing the metal–clay suspension with deionized water a minimum of six times. A sample was

---

[1] Present address: Texaco Inc., P.O. 509, Beacon, NY 12508.

0021-9517/88 $3.00

analyzed by atomic adsorption to determine the amount of platinum exchanged on the clay. All other loadings of Pt were prepared by addition of an appropriate volume of tetrammine salt and equilibration for 24 h, followed by washing until salt free.

All gas reagents were obtained from Linde Corp. in the highest grade available and were used without further purification, with the exception of hydrogen which was passed through a zeolite–liquid N_2 trap.

Air-dried samples were reduced by slowly heating to 140°C under vacuum (1×10^{-5} Torr, 1 Torr = 133.3 N m^{-2}) and held there for a minimum of 6 h. Dry hydrogen was added to the system (100 Torr) and allowed to contact the sample for 6 h at 140°C. The entire system was completely evacuated and an additional 100 Torr H_2 was added and remained for 3 h. At this point, the sample was evacuated to less than 10^{-5} Torr for 4 h and was ready for further treatment.

For infrared analysis, self-supporting films were made by drying a dilute suspension of the metal-exchanged clay on Mylar film. By this method, the clay dried with a high proportion of the basal planes of the silicate layers aligned parallel to the plane of the Mylar film. A stainless-steel evacuable cell fitted with KRS-5 windows permitted the recording of IR spectra in the presence of different gases. Spectra were recorded on a Perkin–Elmer 567 IR spectrophotometer.

X-ray analyses were obtained on a Diano XRD-700 X-ray diffractometer using Ni-filtered Cu$K\alpha$ radiation. Basal spacings, $d(100)$, were determined on oriented samples by using at least four orders of reflection. The presence of metal crystallites was always checked by scanning over the angles expected for the (111), (200), (220), and (311) reflections of the metal. Diffractograms of evacuated samples were obtained by transferring the sample from the vacuum rack to a He-filled glove bag attached to the X-ray sample mount.

Transmission electron micrographs were taken at magnifications ranging from 50 to 100 K with a JOEL 100C electron microscope operated at 40 kV. Samples were deposited on Formvar-coated copper grids and examined without further treatment. Average platinum particle diameters for each loading were calculated by using the formula (*9*)

$$d_{\mathrm{avg}} = \frac{\Sigma n * d_i^3}{\Sigma n * d_i^2},$$

where d_i is the diameter of particle i measured from the electron micrograph and n is the number of crystallites in the range d and $d + 10$ Å.

The stoichiometry of reduction was determined by adding H_2 to a fully exchanged $Pt(NH_3)_4^{2+}$ montmorillonite (8.6% Pt, w/w) heated to 140°C and trapping the liberated NH_3 at 77°K. Four hours later, flowing He was passed through the trap, as it was warmed to room temperature. The helium flow was then passed through a water trap containing a known amount of acid. The remaining acid was titrated with a standardized base to determine the amount of NH_3 liberated during reduction.

RESULTS

Infrared Analysis

Infrared band positions and their corresponding assignments for the unreduced and reduced platinum-loaded montmorillonite are given in Table 1. The montmorillonite host is characterized by a band at 3625 cm^{-1}, ascribed to the stretching vibration of the structural hydroxyls situated in the octahedral layer of the smectite (Fig. 1). Four distinct clay deformation modes were observed at 920, 885, 850, and 800 cm^{-1} which resulted from bridging hydroxyls associated with different combinations of cations filling the octahedral holes of the mineral. The band assignments (after Farmer (*10*)) for the first two combinations are given in Table 1.

When the mineral was fully exchanged (8.6% Pt) by the $Pt(NH_3)_4^{2+}$ cation, the IR

TABLE 1

IR Band Frequencies for Pt Supported on Wy. Montmorillonite (cm^{-1})

Catalyst	Treatment[a]	ν(OH)	ν(NH)	δ(NH)	$\delta(Al_2OH)$	δ(FeAlOH)
0.6% Pt · Wy. montmorillonite	Untreated (RTP) evacuated	3625	3260	1425,1370 1425,1345	920	885
	Reduced	3625	3260	1425	920	885
1.0% Pt · Wy. montmorillonite	Untreated (RTP) evacuated	3625	3260,3220	1425,1370 1425,1345	920	885
	Reduced	3625	3260	1425	920	885
3.0% Pt · Wy. montmorillonite	Untreated (RTP) evacuated	3625	3300,3260,3220	1425,1370 1425,1340	920	885
	Reduced RTP	3620 3625	3260	1425	915 920	890 885
8.6% Pt · Wy. montmorillonite	Untreated (RTP) evacuated	3625	3290,3220 3330,3300,3220	1370 1335	920	885
	Reduced RTP	3600 3625	3260	1425	915 920	absent 885
NH_4^+ · Wy. montmorillonite	Evacuated	3625	3260	1425	920	885

[a] Untreated refers to the cationic $Pt(NH_3)_4^{2+}$ form. RTP represents room temperature and pressure conditions.

band positions associated with the mineral remained unchanged. The ammine ligands contributed a doublet to the IR spectrum of the unevacuated sample located at 3290 and 3220 cm^{-1}. These have been previously assigned to the asymmetric and symmetric N–H stretching vibrations, respectively (*11, 12*). A corresponding deformation mode was found at 1370 cm^{-1}. Upon evacuation, the ammine stretching vibrations appeared as a triplet, located at 3330, 3300, and 3220 cm^{-1}, and the deformation band shifted from 1370 to 1335 cm^{-1}. Unfortunately the Pt–N stretching fundamentals were obscured by low-frequency vibrations of the aluminosilicate framework.

At lower metal loadings (3.0, 1.0, and 0.6% Pt), there were no significant changes in the IR spectrum relative to the air-dried unreduced 8.6% Pt montmorillonite, albeit the N–H stretching vibration of the residual ammonium cation largely obscured the ammine fundamentals in the samples containing 3.0% or less metal. However, the position of the ligand ammine stretching vibration was elucidated by substituting Na^+ for NH_4^+ as the residual interlayer cation. The only changes in the IR spectrum of these metal-loaded samples with evacuation was the removal of the H_2O de-

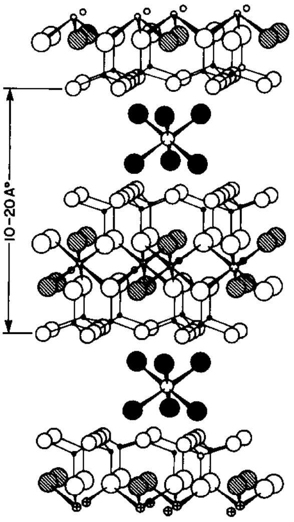

FIG. 1. The structure of a smectite mineral illustrating the two tetrahedral silica sheets linked to the central octahedral sheet through oxygen apices. Shaded circles in the octahedral sheet represent hydroxyl groups bridge-bonded to adjacent structural cations. Hydrated cations are seen positioned between stacked smectite layers.

formation mode, a narrowing of the ammine $\nu_a(NH_3)$ and $\nu_s(NH_3)$ fundamentals, and a shift of the ammine $\delta_s(HNH)$ from 1370 to 1345 cm^{-1} (Table 1).

Moderate reducing conditions (140°C, 100 Torr H_2) produced pronounced changes in the IR spectrum at all metal loadings (Table 1). Although the four catalysts examined differed widely in platinum concentration, the IR spectrum of the fully loaded 8.6% Pt montmorillonite reflected the majority of changes in the lower loadings when reduced. The most notable feature was the appearance of a single broad band centered at 3260 cm^{-1} and a sharp band at 1425 cm^{-1}. Missing from the spectrum were the bands associated with stretching and bending fundamentals of the ammine ligands. In addition, there were pronounced changes in the IR bands attributed to the mineral vibrations. An apparent downward shift in the $\nu(OH)$ occurred with a corresponding upward shift (or disappearance) of the deformation mode belonging to the $\delta(FeAlOH)$ combination. An NH_4^+ montmorillonite subjected to identical treatment conditions showed no change in its IR spectrum. Exposure of the reduced 8.6% Pt montmorillonite to the atmosphere for 24 h restored the hydroxyl bands to their original positions.

Reduction of 0.6, 1.0, and 3.0% Pt montmorillonites showed similar shifts in the FeAlOH deformation band although this band did not completely disappear. Rather, the band was broadened and decreased in intensity. As with the 8.6% Pt montmorillonite, exposure to the atmosphere at room temperature restored the $\delta(FeAlOH)$ hydroxyl band to its original position and intensity.

Stoichiometry of Reduction

Three separate quantitative titrations of the ammonia released upon reduction of 1.000 g, 8.6% Pt montmorillonite yielded an average of 0.292 ± 0.02 mmole NH_3. Using a previously determined cation exchange capacity of 0.85 meq/g, this represented only 17% of the total ammine ligand. The remaining 83% was assumed to be converted to the ammonium cation during the reduction process.

X-Ray Diffraction Analysis

A fully saturated 8.6% $Pt(NH_3)_4^{2+}$ montmorillonite heated at 80°C *in vacuo* exhibited a well-ordered basal spacing of 12.1 Å (Table 2). Since the ideal thickness of a smectite sheet is 9.6 Å, the basal expansion of 2.5 Å is attributed strictly to the presence of the metal ammine cation in the interlayer.

Lower loadings of tetraammine cation produced diffractograms indicative of a less well-ordered structure. In most cases the higher order reflections were broad, often exceeding several degrees of 2Θ in width. This was particularly true when the samples were evacuated at moderate temperatures (110°C, 1×10^{-5} Torr). In general, the basal spacing of the evacuated sample decreased with decreasing platinum content. As Table 2 demonstrates, the (001) reflection of 0.6% Pt montmorillonite approached the basal spacing of an NH_4^+ montmorillonite (10.7 Å).

The addition of 100 Torr H_2 at 140°C decreased the basal spacing of the sample from 12.1 to 10.6 Å in the absence of water vapor (Table 2). A similar value was found for an NH_4^+ montmorillonite treated under the same conditions. However, the fourth-order reflection in this diffractogram was absent.

The reduced 8.6% Pt catalyst showed only limited swelling properties when rehydrated for 24 h at 97% RH and 25°C. The basal spacing increased to only 12.3 Å under these conditions whereas an identically treated NH_4^+ montmorillonite increased to 13.8 Å.

The formation of metal crystallites >50 Å was indicated for the 8.6% Pt catalyst by the appearance of a weak diffuse peak at 39.8 2Θ representing the (111) reflection of well-crystallized platinum. No other reflections attributable to the metal were observed at higher angles. High noise levels at more sensitive instrument settings made

TABLE 2

X-Ray Diffraction Analysis of Pt-Loaded Wy. Montmorillonites

Catalyst	Treatment[a]	Basal spacings (Å)			
		1st order	2nd order	3rd order	4th order
0.6% Pt · Wy. montmorillonite	Untreated (RTP)	12.62	6.12	4.20	3.20
	evacuated	10.68	5.31	—	2.62
	Reduced (97% RH)	13.85	6.87	—	3.52
	evacuated	10.62	5.33	3.17	—
1.0% Pt · Wy. montmorillonite	Untreated (RTP)	12.62	6.10	4.15	3.11
	evacuated	10.77	5.32	—	2.67
	Reduced (97% RH)	13.25	6.66	—	3.35
	evacuated	10.60	5.27	3.19	—
3.0% Pt · Wy. montmorillonite	Untreated (RTP)	12.71	6.43	4.31	3.32
	evacuated	11.51	—	—	2.85
	Reduced (97% RH)	12.66	6.33	—	3.16
	evacuated	10.58	5.32	3.20	—
8.6% Pt · Wy. montmorillonite	Untreated (RTP)	12.62	6.30	4.23	3.14
	evacuated	12.05	6.00	—	3.04
	Reduced (RTP)	11.10	5.52	3.67	—
	evacuated	10.64	5.21	3.14	—
	(97% RH)	12.27	6/10	—	3.08

[a] Untreated refers to the cationic $Pt(NH_3)_4^{2+}$ form. RTP represents room temperature and pressure conditions. The 97% RH refers to the relative pressure of water at 25°C.

line broadening measurements prohibitive. The catalysts loaded at lower Pt contents exhibited a pronounced narrowing of the clay (001) basal reflection upon metal reduction. When thoroughly evacuated all reduced catalysts exhibited basal spacings of 10.6 Å, identical to the value observed for the 8.6% Pt montmorillonite after reduction and evacuation. Diffraction lines associated with bulk Pt formation were never observed for the 0.6, 1.0, and 3.0% Pt catalysts.

Transmission Elecrtron Microscopy (TEM)

Crystallite size distributions, deduced from electron micrographs (Fig. 2) are shown for each catalyst loading in Fig. 3. A narrow distribution was obtained for the 0.6% Pt montmorillonite with 95% of the particles having diameters less than 30 Å. The average crystallite size (*d*) at this loading was 22.9 Å. A small increase in platinum concentration to 1.0% Pt considerably broadened the distribution and resulted in an overall increase in crystallite dimension. The average diameter at this loading was 42.7 Å with only 54% of the particles having a diameter less than 30 Å. At the 3.0% Pt level, 58% of the particles examined were less than 35 Å, yet the average particle diameter was 97.9 Å. This is a consequence of the appearance of a small number of clusters larger than 80 Å which are heavily weighted when calculating the average particle sizes. If only crystallites less than 80 Å were counted the average diameter at the 3.0% level would be 42.8 Å. A similar effect was observed in the 8.6% Pt montmorillonite; the appearance of large clusters was not infrequent. In fact, aggregates as large as 300 and 400 Å were not uncommon. They appeared as bands and films rather than well-defined metal particles and were thought to have coalesced after the initial reduction of the metal.

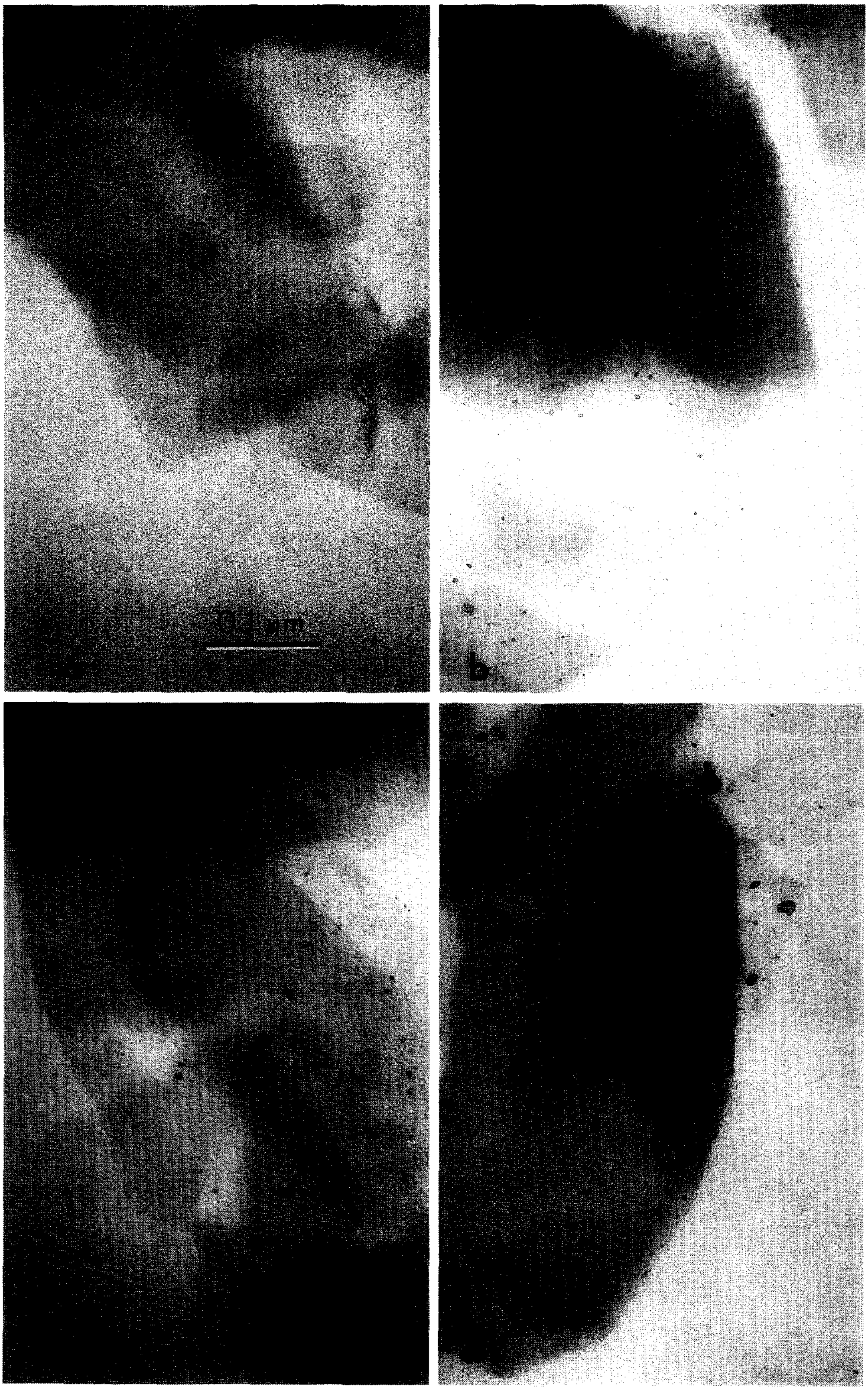

FIG. 2. Transmission electron micrographs of four metals loadings on Wy. montmorillonite: (a) 0.6% Pt, (b) 1.0% Pt, (c) 3.0% Pt, (d) 8.6% Pt.

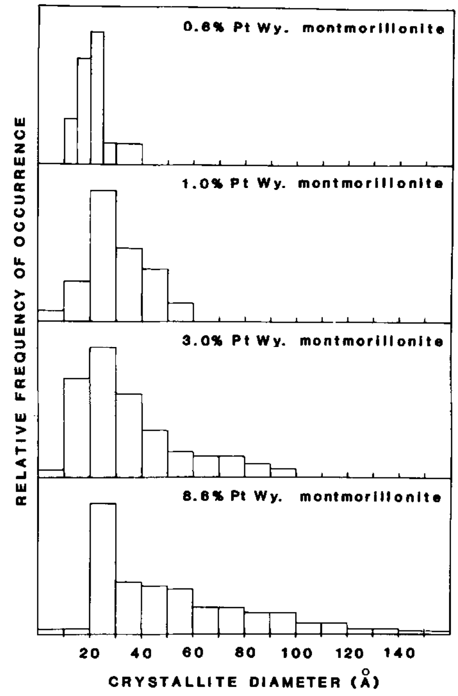

FIG. 3. Particle size distributions for four loadings of platinum supported on Wy. montmorillonite. Metal crystallites larger than 160 Å were counted in the last column.

DISCUSSION

From collected infrared and Raman data the $Pt(NH_3)_4^{2+}$ cation has been shown to be a square planar complex belonging to the D_{4h} point group (*11, 12*). When discussing the ammine ligands it is convenient to describe them in terms of a 1 : 1 model (metal : ligand) with local symmetry C_{3v} (*13*). Of particular interest in this study are the doubly degenerate E antisymmetric stretching vibration, the A_1 symmetric stretching mode, and the symmetric A_1 deformation mode predicted for C_{3v} symmetry. These appeared in the IR spectrum of the air-dried 8.6% Pt montmorillonite as a doublet at 3290 and 3220 cm^{-1} and a single band at 1370 cm^{-1}, respectively (Table 1). Therefore, under air-dried conditions the ammine ligands of the $Pt(NH_3)_4^{2+}$ cation retained their C_{3v} symmetry within the montmorillonite interlayer. Since all four ligands are symmetry equivalent, it is believed that under air-dried conditions, the D_{4h} symmetry of the cation is preserved.

Thorough evacuation of the catalyst at 80°C effected a splitting of the degenerate antisymmetric fundamental with bands appearing at 3330, 3300, and 3220 cm^{-1}. The lifting of the degeneracy by the removal of interlayer water reflects a reduction in ligand symmetry as the metal–ammine complex was sandwiched between the interlamellar surfaces. This can be explained in part by restricted rotation of the complex and ligands as the mineral is dehydrated.

The symmetric deformation fundamental was particularly sensitive to the hydration status of the mineral. Not unexpectedly, dehydration of 80°C *in vacuo* shifted the bending mode to lower frequency (from 1370 to 1335 cm^{-1}) indicative of decreased hydrogen bonding with H_2O molecules.

At lower platinum loadings (0.6, 1.0, and 3.0% Pt) these effects were not nearly as distinct due to an overlap of the stretching vibration of the residual ammonium cation and a decrease in the intensity of the ligand vibrations. When the interlayer ammonium cation was replaced by the sodium ion, the IR spectrum showed ammine stretching vibrations at frequencies similar to those found in the air-dried 8.6% $Pt(NH_3)_4^{2+}$ montmorillonite IR spectrum. As a significant splitting of the $\nu_a(NH_3)$ vibration was not observed with evacuation, it appears that the residual interlayer cation (NH_4^+ or Na^+) prevented the complete collapse of the interlayer upon dehydration at 80°C. This was also reflected in the decreased shift of the δ_s(HNH) with evacuation compared to the shift observed for the 8.6% Pt sample. It is concluded that interlayer water associated with the residual cations must remain partially hydrogen bonded to the ammine ligands under these conditions.

As shown in Table 2, the addition of H_2 at 140°C produced significant changes in the IR spectrum of the 8.6% Pt montmorillonite. Foremost, the appearance of IR bands at 3260 and 1425 cm^{-1} coupled with the disappearance of the bands associated with the ammine ligand vibrations indicated the formation of the ammonium cation. An independent titration of ammonia released during deduction confirmed the formation of the ammonium cation. However, it was noted from these results that nearly 83% of the ammine ligands were protonated and retained by the mineral as ammonium, thereby suggesting a net increase in layer charge. Rozenson and Heller-Kallai (*8, 14*) demonstrated the reduction of octahedral iron in a natural montmorillonite by aqueous solutions of hydrazine, sodium dithionite, and sodium sulfide at 70°C. They found that the Fe^{3+}AlOH bending mode at 880 cm^{-1} disappeared with treatment by all of the reducing agents investigated. In each case the results indicated that reduction was accomplished by protonation of an adjacent OH group which was reversible upon oxidation with H_2. The 885-cm^{-1} band disappeared in the spectra when H_2 was added to the 8.6% Pt montmorillonite at 140°C, but in this case it appears that the increase in layer charge is satisfied by the formation of the ammonium cations rather than protonation of hydroxyl groups.

Calculation of the amount of ammonium formed when all of the octahedral iron (0.54 mmole Fe^{3+}/g clay) is reduced together with the quantity of ammonium formed upon reduction of the platinum (0.882 mmole NH_4^+/g clay) yields a value agreeing well with the amount predicted from the titration results, 1.472 mmole/g clay). The decrease in the hydroxyl stretching frequency observed with the concurrent high-frequency shift or disappearance of the FeAlOH mode has been attributed to the reduction of structural Fe^{3+} (*15*). The presence of the metal–ammine complex in the interlayer region apparently facilitated the reduction of the octahedral iron, in part, by propping the interlayer apart, because an NH_4^+ montmorillonite, treated under the same reducing conditions as the 8.6% Pt catalyst, showed no change in its IR spectrum indicative of structural iron reduction.

The changes in the IR spectra of the 0.6, 1.0, and 3.0% Pt montmorillonite upon reduction are quite similar to those of the 8.6% Pt sample although the FeAlOH deformation band never completely disappeared in the spectra of the lower loading rates. Rather, the decrease in intensity of the band was proportional to the metal content of the catalyst. As the results given above establish the involvement of the interlayer metal in the reduction of structural iron, this observation is not unexpected.

Several studies have established that Cu(II) square planar complexes adsorbed on montmorillonite orient with the metal–ligand bonds parallel to the silicate sheets and the vacant d_{z^2} metal orbital perpendicular to the interlamellar surface (*16, 17*). The 2.5-Å interlayer separation observed for the 8.6% $Pt(NH_3)_4^{2+}$ montmorillonite would seemingly substantiate this orientation. By analogy, lower contents of $Pt(NH_3)_4^{2+}$ would also be expected to attain this configuration although X-ray data for these samples cannot confirm their orientations due to the uncertainty in the basal spacings.

It is evident that reduction of all catalysts produced a decrease in the interlayer spacing which under vacuum approached a value nearly identical to an evacuated NH_4^+ montmorillonite. In light of the TEM results, the reduction of the metal is envisaged as diffusion of metal atoms and crystallites out of the interlayer through the edge openings, followed by distribution of individual crystallites to areas on the external clay surface and edge sites of lower electron density. Therefore, the narrowing of the (001) reflections with reduction of 0.6, 1.0, and 3.0% Pt catalysts resulted from an increase in the overall ordering or regularity of the interlayer dimension produced by the collective migration of the metal out of this region. This fact, coupled with the collapse of all catalyst basal spacings to identical values, rules out the possibility that a high proportion of the metal remained in the mineral interlayer as individual atoms or crystallites. Indeed, a priori, the high charge density found within the interlamellar regions would be expected to destabilize the metal and favor its redistribution to external surfaces.

TEM results clearly show that a large porportion of the reduced metal accumulates at the edges of the mineral after diffusion out of the interlayer. This apparently imparts limited swelling properties to the mineral upon rehydration. Although the montmorillonites are ammonium saturated, equilibration with water vapor did not restore the basal spacing to the value observed for a similarly treated NH_4^+ montmorillonite.

CONCLUSION

The results of this study have shown that interlayer $Pt(NH_3)_4^{2+}$ was readily reduced with hydrogen at 140°C according to the equation $Pt(NH_3)_4^{2+} + H_2 \rightarrow Pt + 2NH_4^+ + 2NH_3$. The reaction was accompanied by the concurrent reduction of structural iron thereby increasing the layer charge of the mineral. Charge balance was maintained by the additional formation of ammonium cations produced by protonation of the ammine ligands.

During metal reduction, platinum atoms or crystallites migrated out of the interlamellar region and were distributed on the external surface and edge sites, presumably of lower negative charge. At low metal loadings of 0.6 and 1.0% Pt, high dispersions were obtained with minimal pretreatment. Reduction at higher metal loadings, however, resulted in poor metal dispersion and in many instances clustering of smaller crystallites into films of undetermined thickness. Nonetheless, approximately 50% of the crystallites examined were less than 30 Å.

Finally, X-ray diffraction analysis demonstrated that the interlayer swelling capacity of the montmorillonite mineral is not completely impaired, thus permitting the suspension of the catalyst in solution and suggesting that this support might be particularly well suited to condensed phase hydrogenation reactions.

REFERENCES

1. Mortland, M. M., and Pinnavaia, T. J., *Nature (London), Phys. Sci.* **229,** 75 (1971).
2. Pinnavaia, T. J., and Mortland, M. M., *J. Phys. Chem.* **75,** 3957 (1971).
3. Pinnavaia, T. J., Hall, P. L., Cady, S. S., and Mortland, M. M., *J. Phys. Chem.* **78,** 994 (1974).
4. Berkheiser, V. E., and Mortland, M. M., *Clays Clay Miner.* **25,** 105 (1977).
5. Berkheiser, V. E., and Mortland, M. M., *Clays Clay Miner.* **26,** (1978).
6. Krenske, D., Abdo, A., Van Damme, H., Cruz, M., and Fripiat, J. J., *J. Phys. Chem.* **84,** 2447 (1980).
7. Pinnavaia, T. J., and Welty, P. K., *J. Amer. Chem. Soc.* **97,** 3819 (1975).
8. Rozenson, I., and Heller-Kallai, L., *Clays Clay Miner.* **24,** 271 (1976).
9. Primet, M., Bassert, S. M., Garbowski, E., and Mathieu, M. V., *J. Amer. Chem. Soc.* **97,** 3655 (1975).
10. Farmer, V. C., *in* "Infrared Spectra of Minerals," Chap. 15, Monograph 4. Mineralogical Society, London, 1974.
11. Hiraishi, J., Nakagawa, I., and Shimanovchi, T., *Spectrochim. Acta A* **24,** 819 (1968).
12. Poulet, H., Delorme, P., and Mathiev, J. P., *Spectrochim. Acta* **20,** 1855 (1964).
13. Nakamoto, K., *in* "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed., p. 199. Wiley, New York, 1978.
14. Rozenson, I., and Heller-Kallai, L., *Clays Clay Miner.* **24,** 283 (1976).
15. Stucki, J. W., Roth, C. B., and Baitinger, W. E., *Clays Clay Miner.* **24,** 289 (1976).
16. Clementz, D. M., Pinnavaia, T. J., and Mortland, M. M., *J. Phys. Chem.* **77,** 196 (1973).
17. Burba, J. L., III, and McAtee, J. L., Jr., *Clays Clay Miner.* **25,** 113 (1977).