Nitrogen Retention by an Osmium Complex Supported on Sepiolite

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Magnesian layer lattice silicates such as chrysotile or sepiolite can be transformed into high-surface-area solids covered with
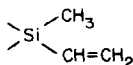
groups. Osmium tetroxide can be added to the vinyl C=C bond and electron micrographs of the OsSS ("osmium supported on sepiolite") samples prepared in that way have revealed a rather regular distribution of vinyl groups. It is now shown that upon drying OsSS at 200°C, the methyl group is oxidized, leading to a surface species with the probable structure
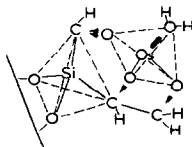
Os passing from the eighth to probably the sixth, then finally to the second oxidation state. This structure has interesting properties: (a) at −196°C it adsorbs H_2 in the ratio of $4H_2$ per osmium atom under 400 Torr H_2; (b) when treated at 200°C at the same pressure with H_2, H_2 is consumed in the ratio of 1 mole H_2/one osmium atom. It is suggested that during the reduction treatment, the water molecule adsorbed on an osmium atom is replaced by one molecule of hydrogen, less strongly attached. "Reduced" OsSS adsorbs dinitrogen reversibly and under a pressure of 400 Torr N_2, one N_2 molecule is retained per four osmium atoms at *room* temperature. It is proposed that N_2 forms

-bridged structures.
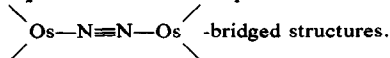
INTRODUCTION

Adsorption of dinitrogen (N_2) at temperatures appreciably higher than the boiling point of the liquefied gas has been reported on zinc oxide pretreated by hydrogen (*1*). Vicinal H—Zn—OH—Zn sites are produced and Zn—H can be replaced by Zn—N≡N terminal ligands as evidenced by the observation of the N≡N stretching band at 2337 cm⁻¹. Water is a strong poison for dinitrogen adsorption. In an early study by Beebe and Dowden (*2*), chromic oxide was found to retain small amounts of N_2 at

0°C. As far as we are aware there are no other examples of N_2 adsorption by oxide above 200 K.

On the other hand, numerous metal complexes are known to accept dinitrogen as a ligand in solution (*3, 4*). It was very tempting to synthesize a complex of this kind on the surface of a high-specific-area solid and to observe its behaviour with respect to molecular nitrogen. Osmium (II) was a good candidate for such an attempt. Indeed, osmium tetroxide OsO_4 is easily added to a carbon–carbon double bond (*5*). On the other hand, techniques for grafting

vinyl groups on the surfaces of magnesian layer lattice silicates are well documented (6–8). Therefore, it should be possible to support Os^{IV} on a solid surface and furthermore to study the influence of the reduction into Os^{II} on the adsorption of molecular nitrogen. The aim of this paper is to report the experimental results obtained so far.

Much remains to be done especially as regards the catalytic properties. Also the behaviour of ReO_4 and RuO_4 on the same grafted support deserves to be investigated.

EXPERIMENTAL

Sample Preparation

In the present experiment, sepiolite from Vallecas, Spain, was used as a support because of its initial high surface area ($\sim$280 m²/g). It is a magnesium hydrated silicate with a fibrous morphology, whose octahedral layers are discontinuous and the open channels extend longitudinally in the direction of the fiber axis. According to Brauner and Preisinger (9), the ideal formula of the half-cell corresponds to $Si_{12}Mg_8O_{30}$ (OH)$_4$ · (H$_2$O)$_4$ · 8H$_2$O.

It should be emphasized that acid-leached chrysotile (7) is most probably as good a support as sepiolite.

The experimental procedure to graft methyl silyl groups starting from methylvinyldichlorosilane has already been reported (8, 10). The surface grafted silicate was air dried and brought into contact with osmium tetroxide dissolved either in carbon tetrachloride or in ether. It had been shown previously (11) that an ordered distribution of OsO_4 was obtained from the carbon tetrachloride solution. A high-resolution electron micrograph is shown in Fig. 1. The black points exhibit the approximate size expected for individual OsO_4 particles ($\sim$10 Å diameter).

It is this solid containing 7% Os (g/g of air-dried sepiolite) which has been used throughout the present study. The osmium content was thus 0.37×10^{-3} Os atom (g/g). As about 0.7×10^{-3} g · eq —HC=CH$_2$

groups were fixed on the surface, only 50% of them were available for the OsO_4 fixation.

Samples prepared as described above are abbreviated as OsSS. Due to its high toxicity, precautions must be taken when handling OsO_4.

Again it should be emphasized that solids containing at least two and perhaps three times as many Os atoms could be prepared by using thoroughly grafted sepiolite or chrysotile skeleton. Indeed, as shown by Ruiz-Hitzky and Fripiat (10), the amount of organic matter grafted, and hence the number of C=C bonds, depends on the extent of the external surface area exposed to the methylvinyldichlorosilane and on the number of accessible silanol sites, which, in turn, is ruled by the hydrolysis conditions.

Adsorption Measurements

The nitrogen and hydrogen adsorption isotherms were carried out in a conventional all-glass volumetric apparatus equipped with greaseless stopcocks. All pretreatments and adsorption measurements were performed below 200°C in order to avoid pyrolysis of the organic fragments which, as shown elsewhere (9), occurs at around 280°C.

Infrared Spectroscopy

The ir spectra were recorded on a Beckman IR 12 double-beam grating spectrometer. Self-supporting thin wafers of OsSS (10–20 mg/cm²) were placed in a Pyrex ir cell that could be outgassed and in which N$_2$ and H$_2$ adsorptions could be carried out.

RESULTS

Molecular Nitrogen and Hydrogen Low-Temperature Adsorption

A 0.3-g sample of OsSS was outgassed at 120 and 180°C. The experimental isotherms obtained for N$_2$ and H$_2$ at -196°C are shown in Figs. 2 and 3, respectively.

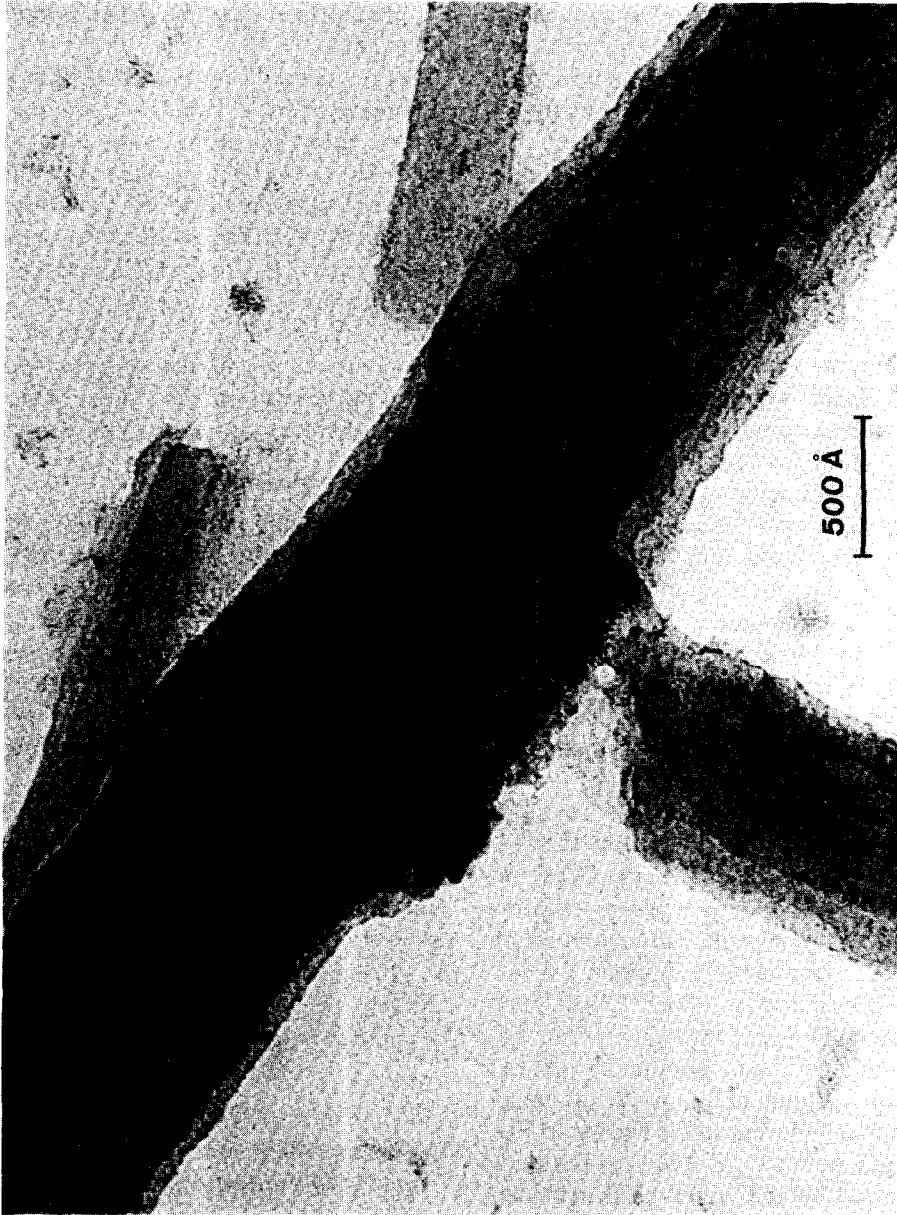That higher amounts of N$_2$ are adsorbed after outgassing at 180°C is probably due to

FIG. 1. High-resolution electron micrograph showing the presence of black spots of about 10 Å diameter or less associated with the presence of osmium oxide.
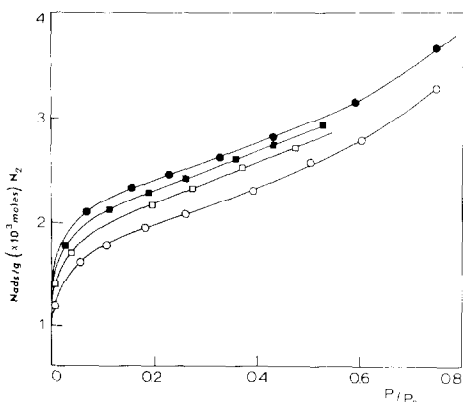
FIG. 2. N_2 adsorption isotherms at $-196°C$ on OsSS prepared either from OsO_4 dispersed in CCl_4 and outgassed at 120°C □, and at 180°C ■ or from OsO_4 dispersed in ether and outgassed at 120°C ○ and at 180°C ●.

the greater removal of the "zeolitic" water molecules filling the porous volume of the solid achieved at that temperature.

The results obtained for H_2 are surprising since, in spite of the fact that the H_2 isotherms have been carried out well above the critical temperature, nearly as much H_2 as N_2 is absorbed at $-196°C$. For an unexplained reason, the ether-prepared OsSS is slightly more sensitive towards the outgassing temperature than the CCl_4-prepared one. This is inferred from the differences between the amounts of H_2 and N_2 adsorbed after outgassing at 120 or 180°C which are more pronounced for ether–OsSS than for CCl_4–OsSS.

Reducing Treatment and H_2 Adsorption Isotherms at 22°C

Samples (~ 0.3 g) of OsSS were treated at $\sim 180°C$ under a pressure of about 400 Torr H_2 and the gas consumption was measured. Almost exactly 1 mole H_2 was consumed per Os atom present in the sample.

H_2 adsorption isotherms were measured on unreduced and reduced OsSS. They belong to the Langmuir type (with a fast-rising initial portion). The saturation values are given in Table 1.

Obviously reduction promotes the H_2 adsorption but the amounts of H_2 retained are at least four times smaller than the amount of Os on the surface. As observed for the ether-prepared OsSS, a second reducing treatment at 180°C followed by an outgassing still improves the quantity of H_2 adsorbed.

N_2 Adsorption Isotherms at Room (22°C) and at Higher Temperatures

Dinitrogen is adsorbed by reduced OsSS at 22°C and even at 180°C. Adsorption isotherms obeying Henry's law are shown in Fig. 4.

Up to 400 Torr the linearity with respect to the pressure is well obeyed for isotherms 1, 2 and 3 but only partly so for isotherm 4, where departure from linearity occurs above 250 Torr. At 22°C and 400 Torr N_2 (isotherm 1) there is nearly 1 mole adsorbed per four osmium atoms. This is about the
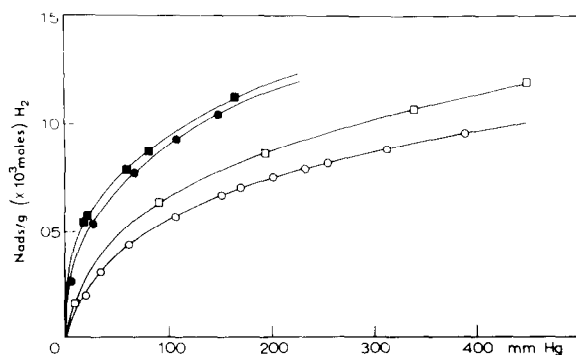

FIG. 3. H_2 adsorption isotherms at $-196°C$ for the same samples as in Fig. 2.
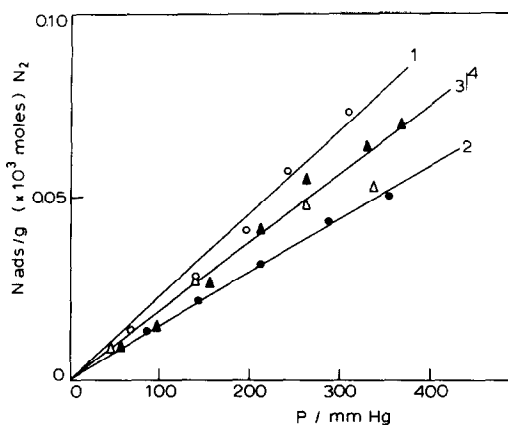
FIG. 4. N_2 adsorption isotherms: (1) ○ at 22°C on OsSS outgassed at 180°C for 15 h and reduced at 180°C for 5 h by 370 Torr H_2; (2) ●, the same sample as (1) but after outgassing at 180°C for 15 h, the isotherm being measured at 180°C; (3) ▲, the same sample as (2) but after 51 h of reduction with 360 Torr H_2 at 180°C; (4) △, the same sample as (3) but the isotherm is measured at 22°C.

same ratio as that found for H_2 at the plateau of the Langmuir isotherm. At 180°C and 400 Torr N_2 (isotherm 2), only one N_2 molecule is adsorbed per six osmium atoms.

INFRARED SPECTROSCOPY

Infrared spectra of self-supporting wafers of OsSS recorded under different conditions are shown in Fig. 5. Four important features of the OsSS samples are easily detected by comparing spectra 1 and 4:

(i) the H—C≡C stretching band at 3058 cm^{-1} and the C—H methyl stretching at 2968 cm^{-1} observed in the initial grafted sepiolite are replaced in OsSS by —CH_2 and —CH stretches at 2920 and 2850 cm^{-1}.

(ii) A carbonyl band appears clearly at 1685 cm^{-1}.

(iii) The two H_2O bending bands observed in the grafted as well as in the nongrafted sepiolite (12) at 1615 and 1640 cm^{-1} are replaced by a single band at 1615 cm^{-1} in OsSS.

(iv) In the OH stretching region, two bands appear at 3430 and 3640 cm^{-1}. They are superimposed on the OH stretching

bands of the support at 3680, 3600, and 3540 cm^{-1}.

The reduction of OsSS by H_2 at 200°C for 16 h in the presence of 400 Torr H_2 brings about some important modifications mainly in the OH region (spectrum 2). The OH stretching vibrations at 3640 and 3430 cm^{-1} are removed whereas the OH bands of the support remain. The H_2O bending at 1615 cm^{-1} is not noticeably altered. This may be observed by comparing spectra 1 and 2. Rehydration followed by an outgassing does not remove water (spectrum 3).

Treatment at 260°C in the presence of O_2 (spectrum 5) removes the organic radical and OsO_4 is vaporized. The resulting spectrum is very similar to that of the starting sepiolite (10). Accordingly, the black color characteristic of OsO_4 disappears.

Attempts to record EPR spectra of OsSS before or after reduction, in the presence or absence of either H_2 or N_2, failed to give any characteristic signal. Infrared adsorption in the spectral domain where either the N≡N stretch, as a terminal ligand, or the Os—H stretch could be expected was carefully studied (1700–2300 cm^{-1}). No absorption band was observed.

Unsuccessful also were the attempts to record the Raman spectra in the region where the —N≡N— stretching vibration of bridged dinitrogen infrared inactive is expected to occur, i.e. between 2000 and 2300 cm^{-1} (4). The high noise and possibly the low N_2 content may explain the negative result.

DISCUSSION

Since the ir spectra of unreduced but dried OsSS have shown the simultaneous transformation of the carbon–carbon double bond into a single bond and the disappearance of the methyl group, the formation of the carbonyl group results probably from the methyl-group oxidation by the osmium tetroxide fixed by the double bond.

In order to preserve the tetrahedral oxygen environment of the Os atom, it may be
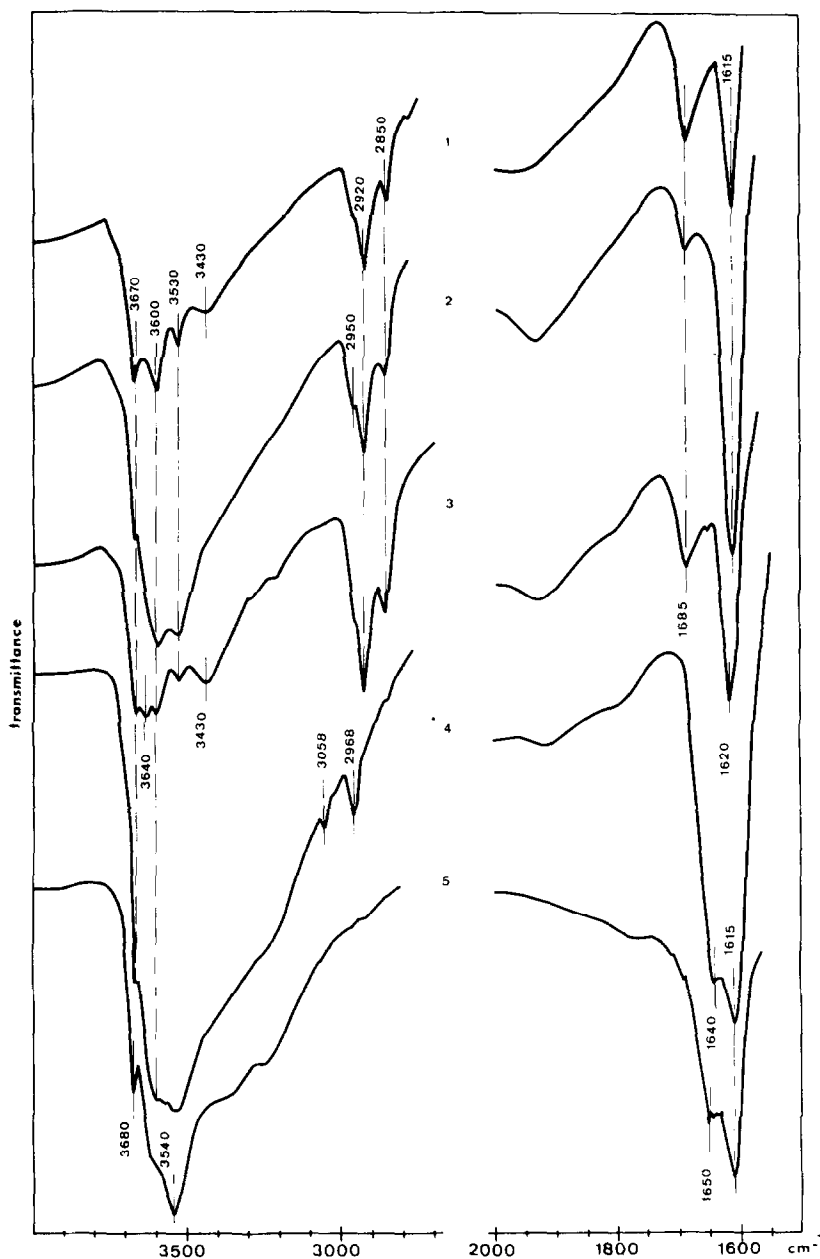
FIG. 5. Infrared spectra: (1) OsSS outgassed at 200°C for 16 h under vacuum; (2) the same sample as (1) but reduced at 200°C in the presence of 400 Torr H_2 for 16 h; (3) OsSS partially rehydrated and outgassed at 200°C for 16 h; (4) sepiolite grafted by methylvinyldichiorosilane and dried at 200°C; (5) OsSS dried at 260°C in the air and then dispersed in Fluorolube.

suggested that two hydrogen atoms of the methyl group are captured by one of the Os=O bonds, forming a strongly coordinated water molecule.

These transformations, illustrated in Fig. 6, would account for the main infrared features and, in particular, for the appearance of OH stretching bands at 3430 and

Pretreatment	Saturation values (10^{-4} mole/g)
OsSS (CCl₄ dispersed)	
Outgassed at 115°C for 16 h	0.16
Same sample after outgassing at 180°C for 15 h	0.36
Same sample, first reduced at 185°C for 5 h in the presence of 390 Torr H_2, and then outgassed at 185°C for 5 h	0.58
OsSS (ether dispersed)	
Outgassed at 180°C for 16 h	0.30
Same sample, first reduced at 180°C for 5 h in the presence of 500 Torr H_2, and outgassed at 180°C for 5 h	0.78
Same sample, reduced again at 180°C for 5 h with 380 Torr H_2, and outgassed at 180°C for 5 h	1.10

3640 cm^{-1}. The bending vibration band of coordinated water could be superimposed on that of water coordinated to magnesium in the sepiolite lattice (12).

Further treatment by H_2 at 200°C would displace quantitatively the coordinated wa-

FIG. 6. Proposed reaction mechanisms and associated structures.

ter, as shown by the disappearance of the 3430- and 3640-cm^{-1} bands, leaving coordinately unsaturated osmium atoms. This hypothesis is supported by the 1/1, H_2/Os ratio observed upon reduction at 180°C. The water displaced by H_2 is probably adsorbed by the exposed Mg atoms of the sepiolite lattice since it is known that a water molecule in this situation is not removed below 300°C (13).

In Fig. 6 it is suggested that the H_2 and N_2 adsorption sites at room temperature are the oxygen vacancies created at the tetrahedral osmium atom by the removal of the coordinated water. This is supported by the fact that no N_2 is adsorbed unless the H_2 treatment between 100 and 200°C is carried out and that the extent of H_2 chemisorption is affected by this treatment.

The low-temperature (-196°C) H_2 adsorption proceeds most probably in a different manner. Indeed, no drastic effect caused by a H_2 pretreatment at 120°C was experimentally observed. The reason why H_2 retention at -196°C greatly exceeds the number of Os atoms on the surface is not clear.

Figure 7 compares the adsorption isotherms at -196°C of the grafted sepiolite (without Os) and OsSS. In both cases, the solid was outgassed at 180°C for 15 h. At 300 Torrs H_2, 1.23 and 1.02 mmole H_2/g are adsorbed by OsSS and the methylvinyl derivative, respectively. The difference, 0.2 mmole, corresponds approximately to a H/Os ratio of 1. That 1 mmole H_2 is adsorbed on the grafted sepiolite cannot yet be explained. Since -196°C lies well above the liquefaction temperature of H_2, capillary condensation occurring in the narrow pores could hardly be involved.

An interesting difference between the H_2 and N_2 adsorptions at room temperature must result from the different shapes of their adsorption isotherms. If —N≡N— bridges as proposed in Fig. 6 are formed between two adjacent Os atoms, the maximum number of adsorption sites would be 0.18 × 10^{-3}/g OsSS. A linear isotherm
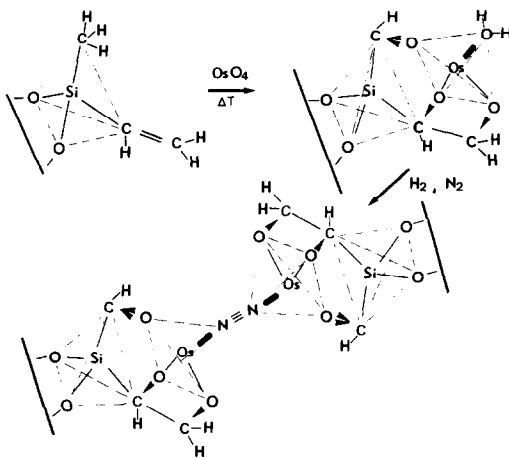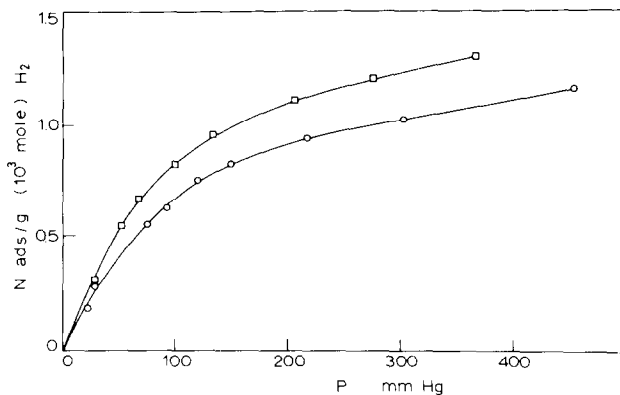
FIG. 7. H_2 adsorption isotherms at $-196°C$ on the methylvinyl derivative (O) and OsSS ($\square$), after outgassing at 180°C for 15 h.

could account for the formation of these bridges. Bridged N_2 would also explain why no ir-active —N≡N vibration of a N_2 terminal ligand has been observed.

In spite of the fact that no direct spectroscopic evidence for nitrogen-bonded end-on either as —Os—N≡N or as —Os—N≡N—Os— could yet be provided, it should be noted that dinitrogen-bridged complexes have been reported in the literature (4, 14). In particular the configuration of N_2 which is proposed for the Os-grafted sepiolite is similar to the one existing, e.g., in [(NH$_3$)$_5$ Ru—N≡N—Ru(NH$_3$)$_5$]$^{4+}$ (15) or in [(C$_6$H$_{11}$)$_3$P]$_2$—Ni—N≡N—Ni—[P(C$_6$H$_{11}$)$_3$]$_2$ (16) complexes.

In the [N$_2$(NH$_3$)$_4$—Os—N≡N—Os—(NH$_3$)$_5$]$^{5+}$ complex studied by Magnusson and Taube (17), both end-on and bridged dinitrogen are simultaneously present.

On the other hand, the room temperature H_2 adsorption isotherms have the Langmuir shape, classical for a homogeneous surface with little interaction between chemisorbed species. This suggests that H_2 would not form bridges, the molecules, however, remaining intact since no dissociative adsorption has been observed.

CONCLUSION

The OsSS catalyst described here offers interesting features to combine the possibility of accommodating dinitrogen as a bridg-

ing ligand and to adsorb molecular H_2 without dissociation at room or higher temperatures. The supported osmium shares these characteristics with some osmium (II) complexes in solution.

REFERENCES

1. Chang, C. C., and Kokes, R. J., J. Phys. Chem. 77, 2640 (1973).
2. Beebe, R. A., and Dowden, D. A., J. Amer. Chem. Soc. 60, 2912 (1938).
3. McGinnety, J. A., in "Transition Metals," Inorganic Chemistry Series One, Vol. 5, p. 261. Univ. Park Press, Baltimore, 1972.
4. Henrici-Olivé, G., and Olivé, S., in "Coordination and Catalysis," p. 289. Monographs in Modern Chemistry, V9, Verlag Chemie, Weinheim/New York, 1977.
5. Sykes, P., in "A Guidebook to Mechanism in Organic Chemistry," p. 186. Longman, New York, 1975.
6. Fripiat, J. J., and Mendelovici, E., Bull. Soc. Chim. Fr. 2, 483 (1968).
7. Zapata, L., Castelein, J., Mercier, J. P., and Fripiat, J. J., Bull. Soc. Chim. Fr. 1, 54 (1972).
8. Ruiz-Hitzky, E., and Fripiat, J. J., Clays Clay Miner. 24, 25 (1976).
9. Brauner, K., and Preisinger, A., Mineral. Petrogr. Mitt. 6, 120 (1956).
10. Ruiz-Hitzky, E., and Fripiat, J. J., Bull. Soc. Chim. Fr. 9, 1341 (1976).

11. Barrios-Neira, J., Rodrique, L., and Ruiz-Hitzky, E., *J. Microsc.* **20,** 295 (1974).

12. Serna, J. C., Ph.D. thesis, Lab. Edafologia CSIC, Madrid 1973.

13. Rautureau, M., and Mifsud, A., *Clay Miner.* **12,** 309 (1977).

14. Sellmann, D., *Angew. Chem. Int. Ed.* **13,** 639 (1974).

15. Harrison, D. F., Weissberger, E., and Taube, H., *Science* **159,** 320 (1968).

16. Jolly, P. W., and Jonas, K., *J. Organometal. Chem.* **33,** 109 (1971).

17. Magnusson, R. M., and Taube, H., *J. Amer. Chem. Soc.* **94,** 7213 (1972).