Figure 5 represents the change of pressure with adsorption by the film.

It can be emphasized that the pirani gauge with high sensitivity, no pumping action and excellent stability could be quite useful for the studies of adsorption of active gases at very low pressures. Detailed results of adsorption of hydrogen and different gases by evaporated metal films will be described in the near future.

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# Catalytic Properties of Some $Mo_3$-Cluster Compounds Prepared in High Surface Area

A new class of ternary tetravalent molybdates was reported by McCarroll, Katz, and Ward in 1957 (*1*). The formula for these materials is $M_2Mo_3O_8$, where M = Mg, Zn, Mn, Cd, Fe, Co, or Ni. A striking structural feature is the presence of clusters of three Mo cations bonded together with Mo–Mo separation of 2.53 Å. This close approach (smaller than the Mo–Mo distance in molybdenum metal) indicates strong bonding within the $Mo_3$ cluster, explaining its weak paramagnetism.

It seemed interesting to investigate the catalytic properties of these materials. However, conventional preparative techniques, (i.e., heating mixtures of reactant oxide powders), gave surface areas of about 1 $m^2/g$. This was deemed undesirable for catalytic testing. Initial attempts to remedy this involved the use of $MgO$–$MoO_2$ powder mixtures with one component present in 2–4-fold molar excess. After formation of $Mg_2Mo_3O_8$, excess oxide was removed with dilute $HNO_3$. Using firing temperatures of 1100°C, no improvement in product surface area was realized. However, for preparations carried out at 900°C, with either MgO or $MoO_2$ in excess, $Mg_2Mo_3O_8$ surface areas of 4 $m^2/g$ were achieved. Lowering the firing temperature further did not improve upon this.

A different approach was adopted which gave much better results. It was reasoned that the low surface area obtained for complex oxides by ceramic techniques stems from the relatively large particle size of the starting oxides, typically about 2 $\mu$ or more. Reduction of the particle size of either or both oxides would be expected to lead to a lower synthesis temperature and a more finely divided product. A convenient way of effecting this is to start with one of the reactant oxides in high-area (small pore-size) form, and to impregnate this with a solution of a precursor salt of the second oxide. The latter oxide, when formed, will necessarily have particle dimensions no larger than the pore diameter of the first oxide. *Impregnation–synthesis,* as this technique might be termed, thus relies on the fact that high-area oxides, (greater than about 10 $m^2/g$), will have pore diameters in the range 100–1000 Å, and the particle size of any material formed in this pore structure will be smaller by 1–2 orders of magnitude than those used in ceramic techniques.

Impregnation–synthesis of $Mg_2Mo_3O_8$ consists, then, of:

a. Impregnation of MgO (commercially available with surface area of ~50 $m^2/g$) with an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ followed by drying at 110°C.
b. Treatment of the product of Step (a); first with $H_2$, sparged through $H_2O$, at 500°C for 16 hr, and then at 700°C for 16 hr under an inert atmosphere. The $H_2$–$H_2O$ treatment converts the precursor salt to $MoO_2$ ($H_2O$ vapor inhibits further reduction to Mo metal), (2) and the $MoO_2$, present as <100 Å particles due to the pore size of the MgO, will react with contiguous MgO to form $Mg_2Mo_3O_8$.
c. Extraction, with dilute mineral acid, of excess MgO to yield pure $Mg_2Mo_3O_8$. Surface areas of 100 $m^2/g$ have been obtained. X-Ray diffraction reveals $Mg_2Mo_3O_8$ with no other phases present.

The analogous impregnation–synthesis of $Zn_2Mo_3O_8$ has been carried out using, as support, ZnO with surface area of 21 $m^2/g$. The product $Zn_2Mo_3O_8$ had a surface area of 22 $m^2/g$, but X-ray analysis revealed the presence of the spinel, $Zn_2MoO_4$, as an impurity. Pure $Zn_{4/3}Mg_{2/3}Mo_3O_8$ was prepared by impregnation–synthesis using $MoO_2$ (12 $m^2/g$) as support and impregnating this with mixed acetate solution of $Zn^{2+}$ and $Mg^{2+}$. The product, (after removal of excess $MoO_2$ with cold, dilute $HNO_3$), had a surface area of 16 $m^2/g$. X-Ray diffraction indicated only the $Mo_3$-cluster phase; $Zn_2MoO_4$ was absent. This is explained on the basis of excess $MoO_2$, (the support), disfavoring formation of $Zn_2MoO_4$ due to the stoichiometry of this reaction vs that of $Mo_3$-cluster formation.

It was desired to investigate the catalytic activity of some $Mo_3$-cluster phases. The reaction chosen was hydrogenation of cyclopropane. This tests the important catalytic function of hydrogenation–dehydrogenation and can be carried out, for active catalysts, at moderate temperatures. A stainless-steel reactor was employed, with metered gases passing downflow through the catalyst bed. Effluent gases were analyzed by gas chromatography using a 2-m silica-gel column.

To minimize catalyst deactivation, cyclopropane was delivered in pulses of 1–2 min at the conclusion of which the sample was taken. Hydrogen and helium were fed continuously. During the cyclopropane pulse, its partial pressure was 0.10 atm, and those of hydrogen and helium were 0.40 and 0.50 atm, respectively.

Activity for cyclopropane hydrogenation was determined for four $Mo_3$-cluster phases, and an arbitrarily chosen nontransition-metal oxide. As discussed above, the $Zn_2Mo_3O_8$ preparation contained a small amount of $Zn_2MoO_4$ impurity, as revealed by X-ray analysis. The three other $Mo_3$-cluster phases in Table 1 showed no extra phases. $Ni_2Mo_3O_8$, $Co_2Mo_3O_8$, and $Fe_2Mo_3O_8$ were excluded from this study, since reduction to the corresponding ferromagnetic metal would obscure the catalytic results. The two Mg–Zn $Mo_3$-cluster phases are believed to be solid solutions, and not merely mixtures of $Mg_2Mo_3O_8$ and $Zn_2Mo_3O_8$. This

TABLE 1

HYDROGENATION OF CYCLOPROPANE

| Catalyst | $T^*$ (°C) |
|---|---|
| $Mg_2Mo_3O_8$[c] | 130 |
| $Mg_{4/3}Zn_{2/3}Mo_3O_8$[c] | 190 |
| $Mg_{2/3}Zn_{4/3}Mo_3O_8$[c] | 320 |
| $Zn_2Mo_3O_8$[c] | 260 |
| ZnO[a,c] | >500 |
| 10% $Ni/SiO_2$[b] | −5 |
| 10% $Pt/SiO_2$[b] | 18 |
| 10% $Co/SiO_2$[b] | 52 |
| 10% $Cu/SiO_2$[b] | 84 |

[a] ZnO prepared by decomposition of $ZnCO_3$, *in vacuo*. Surface area = 21 $m^2/g$.

[b] Data of Sinfelt, Yates, and Taylor (*3*), recalculated to give $T^*$.

[c] Catalyst pretreated with $H_2$ at 500–550°C for at least 1 hr. The X-ray pattern of $Mg_2Mo_3O_8$ was found to be unchanged by this treatment.

is asserted on the basis of X-ray examination of $MgMnMo_3O_8$, which produced a single symmetrical 100 reflection. This would not be the case for a mixture of $Mg_2Mo_3O_8$ and $Mn_2Mo_3O_8$ which, possessing appreciably different *c* axes, would give two resolvable peaks in this region. The *c* axes of $Mg_2Mo_3O_8$ and $Zn_2Mo_3O_8$ are virtually identical.

The hydrogenation activity of the materials listed in Table 1 is presented in terms of a hypothetical temperature, $T^*$, at which 100 $m^2$ of catalyst, (or supported metal), would convert 0.25 liter/hr (STP) of cyclopropane to propane at $p$(cyclopropane) = 0.10 atm, and $p(H_2)$ = 0.40 atm. The results for the supported-metal catalysts are from the work of Sinfelt, Yates, and Taylor (*3*). $T^*$ values have been calculated from their data, (and adjusted to the different partial pressures used in the present study), using specific activities, activation energies, and exponents on cyclopropane and hydrogen pressures which are contained in their work. A survey of the literature revealed no reference to cyclopropane hydrogenation catalyzed by nonmetals.

The $Mo_3$-cluster compounds reported in Table 1 are seen to be considerably less active for cyclopropane hydrogenation than any of the metals reported by Sinfelt, Yates, and Taylor. Nevertheless, they are definitely catalysts for this reaction. ZnO showed no activity even at 500°C, which suggests that the hydrogenation activity found for $Mg_xZn_{2-x}Mo_3O_8$ is associated either with $Mo_3$ clusters present at the surface, or molybdenum surface species which are formed from these clusters.

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