

Strong Metal-Support Interactions: Occurrence among the Binary Oxides of Groups IIA-VB

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Iridium, supported on a number of oxides from Groups IIA, IIIB, IVB, and VB, exhibits normal H₂-chemisorption (typical of Ir/Al₂O₃ and Ir/SiO₂) following reduction at 200°C. If supported on MgO, Sc₂O₃, Y₂O₃, ZrO₂, or HfO₂, this behavior is not seriously affected by reduction temperatures ≤ 700°C. If, however, the carrier is TiO₂, V₂O₅, or Nb₂O₅, H/M is decreased to near-zero by reduction at 500°C, while Ta₂O₅ requires 700°C for this. This strong metal-support interaction is discussed in terms of the need for a reducible, transition metal oxide support and on the basis of bonding mechanisms suggested by known compounds.

INTRODUCTION

A fundamental property of the Group VIII noble metals is their ability to chemisorb hydrogen and carbon monoxide. On supports such as alumina or silica this provides a means of measuring their dispersion and such techniques are routinely applied in almost every laboratory investigating catalysts of this kind.

When Group VIII noble metals are supported on TiO₂, however, a metal-support interaction occurs which virtually eliminates their normal ability to adsorb H₂ and CO (1, 2). This suppression is not found if the catalysts have been reduced at low temperature (200°C), which leads to hydrogen/metal atomic ratios (H/M) indicative of moderate-to-high metal dispersion. Following reduction at 500°C, however, H/M values are found to be drastically lowered; ≤ 0.01 for Pt, Ir, and Rh, 0.05 to 0.06 for Pd and Ru, and 0.11 for Os. CO chemisorption properties of these catalysts are similarly affected. Trivial explanations, such as impurity effects, or

the agglomeration, encapsulation, or incomplete reduction of the supported phase can be ruled out on the basis of much evidence (2).

Efforts to explain the origin of this strong metal-support interaction have been influenced by consideration of two known classes of compounds. One is the so-called hexagonal barium titanates (3) in which metal-metal bonding occurs between cations of titanium and "donor" cations, of which Pt⁴⁺, Ir⁴⁺, and Co²⁺ are examples, which supply the electrons for this bond. We have suggested that titanium cations at *surfaces* may have similar properties and be capable of covalent interaction involving *d* orbitals centered at these cations and *d* electrons from supported metal atoms or aggregates.

An alternative model for the strong metal-support interaction involves formation of Lewis-acid-base intermetallic compounds (4-6) such as TiPt₃ and TiIr₃. These have been reported to form, from finely ground powders of TiO₂ and the

noble metal in the presence of H_2 , only at temperatures $\geq 1200^\circ C$ (7). Conceivably, the higher metal dispersion in an impregnated catalyst could lead to formation of these phases at much lower temperatures. It is interesting that Brewer's account of these phases (6) involves transfer of d electrons between a metal, e.g., Pt or Ir, with internally paired d electrons and a metal with vacant d orbitals, e.g., Ti or Hf, and is thus analogous to the description of metal-metal bonding in the hexagonal barium titanates.

It is natural to speculate that oxides other than TiO_2 might manifest strong metal-support interaction (SMSI) properties. If titanium cations at the surface are the bonding entities in the noble metal/ TiO_2 systems, the possibility must be considered that other cations are able to participate. The hypothesis (2) that the interaction of an SMSI-active cation involves its d orbitals would restrict participation to *transition metal* oxides.

If SMSI properties are considered to relate to intermetallic compound formation there is scant thermodynamic data available upon which to base predictions of their extensiveness among other oxides. Even in those systems for which such data exists the situation is unclear due to lack of knowledge of kinetic factors and the possibility of altered free energies of formation of quasi-two-dimensional intermetallic phases formed at the metal-support interface.

It is thus necessary to take an empirical approach. In the present report we present the results of an investigation of several oxides belonging to Groups IIA, IIIB, IVB, or VB for SMSI properties. Not all oxides in these groups were suitable for study, some being rejected because of stable carbonate formation (discussed below). Nine were selected and tested for their ability to suppress the chemisorption of H_2 onto iridium, which was supported on them at a concentration of 1 to 2% (wt).

Adsorption of H_2 was measured (at $25^\circ C$) after each of a number of activations in H_2 at progressively higher temperatures. In this way there results not only a delineation between oxides which are SMSI-active and those that are not but, for the former, information concerning the induction of this property as a function of activation temperature. The sequence of several activations and chemisorption measurements was carried out without removing the catalyst from the cell or exposing it to air.

EXPERIMENTAL METHODS

Selection of Binary Oxides

Although the general intent was to investigate binary oxides belonging to Groups IIA-VB, upon reflection it was apparent that some of these would have to be omitted. The deterring factor was the formation of highly stable carbonates on some oxides of Groups II and III. To illustrate this, the temperature required for a dissociation pressure of 1 atm is $230^\circ C$ for $MgCO_3$, $817^\circ C$ ($CaCO_3$), $1258^\circ C$ ($SrCO_3$), and $1297^\circ C$ ($BaCO_3$) (8). Superficial carbonate formation will be unavoidable upon impregnation and subsequent handling of these oxides unless special equipment and procedures are resorted to. In order that the properties of the support reflect an oxidic surface rather than one extensively covered with carbonate groups one must rely upon decomposition of carbonate during *in situ* hydrogen-activation to restore the oxidic surface. As these activations were in the temperature range 200 to $700^\circ C$, there was clearly no interference to be expected from the presence of $MgCO_3$. However, the very stable carbonates of strontium and barium render their oxides unsuitable for study. Calcium oxide is marginal in this respect and was likewise excluded. BeO was not studied because of the high toxicity of the finely divided powder.

In Group IIIB one again finds a strong increase in carbonate stability on proceeding to the heavier members. $\text{Sc}_2(\text{CO}_3)_3$ cannot be formed (9). $\text{Y}_2(\text{CO}_3)_3$ is known but decomposes at relatively mild temperatures with the final stage, leading to Y_2O_3 , occurring at 410 to 450°C (10). Accordingly, Sc_2O_3 and Y_2O_3 were included in the present study. $\text{La}_2(\text{CO}_3)_3$ decomposes to La_2O_3 only at 1000°C (11) and this oxide was omitted. Carbonate formation is not a problem with any of the oxides of Group IVB or VB.

Preparation of Supports

The oxides used as supports in this study were those of magnesium, scandium, yttrium, titanium, zirconium, hafnium, vanadium, niobium, and tantalum. These were obtained and characterized as follows.

MgO. Reagent grade magnesia (Matheson, Coleman and Bell, Norwood, Ohio) was calcined in air at 600°C, then pretreated ~3 hr in H_2 at 730°C. Surface area (BET) was 31 m^2/g .

Sc₂O₃. Scandium oxide (99.9%, Research Organic/Inorganic Chemical Corp., Belleville, N. J.) was dissolved in hot 4 *N* HCl and scandia gel was precipitated with excess NH_4OH . The product was calcined in air at 520°C. XRD showed cubic Sc_2O_3 plus a very small signal at $2\theta = 16^\circ$ and a trace signal at $2\theta = 26^\circ$ (both present in scandium oxide as received). The surface area (BET) was 70 m^2/g . This material was pretreated ~3 hr in H_2 at 550°C.

Y₂O₃. Yttrium oxide (99.99%, Ventron Corp., Danvers, Mass., surface area = 5.9 m^2/g) was dissolved in hot 2.5 *N* HCl and yttria gel was precipitated with excess NH_4OH . This was calcined in air at 520°C. XRD showed cubic Y_2O_3 , no other phases. Surface area (BET) was 54 m^2/g . This material was pretreated ~3 hr in H_2 at 750°C.

TiO₂. Titanium dioxide (National Lead Co., Perth Amboy, N. J.) was calcined ~3 hr in air at 500°C. XRD showed anatase, no other phases. Surface area (BET) was 145 m^2/g .

ZrO₂. Zirconia gel was precipitated from a methanolic solution of ZrCl_4 with excess NH_4OH . This was calcined in air at 520°C. XRD showed monoclinic ZrO_2 , trace of tetragonal ZrO_2 , no other phases. Surface area (BET) was 41 m^2/g . This material was pretreated ~3 hr in H_2 at 750°C after which the surface area was 36 m^2/g .

HfO₂. Hafnia gel was precipitated from a methanolic solution of HfCl_4 with excess NH_4OH . This was calcined in air. XRD showed $(\text{HfO}_2)_{12}M$, some $(\text{HfO}_2)T$, no other phases. This material was pretreated ~3 hr in H_2 at 500°C.

V₂O₅. Reagent grade ammonium metavanadate (Matheson, Coleman and Bell, Norwood, Ohio) was calcined in air to obtain V_2O_5 (surface area (BET) = 11 m^2/g). This was pretreated ~3 hr in H_2 at 540°C. XRD showed V_2O_5 plus very small signal at $2\theta = 27^\circ$. Surface area (BET) was 6.7 m^2/g .

Nb₂O₅. Niobium oxide gel was precipitated from a methanolic solution of NbCl_5 with excess NH_4OH . This was calcined ~3 hr in air at 540°C. XRD showed Nb_2O_5 , no other phases. Surface area (BET) was 26 m^2/g .

Ta₂O₅. Tantalum oxide gel was precipitated from a methanolic solution of TaCl_5 with excess NH_4OH . This was calcined in air at 500°C. The surface area (BET) was 135 m^2/g . This material was pretreated ~3 hr in H_2 at 750°C.

Preparation of Catalysts and Experimental Procedure

The supports were impregnated with H_2IrCl_6 using the method of incipient wetness. Aqueous solutions were used except for MgO, the slaking properties of which dictated the use of a methanolic

TABLE 1
Hydrogen Chemisorption^a on Supported Iridium Catalysts

Support	Iridium wt%	T_A^b						
		120	203 ± 2	250	300	351 ± 3	501 ± 2	703 ± 3
MgO	2	—	1.05	—	—	0.86	0.75	0.54
Sc ₂ O ₃	2	—	1.44	—	—	1.21	1.10	0.79
Y ₂ O ₃	2	—	—	—	0.90	—	0.88	0.29
TiO ₂	2	1.17	—	0.32	—	—	0.02	—
ZrO ₂	2	—	1.27	—	—	1.12	0.94	0.42
HfO ₂	1	—	1.80	—	—	1.46	1.37	0.67
V ₂ O ₃	1	—	0.84	—	—	0.11	0.046	—
Nb ₂ O ₅	2	—	0.67	—	—	0.040	0.01	—
Ta ₂ O ₅	2	—	—	—	1.01	—	0.060	0.015

^a H/M = atoms hydrogen adsorbed at 25°C/atom iridium in catalyst. The precision of H/M in these measurements is estimated as ±0.01.

^b T_A = temperature of activation in H₂ preceding chemisorption measurement.

solution. After drying at 110°C, the impregnated materials were charged as powders (1–2 g) into the chemisorption cell.

A typical glass adsorption system was used which was capable of attaining a vacuum of 5×10^{-7} Torr. All chemisorption measurements were carried out at ambient temperature and were preceded by 1-hr activation at a specified temperature, followed by evacuation at that temperature to $\leq 10^{-5}$ Torr. The activating gas was flowing hydrogen (20 liters/hr) purified by passage through a catalytic de-oxygenator, a molecular sieve drying trap, and a liquid nitrogen trap.

In a typical experiment an impregnated and oven-dried catalyst was activated in hydrogen and evacuated at 200°C, whereupon hydrogen chemisorption was measured at ambient temperature. The catalyst was next activated in hydrogen and evacuated at 350°C, hydrogen adsorption was again determined at ambient temperature, then activated and evacuated at 500°C, and so on. In all cases activation temperatures were used in ascending sequence.

In several cases the supports were pretreated in H₂ at 750°C. The purpose of this was to structurally stabilize the support

at a temperature exceeding any to which it would be subjected after the introduction of iridium. As SMSI activity was to be inferred on the basis of suppressed H₂ chemisorption following various activations in H₂, it was important to minimize non-SMSI-related changes in H₂ adsorption capacity which might result from these activations. Surface area reduction of the support might lead to agglomeration of the iridium or possibly, if sufficiently drastic, its encapsulation. As the highest activation temperature applied to any iridium-containing sample was 700°C, prestabilizing the support at 750°C will avoid these difficulties. Catalysts that were not activated at 700°C did not, of course, require such pretreatment of the corresponding support. Preliminary results with Sc₂O₃ and HfO₂ indicated that this precaution could be dispensed with for these materials.

Chemisorption Results and X-Ray Spectra of Catalysts

The data relating hydrogen chemisorption to temperature-of-activation for all catalysts is tabulated in Table 1 and plotted in Fig. 1. Data representing Ir/Al₂O₃ and Ir/SiO₂, obtained in our

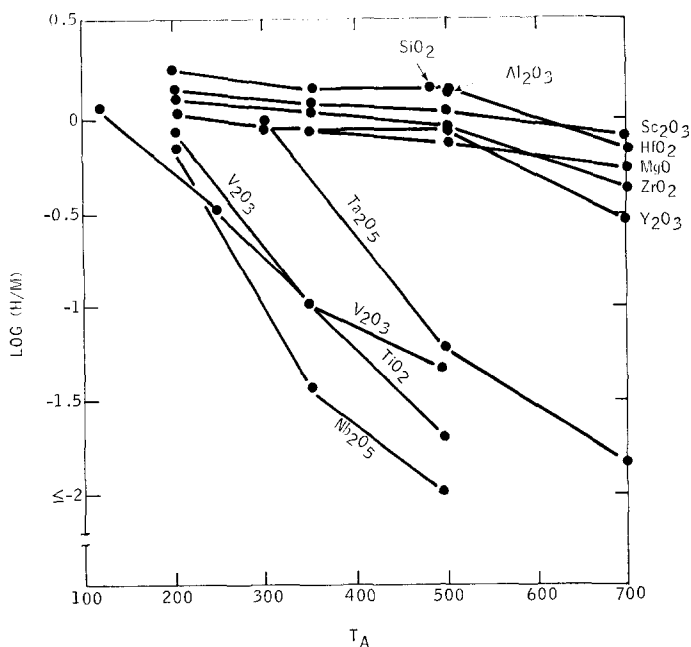


FIG. 1. H₂ chemisorption vs temperature of activation for supported-iridium catalysts. H/M = atoms hydrogen adsorbed at 25°C per atom iridium present in catalyst; T_A = temperature of activation in hydrogen; wt% Iridium = 1 for SiO₂, Al₂O₃, V₂O₃, and HfO₂ and 2 for all other catalysts.

laboratory, is included in Fig. 1 for comparison.

It is apparent that the curves of log (H/M) versus temperature-of-activation (T_A) divide into two groups. In the case of MgO, Sc₂O₃, Y₂O₃, ZrO₂, and HfO₂ the hydrogen chemisorption capacity of the catalyst continues at a high level for $T_A \leq 500^\circ\text{C}$ and then drops somewhat following activation at 700°C. The group comprising TiO₂, V₂O₃, Nb₂O₅, and Ta₂O₅ behaves quite differently. For three of these H/M is reduced to ~ 0.1 by activation at temperatures no greater than 350°C. Ta₂O₅ is clearly more sluggish than the others in this group and reaches this level only after activation at 500°C. The relatively small change in H/M for Ir/V₂O₃ as T_A increases from 350 to 500°C may reflect a small fraction of poorly dispersed iridium (and thus not intimately contacted with the support) due to the low surface area of the carrier (6.7 m²/g).

It will be noted that all catalysts exhibit a hydrogen chemisorption capacity following activation at *some* temperature which is indicative of moderate-to-high dispersion of the supported metal. As in the case of the Group VIII noble metals supported on TiO₂ (2), this observation implies that a low value of H/M, should this occur following activation in H₂ at higher temperature, cannot be attributed to incomplete reduction of the supported phase. The very high values occurring in some cases (Ir/HfO₂, Ir/Sc₂O₃) have been reported previously for iridium-containing catalysts (12).

X-Ray spectra of the catalysts were obtained at the conclusion of the chemisorption experiments. In the cases of 2% Ir/TiO₂, 1% Ir/V₂O₃, 2% Ir/Nb₂O₅ and 2% Ir/Ta₂O₅, all of which exhibited very low H/M ratios, iridium peaks were verified as absent and thus these ratios are not indicative of iridium agglomeration. The

TABLE 2
Correlation of SMSI Properties with Reducibility
for Saturated Transition Metal Oxides

	χ_{1000}^a	SMSI activity
Sc ₂ O ₃	-18.1 (Sc)	Negative
Y ₂ O ₃	-18.0 (Y)	Negative
HfO ₂	-14.0 (Hf)	Negative
ZrO ₂	-13.6 (Zr)	Negative
Ta ₂ O ₅	-6.8 (Ta)	Positive (sluggish)
TiO ₂	-3.9 (Ti ₃ O ₅)	Positive
Nb ₂ O ₅	-1.1 (NbO ₂)	Positive

^a $\chi_{1000} = \log(p_{\text{H}_2\text{O}}/p_{\text{H}_2})$ at which the oxide in column 1 and the phase in parentheses in column 2 exist in equilibrium at 1000 K.

spectra of the 2% Ir/Sc₂O₃ and 2% Ir/Y₂O₃ used-catalysts likewise showed no peaks due to iridium as expected on the basis of their H/M values. In the case of 2% Ir/MgO a broad iridium signal could be detected. In view of the value of H/M (0.54 corresponding to $T_A = 700^\circ\text{C}$) this signal presumably relates to a fraction of the supported iridium with the remainder being in the sub-X-ray-detectable range of crystallite size. In the cases of Ir/ZrO₂ and Ir/HfO₂ interference occurs between the principal iridium peak and peaks due to the support.

DISCUSSION

It is clear that SMSI properties are not unique to TiO₂. Figure 1 suggests the following delineation among the 11 oxides represented.

SMSI	TiO ₂ , V ₂ O ₃ , Nb ₂ O ₅ , Ta ₂ O ₅ (sluggish)
non-SMSI	Al ₂ O ₃ , SiO ₂ , MgO, Sc ₂ O ₃ , Y ₂ O ₃ , ZrO ₂ , HfO ₂ .

It should be stressed that the formulas listed for the SMSI oxides are not intended to identify the actual SMSI-active valencies. These designations merely denote the phases indicated by X-ray inspections

of the catalysts at the conclusion of the chemisorption measurements.

As already noted, the non-SMSI catalysts maintain a high value of H/M for activation temperatures $\leq 500^\circ\text{C}$. Increasing T_A to 700°C leads to a definite decrease, although quite small compared with those found for the SMSI catalysts. It is reasonable to expect a certain degree of metal agglomeration due to activation at 700°C . In agreement with this, electron microscopic examination of a 2% Ir/ZrO₂ sample, following activation in H₂ at 700°C , was performed and yielded an average iridium particle size of ~ 25 to 35 Å. This leads to a calculated H/M ratio of ~ 0.3 to 0.4 , in good agreement with the value tabulated in Table 1.

If one considers the classification of oxides given above, it is seen that although all those exhibiting the strong metal-support interaction are transition metal oxides, the converse is not true. Those transitional oxides, such as Sc₂O₃ and ZrO₂, that are extremely refractory to reduction do not manifest SMSI behavior.

In order to pursue this more explicitly, let us confine our attention to the *saturated* transition metal oxides, i.e., those whose cations formally have zero-*d*-orbital-occupancy before treatment in hydrogen. A discussion of unsaturated oxides such as V₂O₃ will be deferred to a subsequent communication.

In Table 2 the saturated transition metal oxides that we have studied are arranged in order of decreasing resistance to reduction. This is expressed as the logarithm of the ratio $p_{\text{H}_2\text{O}}/p_{\text{H}_2}$ at equilibrium at 1000 K between the saturated oxide and the closest available reduced state. Thermodynamic parameters contained in Reed's monograph (13) have been used and the product of reduction is indicated in parentheses.

For the first five entries in Table 2 no stable lower oxides have been characterized and the calculation relates to reduction to

the corresponding metal. In the case of TiO_2 a large number of intermediate oxides are known. Ti_3O_5 has been arbitrarily selected; choosing $\text{Ti}_n\text{O}_{2n-1}$, $n = 4$ to 7, would lead to higher (less negative) χ values.

A correlation between SMSI activity and reducibility among saturated transition metal oxides is clearly suggested by Table 2. Thus, none of the four most refractory (to reduction) oxides are SMSI-active, the three most reducible are, and the most refractory of these three is relatively sluggish. As the reducibilities relate to bulk phases, and will not precisely apply to the surface, it is appropriate to consider only the relative order among these oxides rather than attach significance to absolute values.

In an attempt to interpret the correlation suggested in Table 2, we may observe that the reduction of the surface of a saturated transition metal oxide will (a) remove the zero- d -orbital-occupancy of the cations; (b) eliminate oxygen anions from the surface via H_2O formation. With regard to the first of these factors, it is conceivable that removal of zero- d -orbital-occupancy is required for effective covalent bond formation between the cation and the supported metal. With regard to the second factor, the significance of oxygen anion removal, in terms of this model, seems rather plausible. Although coor-

dinatively unsaturated cations can simply result from dehydroxylation, it is conceivable that interaction with an *aggregate* of metal atoms requires a high local concentration of such cations, and that reduction of the surface is required to bring this about.

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