

Competition between Electron Localization and Superconductivity

The ability to carry an electrical current without resistance is referred to as superconductivity,^{16c,21} and the temperature at which a material becomes superconducting upon cooling is called the superconducting transition temperature, T_c . It is known that T_c is raised upon increasing the density of states at the Fermi level $n(e_f)$,^{3a,21} and a high transition temperature T_c is likely to occur from a nearly half-filled narrow band⁹ partly because the $n(e_f)$ value of such a band is generally large. As already pointed out, electrons in such a band are also susceptible to electron localization. Thus, competition between superconductivity and electron localization may occur, as observed from several organic salts of tetramethyltetraselenafulvalene (TMTSF) with inorganic ions X^- , i.e., $(TMTSF)_2X$.²² For instance, $(TMTSF)_2PF_6$ undergoes a spin density wave (SDW) transition near 12 K at ambient pressure.²³ However, an applied pressure of ~ 12 kbar is known to suppress the SDW transition and give rise to superconductivity at $T_c \approx 0.9$ K.²⁴ On the other hand, $(TMTSF)_2ClO_4$ becomes superconducting at $T_c \approx 1$ K without any

(21) (a) Krebs, H. *Prog. Solid State Chem.* 1975, 9, 269. (b) Grassie, A. D. C. "The Superconducting State"; Sussex University Press: London, 1975; Chapter 2. (c) Kittel, C. "Quantum Theory of Solids"; Wiley: New York, 1963; Chapter 8.

(22) A recent summary of experimental and theoretical results on $(TMTSF)_2X$ salts is found in *Mol. Cryst. Liq. Cryst.* 1982, 79, 1-359.

(23) (a) Bechgaard, K.; Jacobsen, C. S.; Mortensen, K.; Pedersen, H. J.; Thorup, N. *Solid State Commun.* 1980, 33, 1119. (b) Walsh, W. M., Jr.; Wudl, F.; Thomas, G. A.; Nalewajek, D.; Hauser, J. J.; Lee, P. A.; Poehler, T. *Phys. Rev. Lett.* 1980, 45, 829. (c) Scott, J. C.; Pedersen, H. J.; Bechgaard, K. *Phys. Rev. Lett.* 1980, 45, 1874. (d) Chaiken, P. M.; Grunner, G.; Engler, E. M.; Greene, R. L. *Phys. Rev. Lett.* 1980, 45, 1874.

(24) (a) Jerome, D.; Mazud, A.; Ribault, M.; Bechgaard, K. *J. Phys. Lett. (Orsay, Fr.)* 1980, 41, L95. (b) Andres, K.; Wudl, F.; McWhan, D. B.; Thomas, G. A.; Nalewajek, K.; Stevens, A. L. *Phys. Rev. Lett.* 1980, 45, 1449.

applied pressure.²⁵ It is certainly a challenge to unravel the structural and electronic factors responsible for such delicate changes in the physical properties of $(TMTSF)_2X$.

Concluding Remarks

The electronic structure of a given system is characterized by its orbital occupancy, which is in turn governed by a balance between two opposing energy components. That is, the double occupancy of low-lying orbitals is promoted by orbital energy but opposed by electron-electron repulsion. Since this is true for any material, regardless of whether extended or discrete, it is only natural that similarities do exist between extended and discrete systems in their structural and electronic phenomena. Some of those similarities were identified and analyzed in this article. It should also be noted that common facets exist between molecular ring current and bulk superconductivity²⁶ and that a solid-state polymerization process, as to whether thermally or photochemically allowed, can be discussed in terms of the Woodward-Hoffmann rules.²⁷ Further investigation of such similarities between extended and discrete systems would help us to build true bridges of comprehension between chemistry and physics associated with solid-state materials.

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(25) Bechgaard, K.; Carneiro, K.; Rasmussen, F. B.; Olsen, M.; Rindorf, G.; Jacobsen, C. S.; Pedersen, H. J.; Scott, J. C. *J. Am. Chem. Soc.* 1981, 103, 2440.

(26) Haddon, R. C. *J. Am. Chem. Soc.* 1979, 101, 1722.

(27) Burdett, J. K. *J. Am. Chem. Soc.* 1980, 102, 5458.

Characterization of Chromia and Molybdena Catalysts by Oxygen Chemisorption

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This Account is concerned with the development of methods, based on the selective chemisorption of oxygen, to characterize the specific surface area of chromia and molybdena catalysts. Selective chemisorption techniques, especially for hydrogen and carbon monoxide, are well-known for the characterization of supported metal catalysts. Comparable methods for supported transition-metal oxide and sulfide catalysts have

been relatively neglected, and more study will be needed before we understand in detail what is being measured. The author's interest in this topic originated some 30 years ago in a more general context.

Two papers by Dowden aroused hopes, around 1950, that a unitary electronic theory of catalytic action would be successful.^{1,2} Dowden's approach was based on application of band theory (of electronic energy levels) to insulator, semiconductor, and metal catalysts.³ The author's first work on transition-metal oxide catalysts

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(1) Dowden, D. A. *Research (London)* 1948, 1, 239.

(2) Dowden, D. A. *J. Chem. Soc.* 1950, 242.

(3) Some years later, Dowden gave up this approach in favor of greater emphasis on surface chemistry, expressed in terms of crystal and ligand-field theory.

was initiated under the stimulus of these papers. It seemed useful to start with some material that was known to be catalytically active and whose properties as an n- or p-type semiconductor had been established; to vary the electronic state by appropriate pretreatment at elevated temperatures; and to study catalytic behavior, as a function of pretreatment, under conditions sufficiently mild that the electronic properties would not be changed under the self-leveling effect of reaction conditions.

After exploratory work ruled out several catalytic systems that were too labile toward redox reactions under catalytic conditions, chromic oxide was settled on as a suitable model catalyst.⁴ The research led to a series of papers on unsupported chromia and chromia-alumina.⁵⁻¹² In the course of this research, it became clear that the surface chemistry of chromia was very rich.

Bulk chromium trioxide is unstable on heating in air or oxygen; it loses oxygen at fairly low temperatures to give a variety of intermediate oxides. Chromium dioxide, a well-defined intermediate, itself decomposes to chromic oxide (chromia) with a decomposition pressure of 1 atm at about 430 °C.¹³ Bulk chromia, by contrast, is quite stable even under reducing conditions. In the reduction by hydrogen of bulk chromia to chromous oxide ($\text{Cr}_2\text{O}_3 + \text{H}_2 \rightarrow 2\text{CrO} + \text{H}_2\text{O}$), a water partial pressure of about 2×10^{-5} atm will suffice to prevent reduction of the bulk phase at 500 °C if the hydrogen partial pressure is 1 atm.⁵

These considerations of bulk thermodynamics are useful, but they are not informative about the surface chemistry of chromia. Although bulk chromia is stable in 1 atm of oxygen at 500 °C, the surface Cr^{III} ions are oxidized to Cr^{VI} . Indeed, CrO_3 can be extracted from an O_2 -treated sample and quantitatively measured by iodometric titration.⁸

Adsorption on Chromia

It was suggested some years ago that the catalytically active site in reduced, evacuated chromia is a surface Cr^{III} ion that is not coordinated to hydroxyl ("coordinatively unsaturated").⁸ Chemisorption of oxygen leads to extraction of electrons from Cr^{III} , formation of Cr^{VI} , increased (p-type) electronic conductivity, and loss of catalytic activity. From direct measurements of (a) the amount of chemisorbed or "excess" oxygen, by water extraction and iodometric titration of Cr^{VI} , and (b) total amounts of H_2 and O_2 chemisorbed on reversible cycling at 500 °C, it is possible to construct absolute oxidation-reduction levels for unsupported chromia.

This approach can be extended to chromia-alumina.⁹ Voltz and Weller chose to use the amount of excess oxygen (after O_2 treatment) to estimate the specific

(4) Although chromia was initially selected as a model catalyst only because of its electronic and chemical properties, the research surprisingly led to an improved butane dehydrogenation catalyst that saw commercial use.

(5) Voltz, S. E.; Weller, S. W. *J. Am. Chem. Soc.* **1953**, *75*, 5227.

(6) Voltz, S. E.; Weller, S. W. *J. Am. Chem. Soc.* **1953**, *75*, 5231.

(7) Voltz, S. E.; Weller, S. W. *J. Am. Chem. Soc.* **1954**, *76*, 1586.

(8) Weller, S. W.; Voltz, S. E. *J. Am. Chem. Soc.* **1954**, *76*, 4695.

(9) Voltz, S. E.; Weller, S. W. *J. Am. Chem. Soc.* **1954**, *76*, 4701.

(10) Voltz, S. E.; Weller, S. W. *J. Phys. Chem.* **1955**, *5*, 566.

(11) Voltz, S. E.; Weller, S. W. *J. Phys. Chem.* **1955**, *59*, 569.

(12) Weller, S. W.; Voltz, S. E. *Z. Phys. Chem. (Weisbaden)* **1955**, *5*, 1/2, 100.

(13) Brewer, L. *Chem. Rev.* **1953**, *53*, 1.

Table I
Chemisorption of O_2 on Cr_2O_3 - Al_2O_3 , -195 °C^a

wt % Cr	$V[\text{O}_2]$, mL/g	$S(\text{BET})$, m ² /g	$S[\text{O}_2]$, m ² /g	$S[\text{O}_2]/S(\text{BET})$
100	2.0	20		(1.0)
10.1	3.4	190	34	0.18
5.8	3.3	191	33	0.17
3.6	2.5	204	25	0.12
2.1	1.7	204	17	0.08
0	0	182	0	0

^a Data from Bridges et al.¹⁴ $V(\text{O}_2)$ = volume of O_2 chemisorbed; $S(\text{BET})$ = total surface area; $S(\text{O}_2)$ = specific chromia area, calculated from $V(\text{O}_2)$.

surface area of chromia in a supported catalyst. From measurements of excess oxygen on unsupported chromia of various total (BET) areas, an average value of 0.163 m² chromia area per μmol of excess oxygen was deduced. If the assumption is made that the surfaces of supported and unsupported chromia behave identically, this value can be used as a conversion factor to express the experimentally determined "excess oxygen" for a chromia-alumina sample as a specific area of the chromia in the sample. In this way, it was deduced that in a particular sample having 20 wt % chromia and a BET area of 50 m²/g, the specific surface area of the chromia was about 22 m²/g, or 40-45% of the total surface area.

MacIver and his co-workers extended the work on chromia in a way that lends itself to other systems as well.^{14,15} They observed that after H_2 treatment and evacuation at 500 °C, both unsupported and supported chromia chemisorb oxygen (as well as carbon monoxide) very well even at -195 °C. Again from a comparison of chromia-alumina with unsupported chromia, a calculation can be made of the apparent chromia area in chromia-alumina. As before, the assumption is necessary that the conversion factor, relating chromia area to O_2 chemisorption, is the same for unsupported and supported catalyst. Their results for chromia and for a series of chromia-aluminas with different Cr loadings are summarized, in part, in Table I. $S(\text{BET})$ is the measured total surface area, and $S(\text{O}_2)$ is the specific chromia area, calculated from O_2 chemisorption with the use of the conversion factor for unsupported chromia.

Tejuca and Pajares carried out a particularly systematic and illuminating study of oxygen adsorption on (prereduced, 500 °C and evacuated, 550 °C) unsupported chromia between -195 and +500 °C.¹⁶ Their adsorption isotherms showed asymptotic values for oxygen adsorption that were relatively close over a wide range of temperature, -78 to +300 °C. The average value was about 2.5×10^{18} molecules of O_2 adsorbed per square meter, corresponding to a chromia area per oxygen molecule of 40 Å²/ O_2 .

Oxygen Adsorption on Molybdena

Chromia is an attractive model system because of its stability to bulk-phase changes over a range of temperature and gas atmosphere. Molybdena, which is of comparable practical importance, is much more labile under redox treatments. The problem of attempting

(14) MacIver, D. S.; Tobin, H. H. *J. Phys. Chem.* **1960**, *64*, 451.

(15) Bridges, J. H.; MacIver, D. S.; Tobin, H. H. *Actes Congr. Int. Catal.* **2nd**, **1960**, **1961**, 2161.

(16) Tejuca, G.; Pajares, J. A. *An. Quim.* **1972**, *68*, 1067.

Table II
Area per Chemisorbed Oxygen

compd	temp, °C	area/ mole- cule, Å ² /O ₂	ref
Cr ₂ O ₃	500	23	Weller and Voltz ⁸
	-195	37	Bridges et al. ¹⁵
	-78 to 300	40	Tejuca and Pajares ¹⁶
MoO ₃	-195	51	Parckh and Weller ¹⁷
	-195 to -78	47	Garcia Fierro et al. ¹⁹

to determine the specific surface area of molybdena in reduced MoO₃-Al₂O₃ catalysts was addressed by Parekh and Weller.¹⁷ The approach was essentially that of Bridges et al.¹⁵: prereduction at 500 °C (350 °C for unsupported molybdena) and evacuation at 500 °C; oxygen adsorption at -195 °C, followed by evacuation at -78 °C and readsorption of oxygen at -195 °C. The (constant) difference between the first and second adsorption isotherms was taken as the amount of O₂ chemisorbed. The total area and O₂ chemisorption for unsupported molybdena were assumed to provide a meaningful calibration factor for the calculation of apparent molybdena area in alumina-supported catalysts.

Liu et al.¹⁸ next showed that O₂ chemisorption, for characterization of reduced molybdena-alumina catalysts, is done more conveniently and accurately at -78 °C than at -195 °C. The correction for physical adsorption is much smaller at -78 °C than at -195 °C. Moreover, at -78 °C a dynamic method can be used as well as the conventional static one.

The extension of O₂ chemisorption to reduced molybdena-silica catalysts was made by Garcia Fierro et al.¹⁹ These workers, using a gravimetric method, first redetermined the conversion factor relating O₂ chemisorption to molybdena area for unsupported MoO₃ of relatively high surface area (50–55 m²/g). Their factor, expressed on a volumetric basis, was quite close to that deduced by Parekh and Weller: 12.6 vs. 13.6 mL (STP) O₂ chemisorbed. Application of this factor to chemisorption data for a series of reduced MoO₃/SiO₂ catalysts, of various MoO₃ loadings (4.8 to 13.0%), led to values for equivalent molybdena area (EMA) and apparent dispersion (*D*), defined as the ratio of number of chemisorbed oxygen atoms to total number of Mo atoms in the sample. Within experimental error, the O₂ chemisorption for each sample was independent of adsorption temperature over the range 77–195 K.

It is reasonable to inquire whether this O₂ chemisorption method has an absolute significance, in terms of "titrating" every surface Cr or Mo ion (after appropriate pretreatment). The question is still moot, but several considerations of internal consistency provide a measure of reassurance:

(1) A number of workers have now published data for O₂ chemisorption and total area of unsupported chromia and molybdena. The ratio, area per chemisorbed O₂, may be examined for plausibility and internal consistency. Table II summarizes a number of such studies. The first entry (Weller and Voltz) should probably be disregarded because "excess oxygen" was employed as the measure, rather than O₂ chemisorption at low tem-

perature. The other studies, spanning some 20 years, show surprisingly similar values for the area apparently occupied by one O₂ molecule—40–50 Å²/O₂, or 20–25 Å²/O atom.

(2) Bridges et al.¹⁵ compared the chromia areas calculated from O₂ chemisorption (see Table I), for a series of chromia-aluminas with different chromia content, with the expected values if all of the chromia were present as a two-dimensional surface crystal having the structure of the undistorted (100) plane of α-Cr₂O₃. They state that at chromium contents of about 1% or less (where good dispersion is expected), the areas computed from O₂ adsorption agree quite well with the areas calculated from crystal structure. For example, at 1.1 wt % Cr, the value from O₂ chemisorption was 12 m²/g; the calculated value was 13 m²/g.

Oxygen Chemisorption on Sulfided Catalysts

Alumina-supported molybdena catalysts find use in hydrodesulfurization (HDS) processes. During operation, the molybdena becomes at least partially reduced and sulfided. One may ask whether selective chemisorption of oxygen provides a useful characterization of the sulfided catalyst.

Perhaps the first attempt to measure O₂ chemisorption on a sulfided Co/Mo/Al₂O₃ catalyst was that of Parekh.²⁰ A commercial catalyst (Harshaw 0402 T) was presulfided in flowing H₂S (15%)–H₂ for 2 h at 400 °C and then reduced (H₂) and evacuated at 500 °C before measurement of O₂ chemisorption and total (BET) surface area. The values for chemisorption and surface area were 2.5 mL of O₂ (STP)/g and 143 m²/g for the presulfided sample, as compared with 3.6 mL of O₂ (STP)/g and 178 m²/g for a reduced-only, fresh sample.

Both total surface area and oxygen chemisorption were lower for the presulfided catalyst. The lower surface area was attributed to possible blocking of micropores by MoS₂ present after sulfiding: this Harshaw catalyst has a small average pore size (ca. 60 Å average diameter), and the molar volume of MoS₂ is more than 60% greater than that of MoO₃. The lower oxygen chemisorption could have resulted for several possible reasons. The important point in the present context is the fact that the value is within a factor of 2 (actually, within 30%) of the value for reduced-only catalyst.

To proceed farther, it was necessary to prepare unsupported MoS₂ samples of reasonably high area and to measure oxygen chemisorption on such samples after some appropriate pretreatment. This was done, almost simultaneously, by two groups: Tauster and co-workers^{21,22} and Saforo.²³

Tauster et al.²¹ prepared unsupported MoS₂ of various surface areas by different chemical routes. These samples were then characterized by measurement of activity for the hydrodesulfurization of dibenzothiophene at 350 °C, total surface area, and oxygen chemisorption. Most of the samples were prepared in a conventional way: synthesis and decomposition of ammonium thiomolybdate to MoS₃, followed by heat

(20) Parekh, B. S. Ph.D. Dissertation, State University of New York, at Buffalo, 1976.

(21) Tauster, S. J.; Pecoraro, T. A.; Chianelli, R. R. *J. Catal.* 1980, 63, 515.

(22) Tauster, S. J.; Riley, K. L. *J. Catal.* 1981, 67, 250.

(23) Saforo, E. K. M.S. Thesis, State University of New York at Buffalo, Feb 1981.

(17) Parekh, B. S.; Weller, S. W. *J. Catal.* 1977, 47, 100.

(18) Liu, H.-C.; Yuan, L.; Weller, S. W. *J. Catal.* 1980, 61, 282.

(19) Garcia Fierro, J. L.; Mendioroz, S.; Pajares, J. A.; Weller, S. W. *J. Catal.* 1980, 62, 263.

Table III
O₂ Chemisorption on Unsupported MoS₂

ref	S(BET), m ² /g	O ₂ ads, μmol/g	area/ molecule, Å ² /O ₂
Tauster et al. ²¹	112	31	599
	87	27	535
	112	19	978
	108	41	437
	108	37	485
	14	31	75
	120	35	569
	23	37	103
Saforo ²³	45	123	61

treatment (under HDS conditions) to MoS₂. The samples first were tested for HDS activity, then recovered for measurement of surface area and O₂ chemisorption by a dynamic method. Pretreatment before O₂ chemisorption (but after activity testing) involved in situ treatment with 15% H₂S/H₂ at 350 °C, cooling to ambient temperature under H₂S/H₂, purging with argon for ca. 15 min, and chemisorption measurements with pulses of 10% O₂/argon.

Saforo's preparation and pretreatment differed in significant detail.²³ MoS₃ from ammonium thiomolybdate was reduced in flowing H₂ for 2 h at 400 °C and cooled in H₂. Prior to determination of oxygen chemisorption, the material was heated again in flowing hydrogen for 2 h at 350 °C, evacuated for 1 h at 350 °C, and cooled under vacuum to -78 °C for determination of oxygen chemisorption.

Table III summarizes the data of Tauster et al.²¹ and Saforo²³ for the samples prepared from ammonium thiomolybdate. Included in the table are the BET surface areas, O₂ chemisorption values, and computed area per chemisorbed O₂ molecule. The values of "area/O₂" vary over a 10-fold range for the samples studied by Tauster et al., and they tend to be quite high. For the six samples with total areas exceeding 85 m²/g, the average value for "area/O₂" was about 600 Å²/O₂ molecule. Tauster et al. interpreted their values as a measure of the edge-plane area of MoS₂, with wide variations of the edge-plane/basal-plane ratio for the different samples.

The single result reported by Saforo (Table III) leads to a much smaller value for "area/O₂", 61 Å²/O₂. Comparison with Table II shows this value to be higher than that for O₂ chemisorption on the oxides (ca. 40 Å²/O₂ for Cr₂O₃ and ca. 50 Å²/O₂ for MoO₂), but the value is reasonable in light of the larger atomic volume for Mo in MoS₂ (volume/mol = 33 mL/mol of Mo in MoS₂, 20 mL/mol of Mo in MoO₂).

The divergence between investigators shown in Table III will require further study of unsupported MoS₂. One may speculate that difference in pretreatment will prove to be the key. Tauster et al. measured area and oxygen chemisorption after an HDS experiment, when reaction products may influence the results. They also pretreated with and cooled in H₂S/H₂, purging with argon only at ambient temperature. Saforo pretreated the sulfide with H₂ and evacuated at 400 °C before cooling under vacuum to -78 °C. There may be some question also about the use of ambient temperature for O₂ chemisorption. For supported MoO₂, Parekh and Weller had noted evidence for a slow, bulk phase re-oxidation on exposure of the reduced sample to oxygen

at a temperature as low as 0 °C.¹⁷

Specific Surface Area in Supported Catalysts

The preceding discussion indicates that a series of questions arises in connection with the suitability of selective chemisorption of oxygen for characterizing the specific surface area of chromia and molybdena in supported catalysts. Some of these are the following:

1. What is being measured?
2. How sensitive is it to details of pretreatment?
3. Can unsupported catalyst be used as calibration for supported catalyst?
4. Do the results correlate with activity measurements?

Definitive answers cannot yet be given to any of these questions. As to the first, ever since the work of Bridges et al. on chromia, the author has operated on the hopeful working hypothesis that oxygen chemisorption can be a proper measure of surface Cr^{III} or Mo^{IV} ions in a properly pretreated catalyst. The careful measurements of Tejuca and Pajares on chromia and of Garcia Fierro et al. on molybdena indicates that the desired property of insensitivity to adsorption temperature and gas pressure is reasonably well-satisfied. Sulfided molybdenum catalysts require more study.

The measurement is expected to be sensitive to details of pretreatment. The result should depend on putting the transition-metal ion reliably into a known, lower valence state, and guaranteeing that the ion is free to chemisorb oxygen (i.e., be coordinatively unsaturated). With chromia catalysts, this seems to be easy: hydrogen treatment and evacuation at 500 °C are suitable. For molybdenum oxide on alumina, where interaction with the support is strong, 6–8 h of hydrogen treatment and evacuation at 500 °C appear suitable. The silica-supported material is more easily reduced and should be pretreated at 400–450 °C. Supported molybdenum sulfide is the least studied; the discrepancy between investigators noted in Table III has been tentatively attributed to significant differences in details of the catalyst pretreatment.

It is still not proven that measurements on the unsupported metal oxide or sulfide can be directly translated into an equivalent chromia or molybdena area in the supported catalysts. The dispersion values deduced by Bridges et al. for chromia on alumina at low loading (1%) are consistent with this assumption. There is, as yet, no internal inconsistency in the results reported for the dispersion of supported MoO₂ or MoS₂ that would deny one the use of this attractive approach.

The last question deals with the utility of the method: Do the results correlate with catalytic activity, as one would hope? The answer so far seems to be affirmative. For example, in the work of Tauster et al. with unsupported MoS₂, although the HDS rate constant showed almost no correlation with total surface area, the rate constant increased linearly with oxygen chemisorption value.

Another example comes from a 1980 paper of Liu and Weller,²⁴ who characterized reduced molybdena-alumina for oxygen chemisorption and cyclohexane dehydrogenation activity. For a series of catalysts containing from 4% to 15% MoO₃, the dehydrogenation activity varied smoothly with chemisorption value.

(24) Liu, H.-C.; Weller, S. W. *J. Catal.* 1980, 66, 65.

Table IV
Surface Areas of Oxidized and Reduced MoO₃/Al₂O₃^a

wt % MoO ₃	oxidized MoO ₃ /Al ₂ O ₃ , BET areas		reduced MoO ₃ /Al ₂ O ₃ , BET areas	
	m ² /g of cat.	m ² /g of Al ₂ O ₃	m ² /g of cat.	m ² /g of Al ₂ O ₃
0	144	144	144	144
3.9	136	141	142	148
7.5	137	148	147	159
11.4	128	145	146	163
14.9	124	146	141	166

^a Data from ref 24.

Table V
Nature of Mo/Al₂O₃: Amocat 1B^a

run	treatment	S(BET), m ² /g
1	fresh	165
2	reduced, 500 °C	177
3	reoxidized, 500 °C	161
4	sulfided, 500 °C	173
5	reduced, 500 °C	174
6	reoxidized, 500 °C	164

^a Data from ref 27.

Nature of Molybdena-Alumina Catalysts

There has been a consensus that MoO₃ on a high area alumina surface exists as a monolayer, provided that the areal loading does not exceed the monolayer capacity of the surface. There is much less agreement about the structure of reduced or reductively sulfided molybdena on alumina. One may inquire whether useful conclusions concerning the nature of molybdena-alumina catalysts may be drawn from simple measurements of, say, total surface area and oxygen chemisorption.

Liu and Weller²⁴ pointed out, not for the first time,^{25,26} that the addition of increasing amounts of MoO₃ should decrease the total area per gram of catalyst if the MoO₃ exists as a monolayer but should leave the area per gram of alumina essentially constant. Table IV shows some of their results for a series of samples containing up to 14.9% MoO₃, both in the oxidized (MoO₃) state and after hydrogen reduction at 500 °C. The areas for the oxidized samples are consistent with the monolayer model for MoO₃. Those for the reduced samples are not; the area per gram of alumina increases with increased loading, suggesting a contribution to the total area by very small crystallites of MoO₂ in the reduced samples. (This non-monolayer model for the reduced catalyst had been suggested by Parekh and Weller¹⁷ for other reasons.)

Tan²⁷ has extended these results by making a series of treatments on a single sample of 15% MoO₃/Al₂O₃, obtained through the courtesy of Amoco Oil Co. and termed Amocat 1B by them. Tan's data for surface areas are summarized in Table V. The reduced catalyst (run 2) showed an increase in area qualitatively similar to that reported by Liu and Weller. Run 3 confirmed a prediction: if MoO₃-Al₂O₃ interaction is responsible for the initial MoO₃ monolayer, then reoxidation of small crystallite MoO₂/Al₂O₃ should lead again to fo-

mation of the MoO₃ monolayer and to a corresponding decrease in surface area to the original value. Within experimental error, it does.

As indicated above, the structure of MoS₂ on alumina is poorly established. Run 4, Table V, suggests that reductive sulfiding of this catalyst leads to the formation of small crystallites of MoS₂ (or an oxysulfide), with no further change in area on subsequent hydrogen treatment. Finally, reoxidation of the sulfided sample, run 6, appears to result once more in a return to the monolayer MoO₃/Al₂O₃ structure.

Standardization of Catalyst Test Methods

In June 1972, the author, while on leave as a U.N. employee, was privileged to attend a UNIDO Expert Group Meeting on the subject, "Transfer of Know-how in the Production and Use of Catalysts". The meeting, held in Bucharest, had participants roughly equally from major catalyst producers and from developing countries. The author received there his first exposure to the potential acrimony between "haves" and "have-nots" in this field: representatives of developing countries insisted on not being sold "black boxes", and catalyst manufacturers clearly were unwilling to transfer their know-how in the production of catalysts.²⁸ The delicately worded final report did express a consensus that the feasibility of setting up uniform test procedures for catalyst testing should be studied. As is usual in such situations, an international committee was constituted, and the author was invited to convene this study committee (by correspondence).

Two draft reports later, it was clear that the experience had been educational but that progress might better be made on a less global scale. The first AIChE symposium on standardization of catalyst test methods was therefore organized and held in June 1974.²⁹ Walter Cropper, then Director of the Development Operations Division of ASTM, was invited to attend; later in 1974 he organized an informal meeting attended by many in the country who shared an interest in developing standardized testing methods for catalysts. The effort turned out to be a timely one, and ASTM Committee D-32 on Catalysts came into existence in January 1975. The committee membership has been international from the start; it includes representatives from Australia, Belgium, Denmark, France, The Netherlands, and the United Kingdom as well as from the U.S.

It has been clear since at least 1972 that standardized catalyst test methods in various categories would be useful. Makers and users of catalysts had developed their own methods, obviously, but there had been little effort at standardization. It was also clear in advance that it would be easier to achieve agreement in some areas of testing than in others: an innocuous measurement like BET surface area is easier to agree on than a catalytic activity test which might favor one commercial catalyst over another. Nevertheless, much progress has been made in the last few years. Between 1977 and 1980, eight standard test methods received multilaboratory comparisons and have been adopted.

(25) Giordano, N.; Bart, J. C. J.; Vaghi, A.; Castellan, A.; Marinotti, G. *J. Catal.* 1975, 36, 81.

(26) Massoth, F. E. *J. Catal.* 1977, 50, 190.

(27) Tan, H. B. M.S. Thesis, State University of New York at Buffalo, January, 1982.

(28) Dermot O'Sullivan of the *Chemical & Engineering News* London office has kindly informed the writer of a similar confrontation which occurred during the recent UNIDO-sponsored "Second Consultation on the Petrochemical Industry" in Istanbul during June 1981.

(29) Weller, S. W., Ed. *AIChE Symp. Ser.* 1974, 70, n143.

Concluding Remarks

It is generically useful to have some means of estimating the relative surface areas of the catalytically active ingredients in supported catalysts. For supported metals, the methodology for using selective chemisorption of gases for this purpose is well-developed and broadly accepted. Extension of selective chemisorption techniques to transition-metal oxides and sulfides would fill a present void.

Oxygen chemisorption at low (subambient) temperatures on prerduced chromia or molybdena appears to be a suitable method for these materials supported on alumina or silica. Comparable measurements on the unsupported oxides afford the possibility of achieving

absolute measurements of specific surface area, although questions of interpretation remain. Specific chemisorption of oxygen also appears suitable for the characterization of supported molybdenum sulfide catalysts, which are extremely important for hydro-sulfurization and coal conversion processes.

Interest in the methodology of such characterization techniques has led, during the past decade, to substantial international and national efforts to develop broadly useful, standardized test procedures. The perceived common interest of both developed and developing nations is responsible for great progress in standardized methods both in the U.S. and in Europe.

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Asymmetric Hydrogenation

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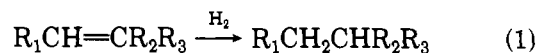
The need to resolve racemic mixtures whenever an asymmetric center is produced has long been a serious limitation to the synthetic chemist. In industry, where usually only one isomer is needed, the problem is particularly severe since resolution, with its numerous recycle loops and fractional crystallizations, is an inherently expensive process. In most cases when a large volume of an optically active substance is required, the chemist has resorted to biochemical routes even though efficient procedures to obtain the DL mixtures are often available. Specific examples are monosodium L-glutamate, L-lysine, and L-menthol, which are all manufactured by biochemical processes¹ on a large scale.

In order to beat "the bug" one needs a catalyst that, when an asymmetric center is formed, directs a reaction to give a predominance of one isomer. For this purpose the 100% efficiency achieved by enzymes would not be necessary to have something of real use. Two developments that occurred in the mid-sixties offered a very attractive approach toward making such a catalyst.

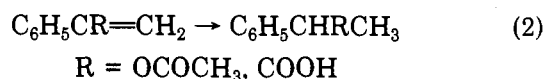
The first was the discovery by Wilkinson² of chlorotris(triphenylphosphine)rhodium, [RhCl(PPh₃)₃], and its amazing properties as a soluble hydrogenation catalyst for unhindered olefins. Homogeneous catalysts had been reported before, but this was the first one that compared in rates with the well-known heterogeneous counterparts.

The other development was the discovery of methods for preparing optically active phosphines by Horner and by Mislow.³ The basic strategy was to replace the triphenylphosphine in Wilkinson's catalyst with a known asymmetric phosphine and hydrogenate a prochiral olefin (eq 1).

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The validity of this thinking was soon verified by using the known methylpropylphenylphosphine and reducing substituted styrenes⁴ (eq 2).



A modest but definite enantiomeric excess (ee) was obtained, and the problem now became one of finding a proper match between ligand and substrate to get synthetically useful efficiencies. As it turned out, good results were achieved only with more highly functionalized substrates than the original models, though the phosphine ligand structures that work well have remained even to this day quite simple, especially if we consider that the job they are doing is usually reserved for enzymes. The best substrate is an enamide precursor of α -amino acids, which is fortunate, since if one had a choice of systems for generating asymmetry one could hardly select a more important area than these protein building blocks.

When a bis(phosphine) ligand called DiPAMP⁵ (III) complexed with rhodium was used, the asymmetric catalysis in eq 3 was accomplished in quantitative yield with an excess of the desired isomer over the ra-

(1) K. Yamada, S. Kinoshita, T. Tsunoda, and K. Aida, "The Microbial Production of Amino Acids", Wiley, New York, 1972.

(2) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(3) N. J. Gallagher and I. D. Jenkins in "Topics in Stereochemistry", Vol. 3, N. L. Allinger and E. L. Eliel, Eds., Wiley, New York, Chapter 1; W. E. McEwen, "Topics in Phosphorus Chemistry", Vol. 2, M. Grayson and E. J. Griffith, Eds., Interscience, New York, Chapter 1.

(4) (a) W. S. Knowles and M. J. Sabacky, *Chem. Commun.*, 1445 (1968). (b) L. Horner, H. Siegel, and H. Büthe, *Angew. Chem., Int. Ed. Engl.*, 7, 941 (1968).

(5) B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman, and O. J. Weinkauff, *J. Am. Chem. Soc.*, 99, 5946 (1977).