Temperature-Programmed Reduction and Oxidation of Metals Supported on γ-Alumina

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Quantitative measurements of temperature-programmed reduction and oxidation (TPR/TPO) at temperatures up to 1200°C were used to characterize 2% metal on γ-alumina catalysts. The TPR/TPO results were also compared with the redox behavior of the bulk compounds. It was found that supported Fe_2O_3, MoO_3, WO_3, and NiO could be reduced to metal only at temperatures near 1100°C. In all cases reduction of supported oxides occurred at temperatures higher than those for the bulk oxides, indicating that interaction of the metal oxides with the support inhibited reduction. However, TPO of the supported metals usually occurred at a temperature lower than those for the bulk metals. This suggests that oxidation diminishes metal–support interaction and the higher rate of oxidation of supported metals reflects their smaller crystallite size. Chemisorption data are also given for the supported oxides after reduction at both moderate and high temperatures. © 1989 Academic Press, Inc.

INTRODUCTION

It has recently been shown (*1, 2*) that catalysts of 2% metal on alumina derived from the carbonyls of Mo, W, and Fe as well as from the salts of Mo, W, Fe, Os, and Co give higher activity (by 4- to 400-fold) for benzene hydrogenation after activation in flowing H_2 at 1000°C than after activation at 400 or 600°C. However, Ni catalysts were about 5-fold less active after reduction at 1000°C. To better understand this synthesis–activity relationship, a study of the redox chemistry of these catalysts was undertaken using temperature-programmed reduction and oxidation (TPR/TPO). In addition, the redox temperatures revealed by TPR/TPO are of general use in planning catalyst syntheses. Results for Mo, W, Fe, and Ni are reported here. Usually, low-valent metals are more efficacious catalysts for hydrogenation than oxides. Thus, it was expected that very high temperatures of activation might lead to increased activity by increasing the extent of reduction for some catalysts. However, high temperatures can

also cause sintering, promote metal–support interactions, and lead to compound formation, all of which can lower activity.

Some of the catalysts studied have been previously investigated. However, in most cases these studies did not encompass the range of conditions reported here, especially reduction at very high temperatures (>1000°C), the use of a low metal loading, cycling TPR with TPO, and quantifying the amount of redox. By application of cycles of TPR and TPO, changes in a catalyst as well as the self-consistency of the data could be assessed. Also, having a number of catalysts studied by a standardized method facilitates comparisons.

EXPERIMENTAL

Materials

The catalysts were prepared by impregnation of γ-alumina (Conoco Catapal 8801K, 60–80 mesh, a_s = 203 m²/g, and average pore diameter = 7 nm after calcination at 500°C, a_s = 98 m²/g after heating at 1100°C for 1 h) with aqueous solutions of metal salts using the incipient wetness technique. After impregnation samples were dried for 24 h at 125°C, bottled, and then

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TABLE 1

TPR Results

Material[a]	Pretreatment heating in O_2	Initial color	H_2 uptake (μmole)	Metal (μmole)	ΔO.N.	Final color	Expt No.
Fe_2O_3/Al_2O_3	2 h, 460°C	Coffee brown	126.6	88.3	2.87	Bluish gray	26A
Fe_2O_3/Al_2O_3	—	Rose red	121.7	88.3	2.76	Bluish gray	26C
Fe_2O_3	1 h, 460°C	Rust brown	166.1	83.2	3.99	Dark gray	18A
Fe_2O_3	—	Rust brown	161.5	83.2	3.88	Dark gray	18C
Fe_2O_3	—	Rust brown	162.0	83.2	3.88	Dark gray	18E
MoO_3/Al_2O_3	1 h, 600°C	White	137.3	41.7	6.59	Black	2A
MoO_3/Al_2O_3	—	White	106.4	41.7	5.11	Black	2C
MoO_3	Vac., 25°C	Bluish gray	55.1	19.9	5.53	Black	1A
WO_3/Al_2O_3	1 h, 600°C	White	72.0	22.0	6.55	Bluish black	3A
WO_3	1 h, 500°C	Lemon yellow	99.5	32.8	6.10	Dark gray	7A
WO_3	—	Yellow	93.6	32.8	5.73	Black	7C
NiO/Al_2O_3	1 h, 500°C	Dirty yellow	96.1	84.2	2.28	Black	14A
NiO/Al_2O_3	—	Light blue	94.7	84.2	2.25	Black	14C
NiO/Al_2O_3	—	Light green	84.3	84.2	2.00	Black	14E
NiO	1 h, 500°C	Greenish gray	33.3	32.3	2.06	Dark gray	15A
NiO	—	Greenish gray	34.8	32.3	2.15	Dark gray	15C
NiO	—	Greenish gray	34.5	32.3	2.13	Dark gray	15E

[a] For supported metals after the preoxidation treatment these oxides are assumed to be present on the surface.

stored in a desiccator. Loadings are 2.0 ± 0.1% metal (loadings are based on the weight of support after drying at 120°C). All samples were first calcined in O_2 flowing at ~50 cc/min at temperatures given in Table 1. The samples were then evacuated for 5 min at temperature, isolated from the vacuum pump, and cooled under vacuum. Catalyst pretreatment and TPR/TPO was done using a stainless-steel reaction/gas manifold equipped with packless diaphragm valves (Matheson Co.) and without removing a catalyst from the reactor. The leak rate under vacuum was $<1 \times 10^{-7}$ cc/s and there was no oil, grease, or mercury in the system. The manifold was pumped by an Edwards Diffstak (Model 63M) with a limiting pressure of $<10^{-7}$ Torr.

The metal compounds were used without further purification. MoO_3 and $(NH_4)_6Mo_7O_{24}$ were obtained from Alfa, $Fe(NO_3)_3 \cdot 9H_2O$ and $Ni(NO_3)_2$ were obtained from Mallinckrodt, and Fe_2O_3 was obtained from J. T. Baker. The bulk metal oxides were all

fine powders. C. P. grade Ar and O_2 were used without further purification. Hydrogen was purified by passing over an oxygen purifier (Matheson gas products, Model OR-10) and then molecular sieves to remove water. Traces of oxygen and water vapor were removed from the He by passage through a Go Getter (General Electric Co.).

TPR/TPO Technique

The principles of the TPR/TPO methods have been described previously (3). For these studies mixtures of 5% H_2 in Ar and 5% O_2 in He were used. The gas flowed at 20 cc/min through the reference side of a thermal conductivity detector (Gow-Mac Model 10-952), through the catalysts, through a cold trap at −78°C (to remove H_2O formed during reduction), and then through the sample side of the detector. The reactor charge was typically 0.25 g of a supported catalyst or 8 mg of a metal oxide. Metal oxide was supported on a plug of

quartz wool inside of a 4-mm-i.d. tube of fused quartz. Catalyst was supported on a sintered frit inside of an 8-mm-i.d. reactor, all made of fused quartz. The heating rate (r) was 15°C/min. In some cases a sample was held at the maximum temperature after temperature programming. The amount of H_2 or O_2 uptake was determined by calibration immediately after a run. Several pulses of H_2 or O_2 were injected into the gas flow so as to give a peak height (with detector polarity reversed) similar to that observed during the run. The results for about three calibrations were then averaged. The results are accurate to ±5%. After a TPR or TPO, the sample was evacuated at 500°C for 5 min prior to starting the next run.

Metal dispersion was measured by CO chemisorption at 23°C using an electronic pressure transducer (Sundstrand, Model 314D). After the first isotherm the catalyst was evacuated for 5 min and then the second isotherm was measured. The dispersions are based on the net amount of chemisorption (difference between the two isotherms) at a pressure of about 200 Torr and assuming a 1:1 CO-to-metal adsorption stoichiometry. The sensitivity of the system for measuring adsorption is about 0.002 cc (STP) of gas.

RESULTS AND DISCUSSION

General

The TPR and TPO results are summarized in Tables 1 and 2, respectively. The figures show the TPR and TPO traces. The letter suffix in the experimental number indicates the TPR/TPO cycle. Thus, A, C, and E refer to the first, second, and third TPR and B, D, and F refer to the first, second, and third TPO. For additional clarity on the figures, a B in parentheses denotes a bulk powder and an S in parentheses denotes a supported catalyst.

Blank runs with pure Al_2O_3 showed a reproducible small and sharp peak at 466°C during TPR and no peak during TPO. The H_2 consumption during TPR was 0.011 cc, about 1% the value observed with a sample. Hence, no correction was made for the blank. It should be noted that peak positions are a function of the heating rate (in addition to other parameters (4, 5). An experiment with MoO_3/Al_2O_3 at r = 5°C/min shifted the TPR and TPO peaks down in temperature by about 80°C.

TABLE 2

TPO Results

Material	Initial color	O_2 uptake (μmole)	Metal (μmole)	ΔO.N.	Final color	Expt No.
Fe/Al$_2$O$_3$	Bluish gray	44.7	88.3	2.03	Rose red	26B
Fe	Dark gray	48.1	83.2	2.32	Rust brown	18B
Fe	Dark gray	48.7	83.2	2.32	Rust brown	18D
Mo/Al$_2$O$_3$	Black	60.0	41.7	5.76	White	2B
Mo/Al$_2$O$_3$	Black	44.3	41.7	4.25	White	2D
Mo	Black	30.4	19.9	6.10	Bluish gray	1B
W/Al$_2$O$_3$	Bluish black	33.6	22.0	6.10	White	3B
W	Dark gray	34.2	32.8	4.20	Lemon yellow	7B
W	Black	39.2	32.8	4.79	Yellow	7D
Ni/Al$_2$O$_3$	Black	36.0	84.2	1.71	Light blue	14B
Ni/Al$_2$O$_3$	Black	35.7	84.2	1.70	Light blue	14D
Ni	Dark gray	15.8	32.3	1.96	Greenish gray	15B
Ni	Dark gray	16.0	32.3	1.98	Greenish gray	15D

Oxidation at room temperature cannot be directly measured with this system since it can occur during the initial stabilization of the recorder baseline. However, in some cases color changes are immediately observed upon introduction of the O_2/He mixture. Also, the amount of undetected oxidation can be inferred from the following TPR if the value for the change in oxidation number (ΔO.N.) for the TPR is consistently higher than that for TPO. In general, it is expected that supported compounds should have a much smaller particle size than a bulk powder. This will favor faster reaction and hence TPR and TPO should occur at lower temperatures. Therefore, if TPR or TPO occurs at a higher temperature for a supported compound, this should indicate a metal–support interaction.

Fe

The TPR of Fe_2O_3/Al_2O_3 is shown in Fig. 1a. The first TPR profile (run 26A) shows mainly two peaks, one near 370°C and a
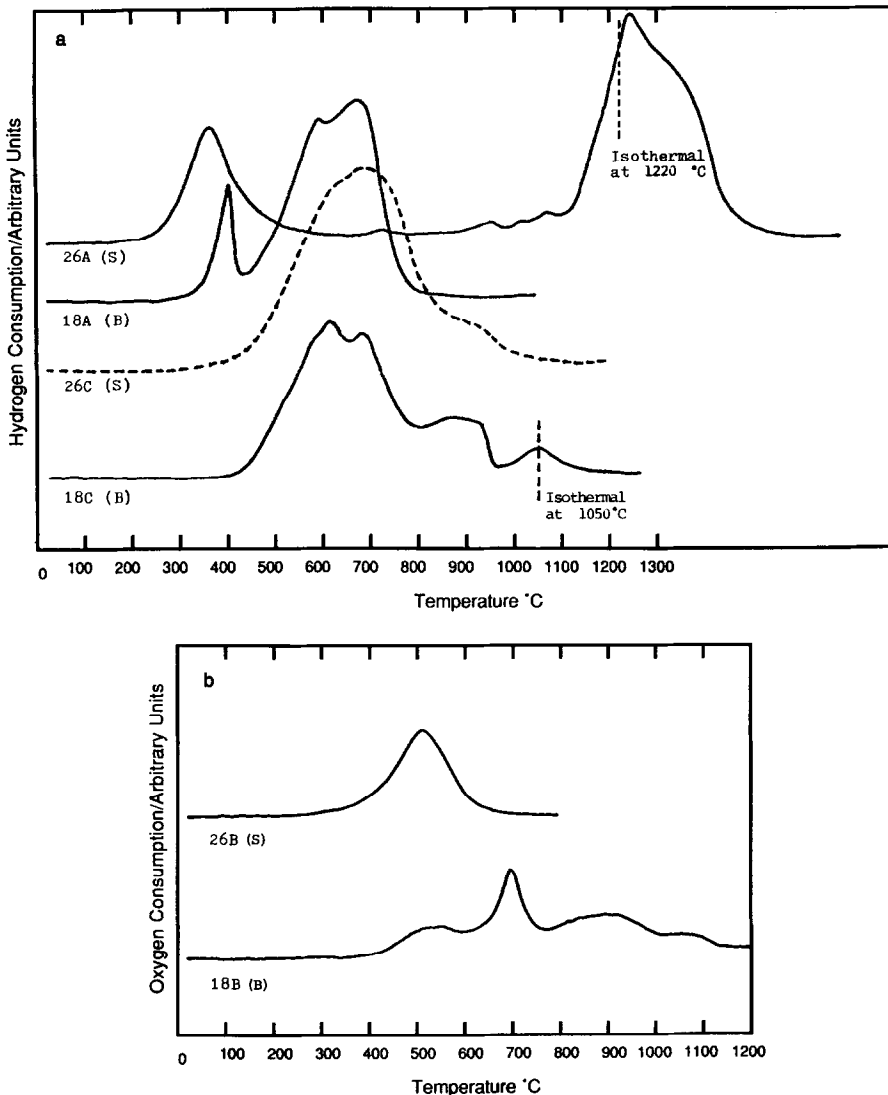
FIG. 1. (a) TPR of Fe_2O_3 and Fe_2O_3/Al_2O_3. (b) TPO of Fe and Fe/Al_2O_3.

larger peak while isothermal at 1220°C for 35 min. For the first peak, ΔO.N. = 1.0, and for the second peak, ΔO.N. = 1.9. Therefore, the reduction of fresh Fe_2O_3/Al_2O_3 to FeO takes place at moderate temperature and further reduction requires a much higher temperature. The total hydrogen consumption (ΔO.N. = 2.9) indicates complete reduction of Fe_2O_3/Al_2O_3 to Fe(0). The second TPR (run 26C) shows a large peak at 690°C and a small shoulder at 900°C. This is similar to the TPR of bulk Fe_2O_3 (runs 18A and 18C) which have their main peaks at 600 to 700°C. The H_2 consumption corresponds to ΔO.N. = 3.9, substantially larger than the theoretical value of 3.0. This is probably due to activated chemisorption of H_2. The reduction of bulk Fe_2O_3 by hydrogen proceeds through the stages $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$ (6). The second TPR of bulk Fe_2O_3 (run 18C) does not show the low-temperature peak, but has shoulders on the main peak at 900 and 1050°C. The reason for this change is unclear. These results suggest that in run 26A the Fe strongly interacted with the Al_2O_3 and this made it more difficult to reduce. However, upon heating to high temperatures the Fe sinters into large crystallites and behaves more like bulk Fe_2O_3. Fe/Al_2O_3 is known to severely sinter above 250°C (7, 8).

Several studies have been made of the reduction of Fe_2O_3/Al_2O_3 (9–12) and in all cases the oxide was only partially reduced. For example, McNicol et al. (9) found that the hydrogen consumption during TPR of a physical mixture of Fe_2O_3 and Al_2O_3 was about half that required for complete reduction. However, their upper limit of temperature was only 700°C. Garten (12) reported that at a metal loading of 0.1% Fe, Fe_2O_3/η-Al_2O_3 was reduced to Fe^{2+} only at 700°C.

The TPO of Fe/Al_2O_3 shows one peak at 510°C (Fig. 1b). The oxygen uptake was only ΔO.N. = 2.03 (Table 2). This is probably due to oxidation at room temperature since the color of the catalyst changed from bluish gray to brownish yellow immediately upon introduction of O_2 into the reactor. Moreover, hydrogen uptake of the second TPR (run 26C) was about the same as that for the first TPR. The oxidation of bulk Fe_2O_3 also has a peak near 500°C, but continues to much higher temperatures. Thus, the oxidation of supported Fe is easier than that for bulk Fe powder, but the reduction of Fe_2O_3/Al_2O_3 is harder than the reduction of the bulk oxide.

Mo

The TPR of MoO_3/Al_2O_3 are shown in Fig. 2a. The first TPR (run 2A) shows two small peaks near 580 and 700°C and a large peak at 1090°C. The low-temperature peaks yield ΔO.N. = 0.7, and complete reduction occurs while isothermal at 1100°C for 30 min (total ΔO.N. = 6.59). The second TPR (run 2C) shows only a single low-temperature peak at 540°C (ΔO.N. = 0.7) and the main reduction occurs at 1010°C. Although the shape of the TPR suggests complete reduction, the consumption of H_2 corresponds to only 85% reduction (ΔO.N. = 5.11) for the second run. This is 78% of the H_2 consumption of run 2A. It should be noted that at temperatures above about 650°C bulk MoO_3 sublimes (13). It is likely that the lower amount of reduction as well as the lower amount of oxidation for the second TPO (run 2D gives 74% of the amount of oxidation of run 2B) is due to about 24% sublimation of MoO_3 from the Al_2O_3. Such sublimation has been visually observed in other runs.

The reduction of MoO_3/Al_2O_3 has been studied by a number of workers. It is well known that at a loading of 8% Mo, MoO_3/ Al_2O_3 is almost quantitatively reduced to Mo(IV) after 1 h in H_2 at 500°C (14–17). As the loading decreases the reducibility monotonically drops, so that at a loading of 2% Mo, ΔO.N. = 0.3 (14). AT 600°C there was evidence for small amounts of Mo(III) (16). Thomas et al. (18, 19) depicted the TPR (r = 5°C/min) of bulk MoO_3 and MoO_3/ Al_2O_3 (as well as MoO_3/SiO_2) over a wide range of loadings. Although no quantitative

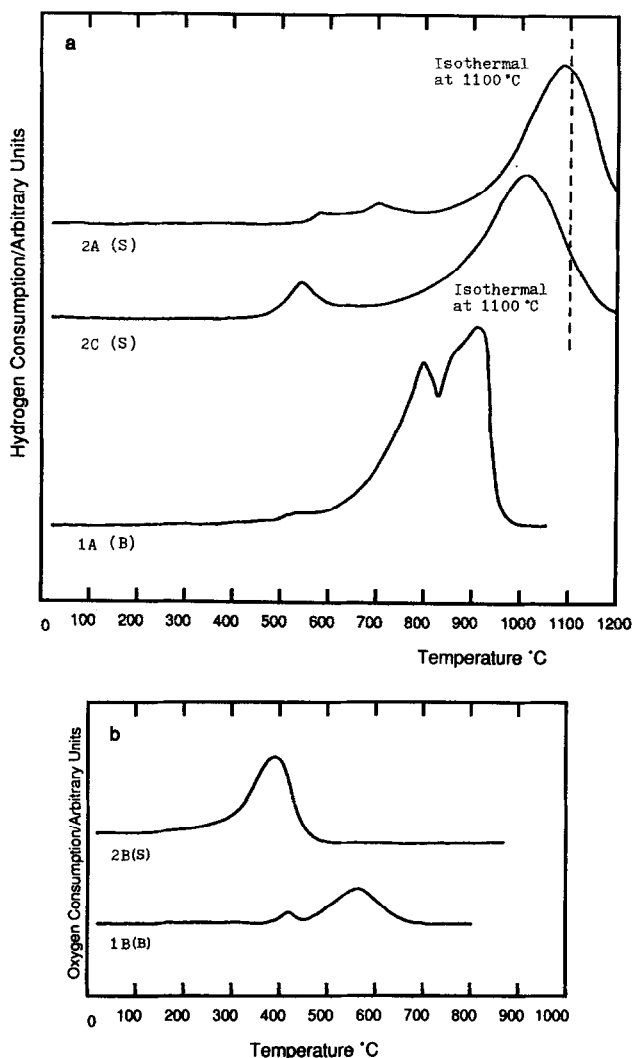FIG. 2. (a) TPR of MoO_3 and MoO_3/Al_2O_3. (b) TPO of Mo and Mo/Al_2O_3.

data were given, the forms of the TPR are close to those reported here. As the loading of MoO_3/Al_2O_3 increased from 0.4 to 20% Mo, the temperature of the high-temperature peak dropped from about 850 to 600°C. Yao (20) has also reported quantitative data for the TPR of MoO_3/Al_2O_3 (r = 10°C/min). As the loading increased from 2.9 to 10.1% Mo, the position of the high-temperature peak, corresponding to complete reduction, dropped from 830 to 730°C. Catalysts containing 1.5% Mo gave an average ΔO.N. = 5.8 after 1 h at 900°C.

The TPR of bulk MoO_3 (run 1A) shows complete reduction occurring in two steps. The two peaks are not sufficiently resolved for accurate deconvolution, but show the second step as consuming more H_2. This is in agreement with well established kinetics for the main steps of reduction in H_2: MoO_3 → MoO_2 → Mo(0) (18, 19, 21, 22). Other intermediate oxides have also been identified by XRD (23).

The TPO of MoO_3/Al_2O_3 (run 2B, Fig. 2b) shows a single peak at 390°C. This is at a temperature lower than that for the TPO of

bulk MoO_3 (run 1B). This is in contrast to the TPR of MoO_3/Al_2O_3 which, except at very high loadings (19), occurs at temperatures higher than those for bulk MoO_3. Thus, the TPR data indicate a metal–support interaction, but TPO of supported Mo is facilitated by the small crystallite size. This result is consistent with extensive studies by Hall (17). Using a variety of techniques, it was shown that MoO_3 is bonded to the Al_2O_3 surface by condensation with hydroxyl groups. However, when MoO_3/Al_2O_3 is reduced this chemical interaction is reversed and free hydroxyl groups on the alumina are regenerated (24).

During TPR/TPO to temperatures above 900°C, the γ-Al_2O_3 loses surface area and other phases (especially δ) begin to appear (25). Due to the higher free energy of the surface relative to the bulk, the surface of γ-Al_2O_3 may begin to restructure before the bulk to approximate the thermodynamically stable phase, α-Al_2O_3. Since α-Al_2O_3 is more inert than γ-Al_2O_3, it is possible that MoO_3 supported on this material would display less metal–support interaction and hence could be reduced at a lower temperature. This concept was tested by preparing MoO_3 supported on Al_2O_3 which had been dehydroxylated by evacuation at 950°C for 1 h following calcination at 500°C. $Mo(CO)_6$ was then sublimed onto the alumina and oxidized to MoO_3. This synthesis avoids the introduction of extraneous solvents and ions into the catalyst system. The TPR of this catalyst (1% Mo) was done up to a temperature of 1000°C. A modest peak was observed at 420°C and a large peak whose amplitude was increasing was observed as the temperature became isothermal at 1000°C. The total reduction was $\Delta O.N. = 1.8$. A similar catalyst prepared on Al_2O_3 which had been calcined only at 500°C showed a tiny peak at 500°C and the leading edge of another peak at 1000°C, yielding a total reduction of $\Delta O.N. = 0.4$ (this experiment can be compared to run 2A of Fig. 2a). Thus, at least in this case pretreatment of the support at high temperatures apparently

reduced the metal–support interaction and aided reducibility.

W

The TPR of WO_3/Al_2O_3 is shown in Fig. 3a. Only a single peak which occurs as the temperature becomes isothermal at 1200°C is observed. After 1 h at this temperature reduction is complete. Bulk WO_3 is completely reduced ($\Delta O.N. = 6.1$) in a two-step process (run 7A) similar to that for MoO_3. Supported WO_3 is substantially more difficult to reduce than the bulk powder, indicating a strong interaction of the metal oxide with the support. WO_3 supported on Al_2O_3 is also more difficult to reduce than its congener, MoO_3/Al_2O_3. This is also true for WO_3 and MoO_3 supported on SiO_2 (26).

Several authors have studied the reduction of WO_3/Al_2O_3, but few quantitative data are available. Biloen and Pott (27) using XPS could detect only slight reduction of WO_3/Al_2O_3 in H_2 at 550°C, even though bulk WO_3 was completely reduced under these conditions. Thomas et al. (18) reported the TPR ($r = 5$°C/min) of both WO_3 and WO_3/Al_2O_3 at loadings from 0.56 to 21.4% W. No quantitative data on the extent of reduction were given. Bulk WO_3 showed a single reduction peak at 530°C. WO_3/Al_2O_3 showed a single peak for loadings <2.9% W. This peak occurred at 1050°C at the lowest loading and shifted to about 730°C at the highest loading. For loadings >2.9% W, a small peak also appeared at about 380°C.

The TPO of supported and bulk WO_3 are shown in Fig. 3b. W/Al_2O_3 is readily oxidized back to WO_3 ($\Delta O.N. = 6.1$) with the main peak being quite broad and centered at 500°C. The broadness probably reflects heterogeneity of the supported WO_3 and may also imply interaction with the support during oxidation. The trace for bulk WO_3 (run 7B) indicates complete reduction over a relatively narrow temperature range near 500°C. However, for unknown reasons (possibly some oxidation at room temperature) the quantitative data show only
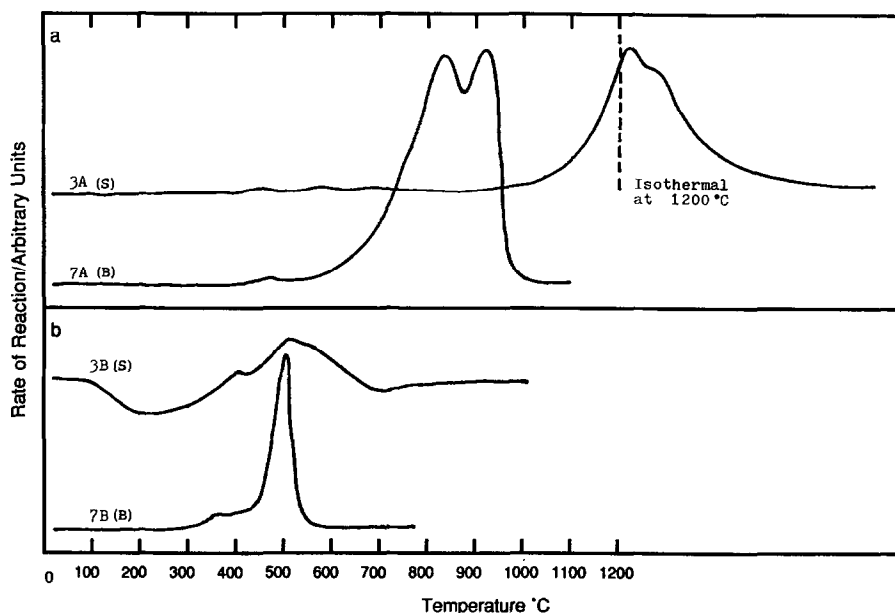
FIG. 3. (a) TPR of WO₃ and WO₃/Al₂O₃. (b) TPO of W and W/Al₂O₃.

ΔO.N. = 4.2. The following TPR (run 7C) shows ΔO.N. = 5.73, within the experimental error for the expected result of ΔO.N. = 6.0. Thus, unlike the case for Fe and Mo, supported W does not oxidize at a temperature lower than that for bulk powder.

Ni

TPR profiles for NiO/Al₂O₃ are shown in Fig. 4a. Reduction for the first TPR (run 14A) commences at about 400°C, but mostly occurs during a peak centered at 1050°C. In subsequent runs (experiments 14C, 14E) the high-temperature peak shifts to about 930°C. In all cases reduction is complete (average ΔO.N. = 2.18) and yields a black catalyst. TPR of bulk NiO (runs 15A, 15C, 15E) gave complete reduction (average ΔO.N. = 2.11) and yielded dark gray Ni. Most of the reduction occurred in a doublet peak at 380°C in the first run, but in subsequent runs the main peak shifted to 420°C and was accompanied by a small peak at 550°C. Several workers have found that NiO displays variable activation

energies during its reduction and this gives rise to local rate maxima (*28–30*). However, Robertson *et al.* (*3*) reported that the TPR of bulk NiO at a heating rate of 5°C/min yielded a single peak at 327°C. Thus, the low-temperature peaks in the TPR of NiO/Al₂O₃ are probably due to some large crystallites which behave like bulk NiO. With the exception of this material, the reduction of NiO/Al₂O₃ is considerably more difficult than the reduction of NiO powder.

A number of workers have studied Ni. Strong interaction with supports has been noted (*31–33*). The reduction of supported NiO has also been described (*3, 9, 31, 34*). At a loading of 9% Ni, NiO/Al₂O₃ is reduced to Ni(0) at 500°C (*31*). This result is not inconsistent with this study, since it is generally found that reducibility becomes more difficult as the metal loading decreases.

The first TPO of supported Ni shows oxidation occurring in two steps centered at 490 and 750°C, (run 14B, Fig. 4b), but the next TPO (run 14D) shows oxidation occurring in a single peak at 450°C. In both cases
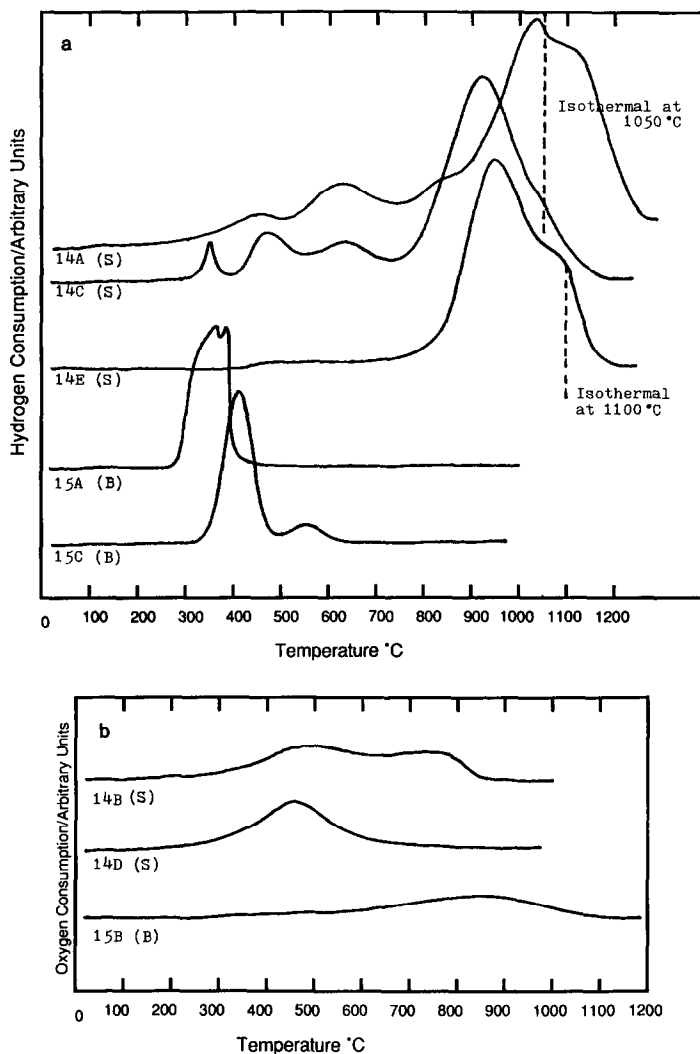
FIG. 4. (a) TPR of NiO and NiO/Al$_2$O$_3$. (b) TPO of Ni and Ni/Al$_2$O$_3$.

oxidation yields a light blue catalyst and the amount of oxidation is ΔO.N. = 1.7. This value is less than that found for TPR and indicates some oxidation at room temperature. In contrast, the TPO of bulk Ni occurs in a broad peak centered at 850°C and ΔO.N. = 2.0 (runs 15B and 15D). The product NiO is greenish gray. The unsupported Ni does not display a measurable amount of oxidation at room temperature. The more facile oxidation of supported NiO (both at room temperature and during TPR) pre-

sumably reflects a much smaller particle size than for bulk Ni.

Chemisorption Measurements

Chemisorption data are reported in Table 3. Separate experiments show that γ-alumina has a small background adsorption of CO at 23°C, about 0.04 cc (STP) per gram of alumina. Other experiments show that a compound will adsorb on some of the same sites which adsorb CO, so the background for a supported catalyst is less and difficult

TABLE 3

Chemisorption Measurement of Dispersion $(D)^a$

Metal	No background correction			With background correction		
	Reduction T (°C)		$\left(\dfrac{D_{1000}}{D_{600}}\right)$	Reduction T (°C)		$\left(\dfrac{D_{1000}}{D_{600}}\right)$
	600	100		600	100	
Mo	1.6	9.4	5.9	1.2	9.0	7.5
W	1.0	4.7	4.7	0.2	3.9	20
Fe	2.3	5.4	2.3	2.1	5.2	2.5
Ni	7.2	4.9	0.7	6.9	4.6	0.7

^{a} Samples are 2% loading on 0.500 γ-alumina; samples are different than those used for TPR/TPO. The catalysts were calcined at 500°C in flowing oxygen for 30 min and then evacuated for 5 min at 500°C prior to reduction at the indicated temperature in flowing H_2. Reduction was for 30 min at 600°C or for 1 h at 1000°C.

to exactly measure. Normally the small background adsorption can be ignored, but for catalysts of either very low loading or low dispersion, it can significantly affect the interpretation. The data in Table 3 show the dispersions as normally reported (without any background correction) and with a background correction of 0.02 cc per gram of support.

The data clearly show the expected increase in dispersion for the oxides of Mo, W, and Fe after reduction at high temperature. However, even though supported NiO is more reduced at 1000 than at 600°C, the high-temperature reduction yields a lower dispersion. Presumably additional sintering at 1000°C is more important for this catalyst than the increased reduction.

CONCLUSIONS

TPR/TPO cycles at temperatures up to 1200°C have been used to study the redox chemistry of 2% metals supported on alumina and to compare the results to the behavior of bulk compounds. Care must be taken to avoid exposure of the samples to contamination and to accurately quantify the changes in oxidation state. However, in a few cases the deviations in the expected value of ΔO.N. exceed the estimated exper-

imental accuracy of 5%. This can usually be explained by either undetected oxidation occurring at room temperature or some sublimation of an oxide during TPO. Supported Fe_2O_3, MoO_3, WO_3, and NiO are all reduced at temperatures higher than those for the bulk compounds. Since the particle size of supported materials should be much smaller than that for the bulk, this indicates strong interaction with the support. Temperatures of about 1100°C were necessary for the complete reduction of these catalysts at a heating rate of 15°C/min. Temperatures of roughly 100°C less should suffice at low heating rates or for isothermal reduction. The additional reduction at high temperatures is consistent with the large increases observed in the activity for benzene hydrogenation over supported Fe, Mo, and W. However, the dispersion and activity of supported Ni were lower after reduction at 1000°C than after reduction at 600°C. Thus, in this case sintering at high-temperatures offset the additional reduction and is the reason for the lower activity.

After the first TPR the reduction temperatures dropped for Fe, Mo, and Ni (not measured for W), also suggesting that the high temperatures induced sintering and caused the reduction profiles to become more like the bulk compounds. In all cases redox was essentially reversible since similar values for ΔO.N. were found for subsequent cycles. Both supported and bulk W oxidize in the same temperature range, but the other metals oxidize at lower temperatures when supported. This is probably due to the smaller crystallite size and suggests that support effects are less important during oxidation. TPR/TPO studies of other catalyst systems will be reported separately.

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