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Oxygen Chemisorption: Its Relationship to Hydrotreating Activity of Alumina-Supported Nickel–Molybdenum Catalysts

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Oxygen chemisorption capacities of sulfided alumina-supported Ni–Mo catalysts were determined by pulse and static adsorption methods at ambient temperatures. The pulse method resulted in lower chemisorption uptakes compared to the static method. Static to pulse uptake ratios of 2.12 to 3.03 were observed for freshly sulfided catalysts while values of 1.70 to 1.92 were obtained for catalysts which had been tested for hydrodenitrogenation (HDN) activity. A general trend of increasing O_2 chemisorption uptake with increasing activity for removal of basic nitrogen, total nitrogen, and sulfur was observed for Ni–Mo catalysts. However, because variations in the specific O_2 chemisorption capacity per activity unit among these three reactions were small (±10%), it does not appear that O_2 adsorption is selective for the active sites of any one reaction, rather, it is probably proportional to the sum of these different sites. Comparison of the O_2 adsorption capacity with the activity data (reproducibility ±3%) indicates the use of O_2 adsorption can distinguish large differences in catalyst activity (>25%) but not smaller differences.

INTRODUCTION

There has been considerable recent interest in oxygen chemisorption as a characterization tool for molybdenum-containing hydrotreating catalysts. It has been shown that O_2 chemisorption capacity correlates with the activity of these catalysts for propylene hydrogenation (*1*), CO hydrogenation (*2*), and thiophene or dibenzothiophene hydrodesulfurization (*3–7*). Moreover, these comparisons appear to be valid for a variety of Mo-containing catalysts including reduced-oxidic Mo/γ-Al_2O_3 (*1*), unsupported MoS_2 (*2, 3*), coked, sulfided Ni–Mo/γ-Al_2O_3 (*4*), Co–Mo/γ-Al_2O_3 (*5*), and Ni–Mo (*5, 7*). Only two exceptions have been reported. Massoth *et al.* (*8*) reported that the correlation of O_2 uptake with thiophene HDS activity of Co–Mo catalysts was only fair; Burch *et al.* (*9*) found no correlation between oxygen uptake and activity of sulfided Ni–Mo catalysts. The lack of correlation in these two cases was explained by a lack of selectivity of oxygen adsorption for the active sites.

This paper reports the results of an investigation into the use of O_2 chemisorption as a tool for measuring active site concentrations of hydrodenitrogenation (HDN) catalysts and compares two techniques (static and dynamic). Comparisons of activity for removal of total nitrogen, basic nitrogen, and sulfur were made with O_2 chemisorption, thus providing a more detailed breakdown of the HDN process than before.

EXPERIMENTAL

Catalysts

The catalysts studied here were prepared by impregnating to incipient wetness a γ-Al_2O_3 extrudate (270 m^2/g) with solutions containing Mo and Ni in aqueous H_3PO_4. A complete description of the preparative

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methods is available in the literature (*23–26*).

Activity Measurements

Activities of the presulfided catalysts were determined in a bench-scale reactor operated at 370°C, 1400 psig H_2 (10.2 mPa), a LHSV of 2, and a H_2/oil ratio of 6000 SCF/bbl. The feedstock used was a California mixed gas oil containing 1875 ppm total nitrogen, 600 ppm basic nitrogen, and 1.3 wt% sulfur with a boiling point range of 150 to 425°C (API gravity of 24.6). The total and basic nitrogen activities were determined as first-order rate constants while the sulfur activity was determined in terms of the $\frac{3}{2}$-order rate constant after 60 h of testing.

O_2 Chemisorption Measurements

Two methods for measuring O_2 chemisorption were investigated: (i) static volumetric adsorption and (ii) dynamic pulse-flow adsorption (*3, 7*). The static adsorption measurements were carried out in a standard Pyrex BET system at ambient temperature as described previously (*2, 7, 10, 11*) while the dynamic, pulse-flow adsorption measurements were determined using a Quantasorb flow adsorption apparatus at 25°C using standard techniques (*3, 7*).

The catalysts were either presulfided *ex situ*, passivated,[3] and reduced *in situ* at 350°C in 60 cm^3/min flowing H_2 for 1 h or presulfided *in situ* with 10% H_2S in H_2 at 350°C for 4 h. Prior to determining the adsorption capacities reduced and sulfided catalysts were cooled to 25°C in H_2S/H_2 and evacuated (static) or purged (dynamic) in He for 15–20 min.

RESULTS

Static oxygen chemisorptions were measured on presulfided Al_2O_3, Ni/Al_2O_3, and Mo/Al_2O_3 catalysts which were constituents of the catalysts used in this study. These data are presented in Table 1. The chemisorption uptake by the alumina base used for the catalysts in this study can be accounted for by the presence of 1.5% Mo which was added in its preparation. Catalyst G which has a Mo content similar to other catalysts in this study (but contains no Ni) chemisorbs ~$\frac{1}{3}$ the quantity of O_2 [compare Table 1(G) and Table 2(D)] as catalysts which contain both Ni and Mo. The O/Mo ratio of Catalyst G is 0.34 whereas the Ni/γ-Al_2O_3 has an O/Ni ratio of 1.5.

Oxygen chemisorption uptakes of presulfided, prereduced Ni–Mo catalysts, determined by either the static, volumetric, or pulse-flow techniques are listed in Table 2. The amount of chemisorbed O_2 measured by the static method is 2–3 times larger than that measured by the pulse-flow method.

Oxygen chemisorption capacities of presulfided, passivated, and *in situ*-reduced catalysts are compared with those of *in situ*-sulfided catalysts in Table 3. These data were obtained using the static method. It is evident that within experimental error, there are no differences in the chemisorption capacities for presulfided, reduced,

TABLE 1

Oxygen Chemisorption on Catalysts which Represent the Constituent Parts of the HDN Catalysts Used in This Study

Chemisorption Uptake (μmol/g)	
Catalyst[a]	Static[b]
F(Ni/Al_2O_3)[c]	355
G(Mo/Al_2O_3)[d]	212
H(Al_2O_3)	21

[a] Catalysts were presulfided prior to the chemisorption measurement as described in the Experimental section.

[b] See Table 2, footnote (*a*), for details.

[c] NiO/Al_2O_3 3.5 wt%.

[d] MoO_3 18 wt%; P/Al_2O_3 3 wt%.

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[3] The term "passivated" refers to a controlled exposure to air resulting in adsorption of O_2 on the surface layer.

TABLE 2

Comparison of Oxygen Chemisorption Uptakes on Presulfided, Reduced Ni–Mo/Al_2O_3 Catalysts Measured by Pulse and Static Techniques

Catalyst	Chemisorption (μmol/g)		Ratio Static/Pulse
	Static[a]	Pulse[b]	
C(Ni–Mo)	380	179	2.12
D(Ni–Mo)	644	242	2.66
E(Ni–Mo)	635	209	3.03

[a] Measurements carried out at ambient temperature, nominally 23°C. Chemisorption determined by extrapolating the isotherm back to zero pressure.

[b] Measurements carried out at 23°C.

TABLE 4

Comparison of the Oxygen Chemisorption Capacities of Used[a] Ni–Mo/Al_2O_3 Catalysts Measured by Static and Pulse Techniques

Catalyst	Chemisorption (μmol/g)		Ratio Static/Pulse
	Static[b]	Pulse[b]	
C(Ni–Mo)	226	123	1.85
D(Ni–Mo)	260	153	1.70
E(Ni–Mo)	295	153	1.92

[a] The term "Used" refers here to catalysts which have been presulfided with 10% H_2S/H_2 and tested for HDN activity as described in the Experimental section.

[b] The same conditions and methods as described in the footnotes of Table 2.

and sulfided catalysts of a fixed composition.

Oxygen chemisorption capacities of used, sulfided Ni–Mo/Al_2O_3 catalysts measured by static and pulse-flow techniques are listed in Table 4. The presence of "coke" apparently lowers O_2 adsorptions obtained by both methods but has had a greater effect on the adsorption obtained by the static method. Thus, ratios of the oxygen chemisorptions by the static and pulse techniques on catalysts which had been used in a HDN reaction for 80–100 h (1.70–1.92) are lower than obtained on freshly reduced samples (compare data in Table 4 with those in Table 2). The observation of a lower oxygen capacity after reaction finds disagreement with the data of Massoth *et al.* (*8*) but is in agreement with the observations of Tauster and Riley (*4*).

Relative catalytic activities of Mo-containing catalysts were determined for the removal of basic nitrogen, total nitrogen, and sulfur. These data along with average activities are listed in Table 5. The range in catalytic activities for catalysts which contain Ni and Mo is twofold at a nominal 90% conversion of total nitrogen. Catalyst G,

TABLE 3

Oxygen Chemisorption Capacities of Presulfided, Reduced,[a] and Sulfided[a] Ni–Mo/Al_2O_3 and Mo/Al_2O_3 Catalysts Determined by the Static Technique

Catalyst	Chemisorption (μmol/g)[b]		Ratio Reduced/Sulfided
	Reduced[a]	Sulfided[a]	
A(Ni–Mo)	358	327	1.09
D(Ni–Mo)	644	634	1.01
E(Ni–Mo)	635	651	0.98
G(Mo)	214	212	1.01

[a] *In situ.*

[b] Measurements carried out at ambient temperature, nominally 23°C. Chemisorption determined by extrapolating the linear portion of the isotherm back to zero pressure.

TABLE 5

Relative Catalyst Activities[a]

Catalyst	Average[b]	Relative weight activity (%)		
		Basic nitrogen	Total nitrogen	Sulfur
A(Ni–Mo)	100	100	100	100
B(Ni–Mo)	125	138	133	103
C(Ni–Mo)	137	152	141	117
D(Ni–Mo)	158	177	164	132
E(Ni–Mo)	191	206	190	177
F(Ni)		Not Determined		
G(Mo)	41	45	46	32
H(Al_2O_3)	0	0	0	0

[a] See the Experimental section for details of the activity measurements.

[b] Average represents relative ranking of overall hydrotreating effectiveness.

which contains no Ni, is one-half to one-quarter the activity of the Ni-containing preparations.

Activity and chemisorption data are compared in Table 6 on the basis of the amount of chemisorption (μmol O_2/g) per relative activity for each catalyst function. The value for Catalyst G (Mo/Al_2O_3) which contains no Ni is substantially out of line with those containing both Ni and Mo. The most reliable data (as indicated by the percentage of the average that the standard deviation represents) is that obtained on used catalysts with the static technique. The deviation for sulfur removal is, in all cases, larger than that found for removal of nitrogen. This is likely due to the nature of the HDN test in which sulfur conversions were in excess of 99%. Based on the data obtained by the static technique, the use of presulfided catalysts decreases the error by a factor of about two over that for reduced catalysts for HDN. However, catalyst pretreatment and adsorption technique apparently have little or no effect on the observed errors for fresh catalysts in HDS, while in the case of used catalysts the static method is the most reliable by a factor of 2 to 3.

Linear least-square fits of the HDS and HDN activity data with the oxygen chemisorption data (by both methods) provided correlation coefficients which exceeded 0.9 and were more generally in the range of 0.95 to 0.99.

DISCUSSION

Relationship between Activity and O_2 Uptake

The data obtained in this study show a trend of increasing activity with increasing oxygen uptake of Ni–Mo/Al_2O_3 catalysts (see Tables 1–4 and 6). This trend is evident for both presulfided/reduced, and sulfided catalysts as well as fresh and used catalysts. This trend is observed using both static and pulse-flow techniques for measuring O_2 adsorption capacities. Moreover, oxygen uptake correlates with the activity of these catalysts for removal of basic nitrogen, total nitrogen, and sulfur. However, based on the variations in the ratio of activity to adsorption capacity (Table 6), the correlation of static adsorption for the used (sulfided) catalysts with activity for nitrogen removal is apparently the most reliable. Since the activity data reported here are valid after 60 h of testing and correspond to the performance of partially coked, "lined-out" catalysts, it is logical that the best correlation is obtained for adsorption on the used catalysts. Tauster and Riley (*4*) also observed a correlation between activity and O_2 uptake of used catalysts.

Measurement of Oxygen Adsorption Capacity: Static versus Pulse-Flow

While the correlation of activity and oxygen uptake is observed using either adsorption method, the amount of oxygen uptake by the static technique is 2–3 times that obtained by the pulse-flow technique for fresh catalysts and 1.7–1.9 times larger for used catalysts. This discrepancy suggests two possibilities: either (i) the surface and bulk layers of the reduced or sulfided catalysts are oxidized during the static measurements or (ii) the pulse-flow measurements are kinetically limited.

The possibility that surface and/or bulk oxidation occurred was investigated by placing a thermocouple in contact with a 1.0-g catalyst bed while the catalyst was thermostated at 25.1°C in a water bath. Exposure to 100 Torr of O_2 caused the catalyst temperature to rise to 45.4°C. Following this increment, the temperature slowly returned to its initial point. This highly exothermic reaction suggests that oxidation of the bulk and surface layers occurred at 25°C. Observations from other studies (*8b*, *10*, *12*) indicate that oxidation of the catalyst probably occurred under these conditions. For example, Weller and Parekh (*10*) observed that the chemisorption of O_2 on reduced Mo/Al_2O_3 decreased with increasing temperature up to about −78°C; however, above −78°C the chemisorption up-

TABLE 6

Oxygen Chemisorption (μmol/g) per Relative Activity Unit on Equal Weight Basis[a]

Catalyst	Sulfided static			Reduced pulse			Reduced static			Used static			Used pulse		
	Bn[b]	TN[c]	S[d]	BN	TN	S	BN	TN	S	BN	TN	S	BN	TN	S
A	3.27	3.27	3.27				3.58	3.58	3.58						
C				1.18	1.27	1.53	2.50	2.70	3.25	1.48	1.60	1.93	0.81	0.87	1.05
D	3.58	3.86	4.80	1.36	1.47	1.83	3.64	3.93	4.88	1.47	1.58	1.97	0.86	0.93	1.16
E	3.16	3.42	3.68	1.01	1.10	1.18	3.08	3.34	3.59	1.43	1.55	1.67	0.74	0.80	0.86
G	4.71	4.61	6.62				4.75	4.65	6.68						
Ave.[a]	3.33	3.51	3.91	1.18	1.23	1.51	3.20	3.39	3.82	1.46	1.58	1.85	0.80	0.87	1.02
σ	0.22	0.31	0.79	0.18	0.17	0.32	0.53	0.52	0.71	0.03	0.03	0.16	0.06	0.06	0.15
% Dev. from ave.	6.6	8.8	20.2	15.2	13.8	21.2	16.6	15.3	18.8	2.0	1.9	8.6	7.5	6.9	14.7

[a] Values do not include Catalyst G which is a different composition (no Ni) and thus does not provide a good activity comparison with O_2 chemisorption to catalysts with Ni; in effect the comparison developed is the best possible.

[b] Removal of basic nitrogen.

[c] Removal of total nitrogen.

[d] Removal of sulfur.

take increased with increasing temperature. This latter behavior was attributed to reoxidation of the reduced catalyst. Zmierczak *et al.* (*8b*) observed a large, fast oxygen uptake followed by a slow continued oxygen uptake of Co–Mo/Al_2O_3 catalysts at room temperature which they attributed to oxidation of the sulfided phases. Bodrero and Bartholomew (*12*) also observed a significantly larger oxygen chemisorption capacity of MoS_2 at 25°C compared to −78°C. It appears that surface and/or bulk oxidation could account, at least in part, for the differences in the chemisorptions observed for static and pulse-flow methods. The lower static-to-pulse ratio of chemisorption in the case of used catalysts has interesting implications in light of the previous arguments. That is, the coking process may involve adsorption of hydrocarbon species on the most easily oxidizable sites, thereby decreasing the static chemisorption capacity more than the pulse chemisorption uptake.

The Nature of Sites Measured by Oxygen Chemisorption

The selectivity of oxygen chemisorption for specific sites (e.g., hydrogenation, nitrogen removal, sulfur removal sites) on the molybdenum sulfided surface has been the subject of considerable, recent controversy (*2, 3, 6–9, 13, 14*). Based on their correlation of HDS activity with oxygen adsorption and a previous single-crystal study by Bahl (*15*), Tauster *et al.* (*3, 14*) claimed oxygen adsorbs selectively on the edge sites which they considered to be active for HDS. Stevens and Edmonds (*6*), however, argued that HDS occurs on the basal planes and therefore oxygen does not adsorb selectively on the edge sites. Good correlations have been reported for O_2 chemisorption with hexane hydrogenation (*8b*) (sulfided Co–Mo/γ-Al_2O_3) and CO hydrogenation (*2*) (MoS_2). These workers (*2, 8b*) concluded that since O_2 adsorption correlates with both hydrogenation and HDS activity, it is selective for neither hydrogenation nor HDS sites, but rather measures both kinds of sites, and is therefore a measure of the dispersion of the sulfided Mo phase. Nevertheless, it has been shown that oxygen adsorbs only on 5 to 10% of Mo-containing surfaces (*1, 2*).

The results of this study showing correlations between oxygen chemisorption and activity for removal of nitrogen and sulfur combined with the results from previous work showing correlations with hydrogenation activity suggest that either oxygen measures all of the different kinds of active sites or that the active sites have a common characteristic.

Two observations provide some insight into the nature of the sites measured by oxygen chemisorption. First, the oxygen chemisorbed by careful exposure to air at room temperature can be removed by H_2 reduction at 350°C to reproduce the adsorption capacity of the *in situ*-sulfided catalyst. Second, the O/Ni and O/Mo ratios observed here vary significantly with the type of catalyst, i.e., Ni/Al_2O_3. Jung *et al.* (*19*) and Hall (*27*) have shown O_2 and NO adsorb on the same sites. Furthermore, it has been shown that these sites contain multiple coordinative unsaturation (*20–22*). Thus one can speculate that the presence of Ni in a Mo catalyst has the effect of increasing the coordinative unsaturation.

The fact that good correlations of oxygen adsorption and HDN/HDS activity were observed in this study suggests that a single sulfide phase of high activity was predominant or that the relative proportions of different phases were constant among the different Ni–Mo catalysts in this study. The considerable previous literature dealing with Ni–Mo and Co–Mo catalysts teaches that the relative proportions of different catalytic phases vary with preparation. Thus, the lack of correlation of oxygen adsorption versus HDS activity reported by Burch and Collins (*9*) for a series of industrial Ni–Mo/Al_2O_3 catalysts and the relatively poor correlation observed by Zmierczak *et al.* (*8b*) for a series of experimental and industrial Co–Mo/Al_2O_3 catalysts may be explained by the variety of preparations and hence proportions of different sulfide phases.

Lastly, although oxygen adsorption clearly correlates with activity, the correlations are not sufficiently reliable to differentiate catalytic activity on catalysts whose activity difference is less than about 15–25%. However, as a rough screening tool the oxygen adsorption capacity can distinguish between catalysts which have activity differences greater than about 15–25%. The error-bar range of 15–25% is arrived at by summing the errors of O_2 chemisorption (±10%) and the activity tests (±3%, determined by long term use of the test over ~10 years).

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