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Specific Surface Area of Reduced Molybdena: O_2 Chemisorption at $-78°C$

A method for determining the "equivalent molybdena area" in reduced, supported catalysts, based on O_2 chemisorption at $-195°C$, has been previously suggested (*1*). This technique has been used subsequently in studies of the sintering of $Co/Mo/Al_2O_3$ and of "shell" Mo/Al_2O_3 catalysts (*2*, *3*). It is the purpose of this note to point out that the determination may be done more conveniently and accurately at $-78°C$ than at $-195°C$ (with the same results), and that a dynamic method can be used as well as the conventional, static one.

EXPERIMENTAL METHODS

Equipment. The glass system previously used for adsorption measurements and pretreatments at 500°C. has been described (*1*). The dynamic measurements of O_2 chemisorption were made with an Isorpta Analyzer, Type IIIA, manufactured by Engelhard Industries. In this apparatus, adsorption is measured from the concentration difference of a 1.5% O_2–98.5% He mixture between the sample side and the reference side of a differential thermal conductivity cell. The catalyst sample is contained in a stainless-steel U tube which can be heated or cooled while any desired gas is flowing through it. During adsorption measurements, varying partial pressures of the gas to be adsorbed (in this case, O_2) are obtained by step changes in total pressure of a single premixed gas (in this case, 1.5% O_2–He) from a cylinder of known composition.

Materials. Two catalyst samples were studied. One was a commercial CoO (3%)–MoO_3 (15%)–Al_2O_3 catalyst (Harshaw 0402T). The other was a sample of MoO_3 (15%)–Al_2O_3, laboratory prepared by impregnation of alumina pellets (Houdry 200S) with aqueous ammonium molybdate ("no excess solution" technique), drying at 110°C (4 hr), and calcination at 500°C (12 hr).

Pretreatment. The "standard" pretreatment involved reduction in flowing H_2 for 6 hr at 500°C; in one case (Run 3b, Table 1) the pre-reduction between O_2 chemisorption runs was carried out for only 1 hr at 500°C. The reduction was followed by 1 hr of evacuation in the glass system, or by 1 hr in flowing He (100 cm^3/min) in the Isorpta apparatus.

Determination of O_2 chemisorption. As described in (*1*), after temperature equilibration is reached at either -195 or $-78°C$, the "first" O_2 isotherm is determined. The sample is then either (a) evacuated for 1 hr at $-78°C$ in the static apparatus, or (b) flushed with flowing He for 1 hr at $-78°C$ in the dynamic system. The "second" isotherm is then determined at the chosen adsorption temperature (-195 or $-78°C$). The value of the "volume of O_2 chemisorbed" is determined as the difference between the (parallel) "first" and "second" isotherms.

RESULTS

The results for O_2 chemisorption in the static apparatus are summarized in Table 1 and illustrated, for Runs 1 and 2, in Figs. 1 and 2. Results in the Isorpta apparatus for the $CoO–MoO_3–Al_2O_3$ catalyst are illustrated in Fig. 3 for triplicate runs made at $-78°C$.

As Figs. 1 and 2 show for the static system, the isotherms for the $Co/Mo/Al_2O_3$ sample are nicely parallel at either -195 or $-78°C$; the values for O_2 chemisorbed, taken as the difference between "first" and "second" isotherms, are quite close (see Table 1). At $-195°C$, however, the correction for physical adsorption ("second" isotherm) is 10–15 times the

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TABLE 1

O_2 Chemisorption in Static, High-Vacuum System

Run No.	Sample		Pretreatment[a] (hr)	O_2 chemisorption[b,c]	
	Identity	Weight (g)		T (°C)	Volume adsorbed [ml(STP)/g]
1	$Co/Mo/Al_2O_3$	1.44	6	−195	4.0
2	$Co/Mo/Al_2O_3$	1.48	6	−78	4.0
3a	Mo/Al_2O_3	3.52	6	−78	1.4
3b	Mo/Al_2O_3	3.52	1	−78	0.8
3c	Mo/Al_2O_3	3.52	6	−195	1.5

[a] Reduced in flowing H_2 at 500°C for time indicated, evacuated 1 hr at 500°C, cooled to test temperature.

[b] O_2 pressure range 1–5 cm Hg at −195°C, 10–40 cm Hg at −78°C. See Figs. 1 and 2.

[c] O_2 chemisorption of 1 ml (STP) corresponds to 44.6 μm O_2. An O_2 chemisorption value of 1.4 ml/g (e.g.) for a 15% MoO_3/Al_2O_3 catalyst would represent an O/Mo atom ratio of 0.12.

chemisorption value (see Fig. 1), a situation conducive to error. By contrast, the correction for physical adsorption is quite small at −78°C (see Fig. 2), and the value deduced for O_2 chemisorption is much better defined. Comparable results were observed for Runs 3a and c, Table 1 (graphs not shown), for the Mo/Al_2O_3 sample, and again the values of O_2 chemisorption at −195 and −78°C are very close. Run 3b, Table 1, confirms the known result that H_2 reduction, even at 500°C, is slow; pretreatment for 1 hr instead of 6 hr results in a notable decrease in the following O_2 chemisorption.

The dynamic method for O_2 adsorption gives almost identical results. The two adsorption isotherms can be measured at −195°C, but the equilibration rates are so slow for the "first" isotherm (>20 min per point to reach the baseline again) that this temperature is not a convenient one. At

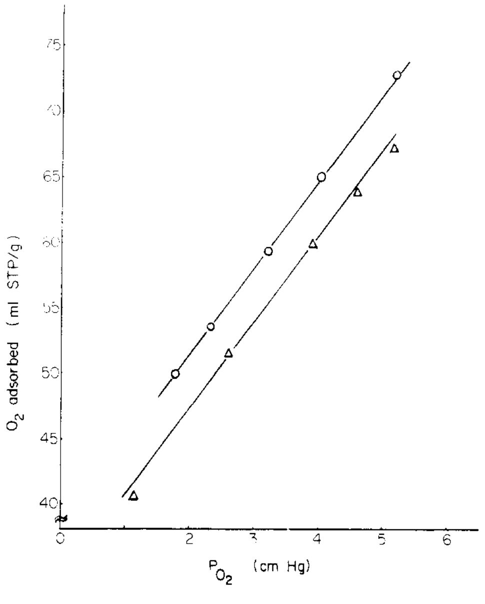

FIG. 1. O_2 adsorption at −195°C, $Co/Mo/Al_2O_3$, static method. ○, O_2 adsorption at −195°C, pump 1 hr at −78°C. △, O_2 adsorption at −195°C.

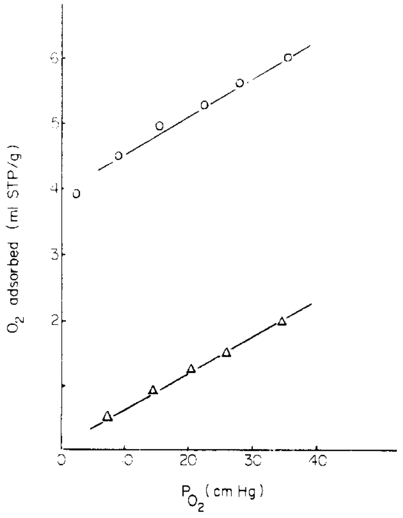

FIG. 2. O_2 adsorption at −78°C, $Co/Mo/Al_2O_3$, static method. ○, O_2 adsorption at −78°C, pump 1 hr at −78°C. △, O_2 adsorption at −78°C.

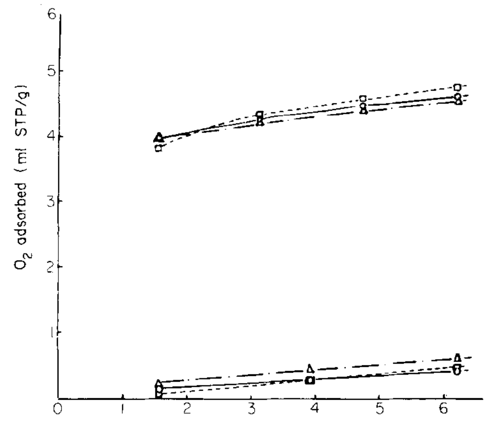

FIG. 3. O_2 adsorption at −78°C, $Co/Mo/Al_2O_3$, dynamic method. O——O, First run: fresh pre-reduced catalyst, sample 1. △——△, Second run: 6-hr reduction at 500°C after first run. □---□, Third run: fresh pre-reduced catalyst, sample 2.

−78°C, by contrast, adsorption equilibration is relatively rapid, and it is easy to trace the two isotherms. Figure 3 is a superposition of three runs with the Isorpta Analyzer showing the agreement obtained for "first" and "second" isotherms with two samples of the $Co/Mo/Al_2O_3$ catalyst. The first run was on fresh pre-reduced catalyst; the second run was with the same sample after intermediate re-reduction at 500°C for 6 hr following the first O_2 chemisorption at −78°C. The third run was on a second sample of fresh pre-reduced catalyst. The reproducibility is good, and the value of O_2 chemisorption, 4.0–4.1 ml STP/g, is very close to the value of 4.0 ml STP/g listed in Table 1 for the static system.

If O_2 chemisorption on a pre-reduced, supported molybdena catalyst is to be used as a measure of the molybdena area, it is recommended that the chemisorption (and the intermediate evacuation or flushing) be carried out at −78°C rather than −195°C. Either a static or dynamic system may be used with equivalent results.

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