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NOTES

Use of Pulsed Reduction to Estimate the Active Surface of Supported Metal Oxides

The specific surface area of metals on metal oxide supports has been the subject of numerous investigations, as pointed out by Boudart *et al.* (*1*). For example, the specific area of platinum metal on an alumina support may be determined by adsorption of hydrogen or carbon monoxide. The information on specific surface area is needed particularly in the evaluation of a series of catalysts which have the same or similar composition, but give different catalytic performance. An analogous need arises in the case of supported metal oxides, wherein one would like to know the specific active surface area, as well as the total surface area of the catalyst in question. Methods for some supported oxides have been evolved such as that for chromium oxide on alumina, silica, and silica-alumina (*2*). However, no general method has been reported for reducible metal oxides on irreducible supports. The preliminary results on pulsed reduction of metal oxides, reported below, indicate that this technique may be of general use for estimating the active areas of reducible oxides on irreducible supports.

EXPERIMENTAL

A chromatograph was modified such that a catalyst sample [0.5–2.0 g] replaced the usual chromatographic packing in the column. The flow path was changed so that the column was exterior to the chromatograph oven and was submerged in a fluidized-sand bath operable up to 600°C. An exterior four-way valve was installed between the chromatograph and the catalyst sample; in one position, hydrogen was vented and the helium carrier gas passed over the sample; in the other valve position, the helium carrier gas was vented and pure hydrogen passed over the catalyst. The flows were preset so that the exit flow rates of hydrogen and helium though the chromatograph were about equal during the tests. This meant that only a fraction of the hydrogen fed reacted with the catalyst, and the partial pressure and flow rate of hydrogen were essentially constant during the pulsed injections.

The hydrogen was switched into the flow circuit for a measured amount of time, then helium switched back in. The amount of reduction that took place was measured by injection of a series of 1-cc or 2-cc slugs of oxygen with a syringe. These were injected through the rubber septum in the injection port of the chromatograph oven. As the catalyst became reoxidized, the recorded peak areas of oxygen reached a plateau and stayed constant. The missing peak areas from the earlier injections then gave a measure of oxygen used for reoxidation. The volume of oxygen used was plotted against various hydrogen injection times.

The catalysts were prepared from reagent grade bismuth nitrate and ammonium molybdate. The silica support was derived from a commercial silica sol. For the unsupported catalysts, proper amounts of the bismuth and molybdenum salts were dissolved in water, precipitated with NH_4OH, filtered, dried, and calcined at 500°C in air. For the supported catalysts, the same salts and silica sol were coprecipitated with ammonia, and given the same finishing treatment as the unsupported catalysts. The two supported catalysts contained by calculation 35% Bi_2O_3 and 50% [$MoO_3 + Bi_2O_3$]; the atomic ratio of Mo/Bi in the latter catalyst was 1.3/1. The silica sol used produces a silica gel with a specific surface are of about 200 m^2/g. The unsupported bismuth oxide and bismuth molybdate both had specific surface areas of about 1.6 m^2/g as determined by nitrogen adsorption isotherms and the BET equation.

RESULTS AND DISCUSSION

The data on pulsed reduction of bismuth molybdate are shown in Figs. 1 and 2; the slopes of the lines are directly proportional to rates of reduction. The initial induction period in the reduction rate has been observed by a number of experimenters (*3*). In Fig. 2 the initial reduction rates were probably not linear as shown, but the linear plots served as a useful approximation. After the induction period, a constant rate of reduction was temporarily achieved at 500°C, as shown by the (upper) linear parts of the plots. As the two figures show, the volume of oxygen used per unit of catalyst weight at the transition point was roughly independent of particle size, flow rate, and sample size. This volume of oxygen corresponded to about 0.54 cc STP/m^2 or 3×10^{15} oxygen atoms/cm^2 of surface for the unsupported bismuth molybdate, based on the BET surface area of the catalyst; this is a reasonable number for the first layer of oxygen in the various phases and crystal planes of bismuth molybdate. It was tentatively postulated that the steady state rate was achieved after removal of the first layer of oxygen atoms. A possible explanation for the induction period and the subsequent constant reduction rate is as follows. It may be that the reduction rate is limited by hydrogen adsorption until the first layer of oxygen is removed. Removal of the first layer of oxygen would increase the metallic character of the surface and probably lead to stronger adsorption of hydrogen. The increased adsorption of hydrogen could then increase the reduction rate until another rate-limiting step is reached, possibly the diffusion of oxygen in the solid phase. This would allow a steady state rate to be maintained for a

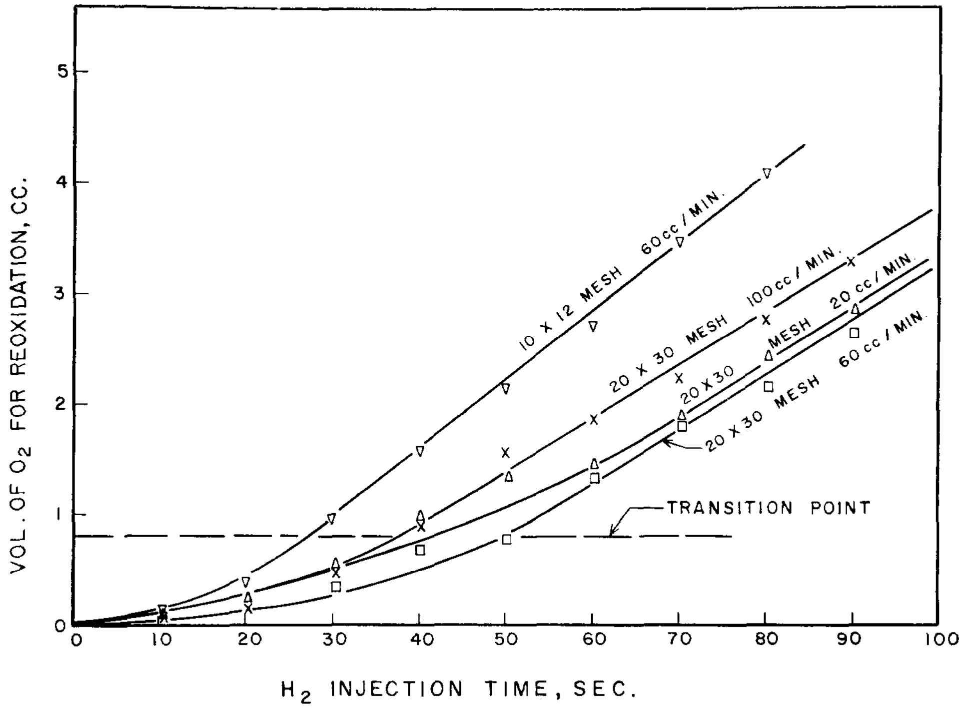

FIG. 1. Reduction of equal weights (0.85 g) of unsupported bismuth molybdate samples by pulsed hydrogen at 500°C. Volumes of oxygen are at 25°C and 1 atm.

TABLE 1
SURFACE AREAS

Catalyst	Surface area (m^2/g)		
	Total	Active	Area/g active ingredient
Uns. bismuth oxide	1.6	1.6	1.6
Supp. bismuth oxide	~130	0.6	1.7
Uns. bismuth molybdate	1.6	1.6	1.6
Supp. bismuth molybdate	~100	3.0	5.9
Silica gel support	~200	—	—

short time, as was found experimentally. As a matter of fact, the intrinsic rates calculated from the linear sections in Figs. 1 and 2 are roughly comparable. The rates of disappearance of oxygen were 0.040 and 0.027 cc STP/sec/m^2 for the 10 × 12 mesh and 20 × 30 mesh sizes in Fig. 1. In Fig. 2, the same rates were 0.065 and 0.045 for the 1-g and 2-g samples, respectively based on the calculated surface areas in Table 1.

The BET surface area and pulsed reduction data for unsupported bismuth molybdate were used with the transition point from Fig. 2 to calculate the active surface of the supported catalyst; the results are given in Table 1. This calculation was based on the assumption that 3×10^{15} oxygen atoms was equivalent to 1 cm^2 of surface of both the supported and unsupported material. Similar results were obtained for unsupported and supported bismuth oxide, as shown in the table. These data indicated that the surface area of the active metal oxides was rather small compared to the area of the support. In addition, preliminary examination of the catalysts by X-ray diffraction gave patterns typical of the respective crystalline compounds, bismuth oxide and bismuth molybdate. It was concluded from

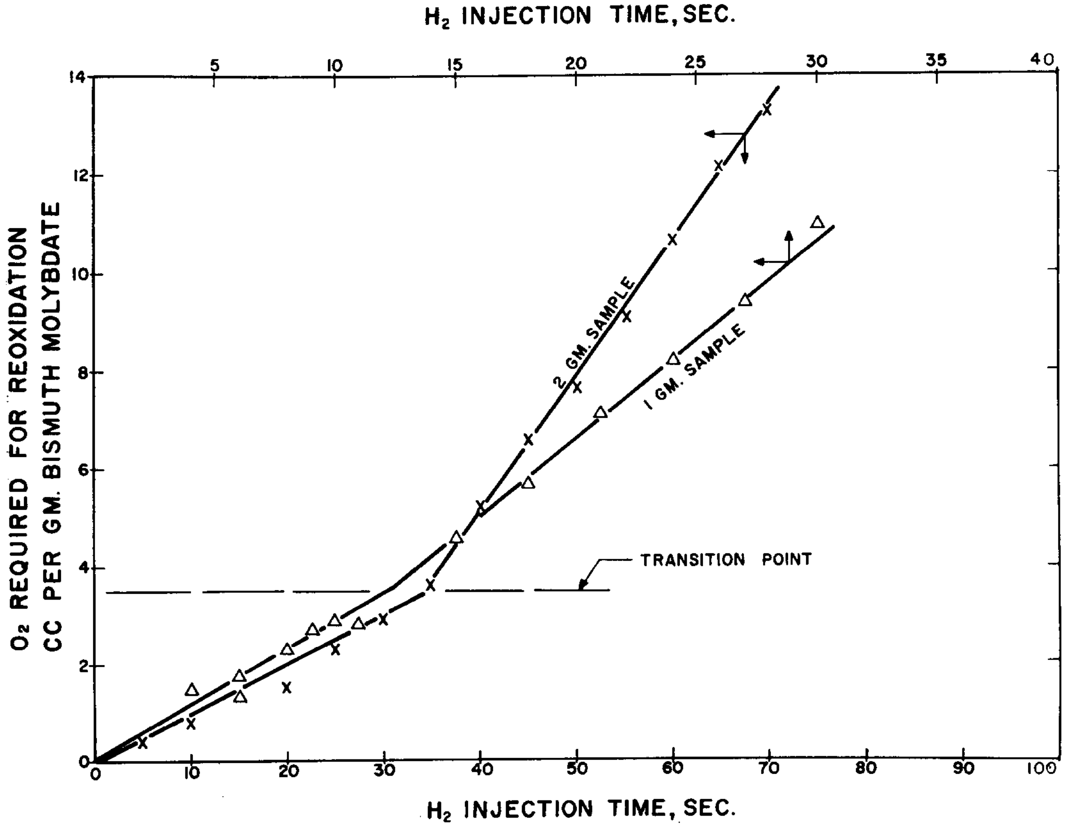

FIG. 2. Reduction of different weights of supported bismuth molybdate by pulsed hydrogen at 500°C. Volumes of oxygen at 25°C and 1 atm.

these data that bismuth oxide and bismuth molybdate crystallites probably existed as isolated clusters throughout the pores of the silica gel support.

Data on more catalysts are obviously needed to prove the validity of this technique for measuring active surface areas. Our work indicates that it would be necessary to experiment with temperature, contact time, and sample size with each catalyst to find the best conditions for detection of the transition point described. Refinements are also needed to improve the accuracy of the method.

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Investigation of Reactions in the Adsorbed Layer: Decomposition of *tert*-Butylbenzene on Silica-Alumina

The cracking of alkylbenzene on silica-alumina catalysts has been investigated by many workers (*1*). The nature of alkylbenzene adsorbed on the catalyst has been discussed indirectly on the basis of the kinetics of the reaction. If the decomposition of adsorbed alkylbenzene can be followed by direct measurements, the information on the reactivity of adsorbed species will be much improved. The present study was undertaken to present such an attempt for *tert*-butylbenzene on a silica-alumina. An investigation along this line has been already carried out by us for the decomposition of formic acid adsorbed on silver and magnesium oxide catalysts (*2*).

The *tert*-butylbenzene was obtained from the Tokyo Kasei Kogyo Co. It was purified by preparative gas chromatography. The purity as checked by gas chromatography was 99.5%. The silica-alumina catalyst containing 13% alumina was obtained from the Shokubaikasei Co. It has a BET surface area of 437 m^2/g. Prior to the experiments, the catalysts were heated in air at 450°C followed by evacuation for 24 hr at this temperature.

Investigation of the decomposition of adsorbed *tert*-butylbenzene (TBB) was carried out as follows: A constant volume apparatus was used. After the adsorption of TBB at room temperature, the desorption experiment was started by immersing a trap attached to the reaction vessel in liquid nitrogen. Analysis of the desorption products collected in the trap was carried out by gas chromatography. It was found that in addition to TBB an appreciable amount of benzene was desorbed from the catalyst, suggesting that even at room temperature the decomposition of TBB takes place. The rate of decomposition of TBB in the adsorbed layer can be given by the rate of appearance of benzene in the gas phase when the adsorption of benzene on the catalyst is negligible. As will be described later, the benzene adsorption can not be neglected at room temperature. In such case the rate of formation of benzene in the adsorbed layer can be obtained in the fol-