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Sintering Studies on a Cobalt Molybdate–Alumina Catalyst

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A commercial cobalt molybdate–alumina has been sintered at 800 or 925°C and characterized with respect to total surface area (BET), specific surface area of molybdena after reduction, redox behavior at 500°C, and X-ray analysis. Marked stabilization of the catalyst against sintering occurs if a small amount (2 wt%) of zirconia is added by impregnation. The redox behavior (H_2, O_2) at 500°C provides a measure of the total amount of accessible, reducible oxides present; O_2 chemisorption at −195°C provides a measure of the accessible molybdena surface area in the prereduced catalyst. The stabilization by zirconia may result from reaction with surface defects or grain boundaries at which the sintering processes originate.

INTRODUCTION

A method has been proposed recently *(1)* to use oxygen chemisorption at −195°C for the measurement of the specific surface area of reduced molybdena in alumina-supported molybdena catalysts. Such a method would be useful, obviously, in characterizing the specific molybdena area as a function of molybdena concentration and distribution in fresh catalysts, and in following changes in molybdena area on deliberate sintering treatment or during process deactivation. The present study is concerned with an application of the oxygen chemisorption method to the sintering behavior of a commercial cobalt molybdate–alumina catalyst, and to the action of added zirconia as an inhibitor of sintering.

EXPERIMENTAL METHODS

Equipment and materials. The adsorption data were obtained using a standard, gas-volumetric, high-vacuum glass system. The detailed description of the apparatus and of the gas purification procedures has been published *(1)*.

The catalyst used was commercial Harshaw 0402T, $CoO(3\%)–MoO_3(15\%)–Al_2O_3$ (stabilized with ca. 5% SiO_2), as received or with 2 wt% ZrO_2. The zirconium oxide-containing catalyst was prepared by impregnating the Harshaw catalyst with aqueous zirconium nitrate solution ("no excess solution" technique), drying at 110°C for 2 hr and then calcining at 550°C for 24 hr.

Sintering. Two samples of each catalyst, with and without added ZrO_2, were sintered at the same time in a muffle furnace, in the presence of air, for 4 hr. The sintering temperatures were 800 or 925°C. After sintering, the samples were cooled and stored in a desiccator.

Redox experiments at 500°C. As a preliminary to the chemisorption measurements, we studied bulk-phase reduction and oxidation of each sample at 500°C,

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starting with the completely oxidized catalyst. These studies were made in a closed system equipped with an electromagnetic circulation pump and an in-line cold trap; details are given in Ref. (*1*).

Oxygen chemisorption at −195°C. The adsorption data were obtained in conventional fashion with about 0.5-g samples of catalyst. Each sample was reduced in flowing hydrogen for 6 hr and then evacuated for 1 hr, all at 500°C. The sample was cooled to liquid nitrogen temperature, and oxygen isotherms were obtained at −195°C, before and after evacuation for 1 hr at −78°C. Following this, the total surface area of the prereduced catalyst was determined by the BET method (N_2 at −195°C).

RESULTS AND DISCUSSION

Harshaw 0402T: Redox Behavior at 500°C and O_2 Chemisorption

The first portion of Table 1 includes data, for dried-only and for air-sintered samples of the commercial catalyst, which give (i) the total surface area, (ii) the H_2 consumption by the catalyst at 500°C after preliminary evacuation for 1 hr at 500°C, and (iii) the O_2 consumption after the H_2 treatment and subsequent evacuation for 1 hr at 500°C. The total area declines greatly ($178 \rightarrow 107 \rightarrow 25$ m^2/g) with increase in the temperature of heat treatment ($110 \rightarrow 800 \rightarrow 925$°C). The decrease in H_2 consumption at 500°C after sintering is much less pronounced, as is true also for the O_2 consumption at 500°C during reoxidation.

The fresh catalyst support is a high surface area, small crystallite size (γ- and η-) alumina. On being heated to high temperatures, the alumina undergoes growth in crystallite size and various phase transitions (*2*, *3*), e.g., to δ-, θ-, and ultimately α-alumina. In 4 hr at 800°C in air, our sample of catalyst decreased in total area from 178 to 107 m^2/g, a decrease of 40%. After 4 hr at 925°C, the total area dropped sharply to 25 m^2/g, a reduction of 86% from the value for unsintered catalyst. The average crystallite size, calculated for the γ- and η-alumina from line-broadening measurements in X-ray diffraction (XRD) examination, increased from 77 Å in the fresh sample, to 129 Å in the sample sintered at 800°C, and finally to 184 Å in the sample sintered at 925°C.

An even more striking effect was reported in the pioneering work of Nahin and Huffman (*4*). For molybdena–alumina

TABLE 1

Sintering of Harshaw 0402T

Heat treatment	S^a (m^2/g)	Consumption at 500°C [ml(STP)/g]		$V_{O_2}{}^b$ [ml(STP)/g]	EMA^c (m^2/g)
		$H_2{}^d$	O_2		
550°C, 24 hr; 110°C, 2 hr	178	28.5	13.2	3.6	49
Sintered at 800°C, 4 hr	107	28.6	11	2.3	31
Sintered at 925°C, 4 hr	25	18.4	8	0.81	11

[a] Total surface area (BET, N_2).

[b] O_2 chemisorption at −195°C on prereduced sample; difference between first and second isotherms.

[c] Equivalent molybdena area (after reduction). Calculated from the ratio of S/V_{O_2} for reduced, unsupported molybdena (*1*).

[d] Theoretical H_2 consumption for $MoO_3 \rightarrow MoO_2$ = 23.4 ml(STP)/g; for $CoO \rightarrow Co$ = 9.0 ml(STP)/g [cf. Ref. (*1*)].

(11.1 wt% MoO_3) catalyst, they found that the total area was reduced from 102 m^2/g after calcination for 6 hr at 875°C to 0 to 4 m^2/g after 6 hr at 900°C. They reported, further, only a γ-phase for the alumina at 875°C and only an α-phase at 900°C, along with a roughly fivefold increase in particle size (by electron microscopy) from 875 to 900°C. The dramatic changes within this narrow temperature range seem surprising, at the least.

The H_2 consumption at 500°C (Table 1, column 3) provides an approximate measure of the total amount of accessible, reducible oxides present, since at 500°C bulk phase reduction of a fresh catalyst goes essentially to completion (*1*). On the simplest view, therefore, one would expect the H_2 consumption, as well as the O_2 consumption during reoxidation, to be independent of sintering treatment. Since this is not strictly the case, one may inquire about the reasons for the decline shown in Table 1.

Calcination of cobalt molybdate–alumina at high temperatures results in solid–solid reactions leading to changes in the structure and composition of the catalyst (*2*, *3*). Moné, in a recent study of reflectance spectra (*5*), has concluded that in $Co/Mo/Al_2O_3$ catalysts calcined above 600°C, cobalt ions move into the alumina lattice, forming a difficulty reducible cobalt aluminate phase (6). Part of the decrease in H_2 consumption (Table 1) may be attributed to this fact. It is also possible that the structural collapse occurring at very high temperatures may result in partial physical entrapment, and loss of accessibility, of the reducible oxides. Finally, we do not as yet know by direct chemical analysis whether any MoO_3 might have been lost by sublimation during the 800 or 925°C sintering treatments. There was no qualitative evidence, such as formation of a yellow deposit external to the catalyst, that significant loss did occur.

The O_2 chemisorption at −195°C, V_{O_2}, and the calculated "equivalent molybdena area," *EMA*, are listed in the last two columns of Table 1. All catalyst samples were prereduced at 500°C, evacuated, and cooled to −195°C for determination of the adsorption isotherms (*1*). By contrast with the H_2 consumption at 500°C, which is a measure of bulk phase reduction, the O_2 chemisorption at −195°C is a measure of molybdena area. It is therefore interesting to note that for the catalyst sintered at 800°C, which had a total surface area loss of 40%, the decrease in V_{O_2} (or in *EMA*) was 36%. Similarly, for the catalyst sintered at 925°C, the decrease in total surface area was 86% and the decrease in V_{O_2} was 78%. To a very rough approximation, the molybdena area decreased in proportion to the total surface area, a result which may be considered as consistent with a monolayer model of MoO_3 on Al_2O_3 for the catalyst before reduction.

The apparent molybdena area of the dried-only Harshaw catalyst is 49 m^2/g catalyst after reduction. This is equivalent to 368 m^2/g MoO_2 (the catalyst contains 15% MoO_3 before reduction, or 13.3% MoO_2 after reduction). The corresponding average particle diameter may be calculated to be about 25 Å for the MoO_2 ($\bar{d} = 6/\rho S$; $\rho = 6.57$ g/ml; $S = 368$ m^2/g). The catalyst sintered at 800°C (and reduced at 500°C) has an apparent average particle diameter of about 40 Å for the MoO_2; and the catalyst sintered at 925°C has an apparent particle diameter of about 110 Å for MoO_2, on the basis of a similar calculation.

Stabilization of Harshaw 0402T with ZrO_2

It was shown many years ago that for chromia–alumina catalysts, the addition of small amounts of HfO_2 or ThO_2 (ca. 1 mole%) results in inhibition of the phase transition from γ- to α-alumina, and in retention of surface area and catalytic activity (*7*, *8*). A recent patent (*9*)

TABLE 2

Sintering of Harshaw 0402T + 2% ZrO_2

Heat treatment	S^a (m^2/g)	Consumption at 500°C [ml(STP)/g]		$V_{O_2}{}^b$ [ml(STP)/g]	EMA^c (m^2/g)
		$H_2{}^d$	O_2		
110°C, 2 hr; 550°C, 24 hr	176	24.3	11	3.1_2	42
Sintered at 800°C, 4 hr	127	22.6	10.6	2.7_5	37
Sintered at 925°C, 4 hr	31	21.5	9.2	1.1_5	16

[a] Total surface area (BET, N_2).

[b] O_2 chemisorption at −195°C on prereduced sample; difference between first and second isotherms.

[c] Equivalent molybdena area (after reduction). Calculated from the ratio of S/V_{O_2} for reduced, unsupported molybdena (*1*).

[d] Theoretical H_2 consumption for $MoO_3 \rightarrow MoO_2$ = 23.4 ml(STP)/g; for $CoO \rightarrow Co$ = 9.0 ml(STP)/g [cf. Ref. (*1*)].

similarly claims that addition of Group IV B metal oxides decreases the rate of deactivation of hydrodesulfurization catalysts. We report here data, summarized in Table 2, for the redox behavior (at 500°C) and O_2 chemisorption (at −195°C) of Harshaw 0402T impregnated with 2 wt% ZrO_2 ex zirconium nitrate.

The total surface area, *S*, again shows a substantial reduction with increase in sintering temperature. However, comparison of these results with the corresponding entries in Table 1 reveals that (i) the total area is better retained in the zirconia-containing samples, and (ii) although the original capacity to react with H_2 and O_2 at 500°C is lower in the catalyst with zirconia, sintering at 800 or 925°C results in a remarkably small decrease in these redox values.

Oxygen chemisorption at −195°C provides further information about the effect of zirconia addition. Comparison of Tables 1 and 2 shows that the equivalent molybdena area of the dried-only catalyst is somewhat lower for the zirconia-containing sample, conceivably because part of the molybdena area is covered by zirconia. Despite this, the zirconia-containing samples sintered at 800 or 925°C show higher equivalent molybdena areas than their zirconia-free counterparts. All of the data are internally consistent in indicating a partial stabilization by ZrO_2 against thermal sintering of $Co/Mo/Al_2O_3$. By the method indicated above, one may calculate that the zirconia-containing sample sintered at 800°C has an average MoO_2 particle diameter of about 33 Å, which increases to about 77 Å for the sample sintered at 925°C.

The data in Table 2 for H_2 consumption at 500°C show that in the presence of ZrO_2, the total amount of accessible, reducible oxides remains remarkably constant on sintering. Even for the 925°C sintered sample, although the total area had decreased by 82%, the H_2 consumption at 500°C decreased only 12%. The equivalent molybdena area suffers more, as is to be expected for a surface rather than a bulk phenomenon; the decrease in EMA at 925°C was 63%.

The stabilization of alumina and alumina-supported transition metal oxide catalysts by small amounts of refractory, tetravalent metal oxides such as ZrO_2, HfO_2, and ThO_2 may be a quite general phenomenon. At the atomic scale, the mode of action of such tetravalent oxides remains an almost complete mystery. The sintering of high-area Al_2O_3 (or Cr/Al_2O_3, or $Co/Mo/Al_2O_3$) involves bulk phase changes as well as loss in total surface area and collapse of micropores (*7, 8, 10*). After sintering, chromia–alumina catalysts become solid solutions of α-(Cr, Al)$_2$O$_3$, for example. When a small amount of a stabilizer such as ZrO_2 is added by impregnation of the catalyst with the nitrate from aqueous solution, and the catalyst is dried at 110°C and calcined at 500 to 550°C, the additive is unlikely to diffuse, to the crystallite interior, from the surface on which it has been deposited. Moreover, no compounds or solid solutions have been reported for such systems as alumina–zirconia, alumina–hafnia, alumina-thoria. If one accepts the thesis that the additive, remaining on the surface, is able to inhibit bulk phase changes occurring during sintering, then one is led to speculate that the sintering of the catalyst originates at surface defects or grain boundaries, which defects can be stabilized by reaction (nature unknown) with the Group IV B additive. One relevant report in the literature is the finding by Rice (*11*) that in MgO containing 2% ZrO_2, an accumulation of a ZrO_2-rich phase is observed at the grain boundaries even after heat treatment at 2300°C.

The presence of MoO_3, ZrO_2, or molybdenum aluminate was not detected in any of our samples by XRD. The calculated crystallite size (by line broadening) for alumina phases after a given heat treatment was, on average, about 15% lower for ZrO_2-containing samples.

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