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Sublimation of MoO_3 from WO_3–MoO_3 Catalysts During the Oxidation of Toluene[1]

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The sublimation of MoO_3 from an equimolar mixture of MoO_3–WO_3 in the temperature range 450–675°C was shown to be remarkably enhanced by the presence of 1% toluene in the air passed over the samples. The presence of a low temperature and high temperature mechanism was observed from Arrhenius plots of the weight loss data, with activation energies of 14.5 and 53 kcal/mole, respectively. In air, an activation energy of 82 kcal/mole was determined. The formation of water vapor as a product of the toluene oxidation resulting in the formation of volatile hydroxide species is proposed as the mechanism by which the sublimation was enhanced.

INTRODUCTION

Both WO_3 and MoO_3 have been characterized as catalysts which show little activity for complete combustion of hydrocarbons, but high selectivity for a number of intermediate oxygen containing products (*1*). MoO_3 has been the more widely studied of the two catalysts in recent years. Much of the interest in MoO_3 has been generated by its importance as a component in the molybdate catalysts, the primary example being bismuth molybdate (*2*). Another example of a catalyst system of increasing importance which contains molybdenum is the molybdenum phosphate system (*3*). Popov (*4*) and Bliznakov *et al.* (*5*) demonstrated that a mixture of WO_3 and MoO_3 had a higher activity for the oxidation of methanol to formaldehyde than either of the pure oxides.

A large number of authors (*6–11*) have treated in some detail the reduction of Mo(VI) to Mo(V) and lower valence states of Mo, however, no mention is made of the loss of MoO_3 by sublimation. In preliminary investigations of mixed WO_3–MoO_3 catalysts for the oxidation of xylenes and toluene, it was sometimes observed that after a few hours of operation at 400–600°C a powder residue was formed on the cooler parts of the reactor. X-Ray diffraction proved this to be essentially pure MoO_3, apparently deposited from the vapor phase. This prompted further investigations of the sublimation of MoO_3 from the surface of supported and unsupported WO_3–MoO_3 catalysts under conditions approximating those in service.

METHODS

Catalysts: Preparation and Characterization

Catalysts used in this investigation were prepared in the conventional manner by decomposing ammonium metatungstate and ammonium paramolybdate in air at 500°C for 2 hr.[2] Mixtures of WO_3 and MoO_3 were prepared from aqueous solu-

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[2] The ammonium metatungstate was obtained from the Sylvania Corp. Ammonium paramolybdate was obtained from Matheson, Coleman, and Bell.

tions of the ammonium compounds. Supported catalysts were prepared by soaking the carrier[3] in the aqueous solutions and vacuum drying before decomposition. X-Ray diffraction patterns of fresh catalysts were obtained using a de Bye Scherrer powder camera and V-filtered Cr*Kα* radiation. With 50 or more mole% WO_3, little evidence of MoO_3 as a separate phase was observed by X-ray diffraction in the freshly prepared catalyst. All X-ray patterns were characteristic of the WO_3 structure with slight modifications, probably due to the formation of crystallographic shear structures in the mixed oxides (*12*).

Thermal Analysis

Differential scanning calorimetry (DSC) of the unsupported catalyst in a feed gas composed of air, and 1% toluene in air was performed to determine the temperature range of interest for catalytic reactions. Isothermal thermogravimetric analysis was then performed at several temperatures within this range in atmospheres of air, 1% toluene in air, and 10% H_2 in N_2. All thermal analysis was performed on a duPont de Nemours 900 thermal analysis system, on samples of approximately 100 mg in size, in atmospheric flow rates of 0.5 SCFH at ambient pressures.

Scanning Electron Microscopy and Chemical Analysis

Scanning electron microscopy (SEM) of supported and unsupported catalysts was performed on a Cambridge Mark IIA scanning microscope equipped with a 190 eV resolution energy dispersive X-ray analysis system. A standard calibration curve of characteristic X-ray intensities vs WO_3/MoO_3 ratios was prepared by using freshly prepared catalyst samples. Chemical analysis of used catalyst surfaces was then performed by aging the catalyst in the aforementioned atmospheres for appropriate times at temperatures of interest. In all cases, the energy dispersive X-ray analysis was performed by scanning a sufficiently large area that masking of the fluorescent X-rays by morphological features would be averaged out for all specimens.

RESULTS

Thermal Analysis

Figure 1 shows the DSC curves obtained when WO_3, MoO_3, and their mixtures were heated in the 1% toluene in air atmosphere. All samples were of approximately the same size, therefore, qualitative comparisons of heats of reaction can be made. No reactions, involving significant heats of reaction, occurred when WO_3 or mixtures of WO_3 and MoO_3 were heated in air, however, when MoO_3 was heated in air, an endotherm was observed at 560°C. When WO_3 was heated in the toluene atmosphere, a broad exotherm, peaking at 480°C was observed. This same exotherm

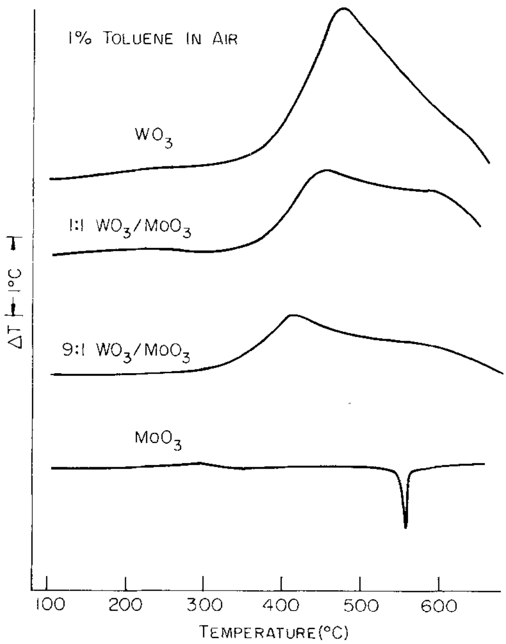

FIG. 1. Differential thermal analysis curves for WO_3, MoO_3, and their mixtures as measured in the DSC cell.

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[3] SA 5103 was obtained from the Norton Co.

appeared on cooling, indicating that a gas phase reaction occurred preferentially on the sample surface. An analysis of the reaction products was not made for the purposes of this study, but it was clearly an oxidation reaction involving toluene. The decrease in ΔT at temperatures in excess of 480°C does not indicate that the rate of the reaction was slowing down, but rather, that the relative rate occurring on the catalyst was no greater than that occurrng homogeneously in the gas phase. The endotherm occurring at 560°C when MoO_3 was heated in air was present at the same temperature in the toluene containing atmosphere. No reference to a phase change occurring at this temperature in MoO_3 was found in the literature, and the nature of this transition is as yet undetermined. It was, however, clearly a phase transition in the MoO_3 phase and no change in this transition was observed with the addition of toluene to the feed gas.

The MoO_3 by itself was obviously a very inactive catalyst, however, it had a marked effect on promoting the reaction when added to WO_3 as was noted by Popov (*4*) and Bliznakov *et al.* (*5*) in the oxidation of methanol. This can be seen from the lower temperature for the exothermic peak for samples containing MoO_3. While unconfirmed at present, it is possible to interpret the curves of Fig. 1 as two overlapping exotherms corresponding to two different reactions in which case the addition of MoO_3 provides the advantage of separating the two reactions, thereby increasing the selectivity for the low temperature product. In any case, Fig. 1 illustrates that MoO_3 is an important component in the catalyst and the loss of MoO_3 by sublimation during service can be an important factor in catalyst performance. It is noteworthy in this regard that the effect of small (10%) additions of MoO_3 was more effective than large (50%) additions in promoting the WO_3 catalyst.

Isothermal thermogravimetric analysis between 450 and 700°C showed a constant rate of weight loss up to at least several percent of the total weight of MoO_3 in the unsupported catalyst when heated in air or 1% toluene in air. When heated above 500°C in 10% H_2 in N_2, the initial weight loss was very rapid, eventually approaching a linear weight vs time curve after several minutes. Samples heated in 10% H_2 in N_2 regained essentially all of their weight when reheated in air, while samples heated in air and 1% toluene in air could not be made to regain any appreciable amount of the weight lost. This, of course, indicates that the samples heated in H_2 were merely reduced while the other samples lost MoO_3 due to sublimation.

To achieve adequate sensitivity in the weight loss measurements it was necessary to go to relatively high concentrations of MoO_3. For this reason, the 1:1 composition of WO_3:MoO_3 was chosen on which to make extensive measurements.

The linear slopes of the weight loss curves obtained on the equimolar mixture are plotted on an Arrhenius plot in Fig. 2. As shown, reduction in H_2 occurs very rapidly at relatively low temperatures apparently reducing the MoO_3 component to a less volatile Mo(IV) species. Furthermore, in air, the weight loss was negligible below 650°C and, in fact, a very slight weight gain was observed below this temperature. When heated in 1% toluene in air, however, an irreversible weight loss was readily observable at temperatures as low as 450°C and the rate of sublimation was dramatically enhanced by the presence of toluene over the entire temperature range studied. Further, in the toluene atmosphere, the data points appear to fall on two intersecting straight lines. This is characteristic of observations made on systems where parallel reaction mechanisms are operative. At low temperatures, the process with the lowest activation energy dominates. At higher temperatures, the high activation energy process is pre-

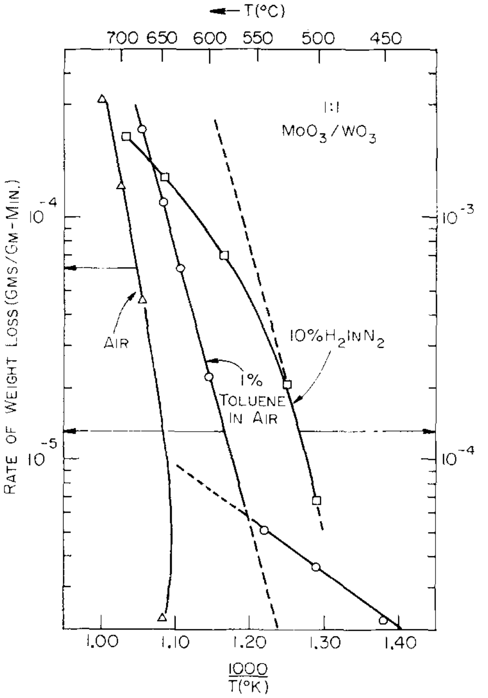

FIG. 2. Rate of weight loss versus 1000/T (°K) for 1:1 MoO_3/WO_3 in air, toluene, and H_2 atmospheres.

dominant. The nonlinearity of the curve for the H_2 atmosphere may be the result of the initial nonlinearity in the high temperature weight loss data complicated by the time involved in bringing the samples to temperature. At lower temperatures, the slope of the Arrhenius plot for the H_2 atmosphere approached the high temperature slope for the toluene atmosphere. The high temperature behavior in toluene was not the result of reduction, however, as the weight loss was not recoverable upon reheating in air.

Were it not for the low temperature mechanism for sublimation in this system when reacted with toluene, the enhancement of the sublimation rate by the hydrocarbon might be little cause for concern. Extrapolating the high temperature portion of the curve to lower temperatures indicates that its contribution would probably be negligible below 500°C, however, from the data presented, it appears that the low temperature mechanism would be significant for long-term service to at least 400°C.

Scanning Electron Microscopy

It was pointed out previously that X-ray diffraction patterns for the mixed catalysts indicated that their structure was closely related to that of WO_3. Even for the 1:1 mixture, the only indication of the possible presence of MoO_3 was a very weak line at 2.291 Å which is the strongest line in the MoO_3 pattern. Scanning electron micrographs of supported catalysts shown in Fig. 3 support this finding. The WO_3 catalyst exhibited a fine grained structure. The MoO_3 catalyst was composed of large crystallites. Mixtures of MoO_3 and WO_3 were similar in appearance to the pure WO_3 catalyst with no semblance of the MoO_3 morphology.

Spectra obtained by energy dispersive X-ray analysis in the SEM on the samples for which thermogravimetric data are presented in Fig. 2 are shown in Fig. 4. Six peaks appeared in this portion of the strip chart curve. The aluminum peak is the result of the use of an aluminum sample holder. The iron peak is the result of the interaction of the primary and backscattered electrons with the specimen stage and final lens area.

The relative intensities of the molybdenum and tungsten lines were a measure of the relative concentrations of these elements in the surface of the samples. The ratios of intensities of the $MoL\alpha/WL\alpha$ lines in Fig. 4 are 2.29, 0.98, and 0.58, for the as fired sample, the sample heated in toluene, and the sample heated in air, respectively. This contrasts with the fact that the total weight loss measured for the samples heated in toluene and in air were 0.68 and 1.55%, respectively.

In an attempt to make these numbers meaningful quantitatively, fresh unsupported catalyst materials of predetermined composition were reacted to 500°C in air,

FIG. 3. Scanning electron photomicrographs of supported (a) WO_3, (b) MoO_3, (c) 1:1 WO_3/MoO_3, and (d) 9:1 WO_3/MoO_3 catalysts (400°C, 2 hr, air).

reground to minimize the effect of any surface depletion during firing, and patterns like those in Fig. 4 were obtained to construct the standard curve shown in Fig. 5. Comparing the observed ratios of intensities from Fig. 4 with the standard curve of Fig. 5, surface concentrations of 42, 21 and 12% MoO_3 are obtained for the as fired sample, the sample heated in toluene, and the sample heated in air, respectively. This illustrates the fact that even for very small losses of MoO_3 due to sublimation,

FIGURE 3b

the surface depletion can be very marked. Even the freshly prepared sample, when not reground to expose new surface showed an appreciable depletion of MoO_3 from the surface.

Energy dispersive X-ray analysis on supported 9:1 W/Mo compositions that had been aged in air at 625°C for 7 and 28 days yielded Mo*Lα*/W*Lα* ratios of 0.14 and 0.13, respectively. Comparison of these values to the standard curve of peak ratio vs percentage of MoO_3 shown in Fig. 5 leads to an Mo content of approximately 4.0 mole%. This is the value reported in

FIGURE 3c

the literature as the maximum obtainable Mo content in a WO_3 lattice (*13*).

DISCUSSION

The primary point to be made from the present paper is that WO_3–MoO_3 catalysts, and perhaps other MoO_3 containing oxidation catalysts, are susceptible to loss of MoO_3 by sublimation even in the absence of MoO_3 as a separate phase. This rate of sublimation may be dramatically enhanced by the presence of the hydrocarbon in the feed gas, even when present in small concentrations. This indicates that

FIGURE 3d

a volatile complex is formed between the MoO_3 and the reactants or reaction products. A number of such complexes might be proposed, but at present there is a great deal of evidence that water has a marked effect on the sublimation of MoO_3 through the formation of $MoO_3 \cdot H_2O$. Since water is one of the products in an oxidative dehydrogenation reaction, it seems likely that it is the component leading to enhanced sublimation of MoO_3.

Mass spectrometric studies of MoO_3 vapors have shown the existence of several polymeric forms of $(MoO_3)_n$ in the

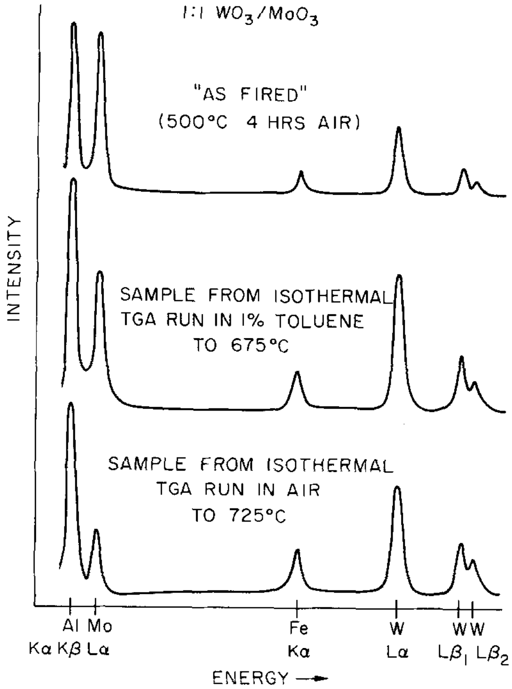

FIG. 4. Results of energy dispersive X-ray analysis of the 1:1 WO_3/MoO_3 catalyst.

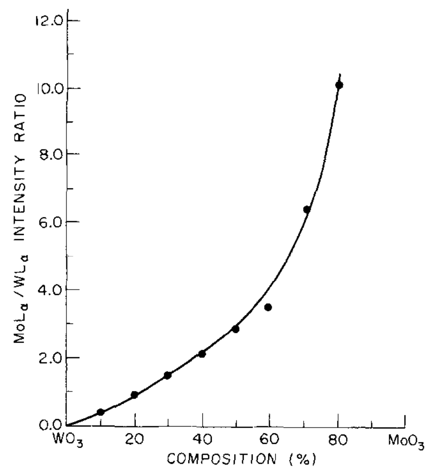

FIG. 5. Standard curve for determining the Mo content by energy dispersive X-ray analysis.

vapor phase but the trimer appears to predominate (*14*). The heat of sublimation of the trimer was calculated to be 80.5 kcal/mole at 850°K. In this light, it may be pointed out that the slope of the Arrhenius plot for the sample heated in air in Fig. 2 yields an activation energy of 82 kcal/mole, however, a more recent determination of the heat of vaporization yielded a value for the trimer of only 68.5 kcal/mole while for the tetramer it was 79.2 kcal/mole (*15*). The activation energy from the high temperature curve for the 1% toluene atmosphere is 53 kcal/mole; for the low temperature curve 14.5 kcal/mole.

The effect of water vapor on the volatility of MoO_3 was first reported by Millner and Neugebauer (*16*). They observed that the addition of 66 vol% of H_2O in air increased the weight lost in 0.5 hr by 17 times at 600°C and over 6 times at 700°C. Oxygen is apparently also required for water to have this effect since it was reported that water–nitrogen mixtures produced no weight loss at 650°C (*17*). The vapor species in the presence of water has been found to be $MoO_3 \cdot H_2O$ (*18,19*).

Several workers have found the hydroxide vapor phase useful in the formation of monolayers of MoO_3 on various supports (*20,21*). Further, Buiten (*20*) found that the excellent activity of MoO_3 monolayers on SnO_2 was obtained only in the presence of water vapor, whereas Pernicone *et al.* (*22*) found a marked inhibiting effect of H_2O on the activity of iron molybdate with excess MoO_3 for the oxidation of methanol. Others have proposed hydroxylated intermediate states of molybdenum as part of the mechanism of reduction (*11*). The lack of sublimation in these studies may be attributed to the absence of O_2 in the reduction of MoO_3 by H_2. In the actual oxidative dehyrogenation of hydrocarbons, however, excess oxygen would be present.

In the WO_3–MoO_3 system, the energy-dispersive X-ray analysis of the catalyst makes it quite clear that the surface concentration of MoO_3 in the catalyst is much lower than in the bulk. It is not clear that this is not beneficial, however. From Fig. 1 it appears that the nominal 9:1 WO_3/MoO_3 composition was more active than the nominal 1:1 composition. Presumably its surface concentration of MoO_3 was even lower. An interesting analogy may be drawn between this observation and the work of Steenhof De Jong *et al.* (*23*), on the oxidative demethylation of toluene over bismuth uranate. Their evidence indicated that bismuth uranate formed a shear structure and that two types of oxygen were present in the catalyst: a relatively nonselective and inactive species associated with the shear planes, and a more selective species located away from the shear planes in the lattice. As previously pointed out (*12,13*), beyond about 4% MoO_3 in the WO_3–MoO_3 system a series of shear structures are produced with the density of shear planes increasing with increasing MoO_3 content. Accordingly, the addition of excess MoO_3 would increase the amount of nonselective lattice oxygen thereby decreasing the concentration of selective oxygen.

Whether the initial loss of MoO_3 from the catalyst is beneficial or not, it has serious implications regarding the long-term behavior and ultimate lifetime of the catalyst. Further study of the mechanism of sublimation could, however, lead to its use for catalyst regeneration.

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