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NOTES

Behavior of Lattice Oxygen in V_2O_5/MoO_3 Mixture and Catalyst

The interaction between V_2O_5 and MoO_3 and the evolution processes of lattice oxygen in V_2O_5/MoO_3 mixtures and catalysts were studied by thermal gravimetric analysis. The evolution of lattice oxygen is promoted by the interaction of V_2O_5 with MoO_3. When the V–Mo–O catalyst is heated to a certain temperature, the sample can absorb or evolve oxygen according to the ambient oxygen partial pressure, and the processes of oxygen absorption and evolution are reversible. Two processes may be involved in the evolution of lattice oxygen for the V_2O_5/MoO_3 mixture and catalyst. © 1989 Academic Press, Inc.

V–M–O catalysts have been used for the selective oxidation of benzene or furfural to maleic anhydride (*1–5*). The main composition phase of the V–Mo–O catalyst is $(Mo_{0.3}V_{0.7})_2O_5$ (*1*), which may be the active phase, as mentioned by Robb (*2*). Some intermediate compounds, such as V_2MoO_8 or $V_9Mo_6O_{40}$, are also observed (*3*). Segregation usually occurs in V–Mo–O catalysts (*4, 5*).

It is generally accepted that, in a selective oxidation reaction, the catalysts give up lattice oxygen to take part in oxidation reaction, and the reduced catalysts can absorb oxygen from the gas phase and transform it into lattice oxygen again (*6*). The evolution of lattice oxygen is usually promoted by the interaction between the metal oxide components of catalysts. In the present paper, we report the promotion of the evolution of lattice oxygen by interaction between V_2O_5 and MoO_3 and the behavior of lattice oxygen in V_2O_5/MoO_3 mixtures and catalysts.

A V_2O_5/MoO_3 mixture was prepared by simply mixing the two oxides in a mortar. The V–Mo–O catalytic samples were prepared as follows: Ammonium metavanadate and ammonium molybdate in the required ratio were put into an aqueous solution of oxilic acid and sufficiently stirred, subsequently dried, ground, and finally calcined in air at 450°C for 2 h.

The processes of evolution of lattice oxygen and oxygen absorption were studied by thermal gravimetric analysis (TGA), which was carried out with a Perkin–Elmer TGS-2 thermobalance under flowing atmosphere of $He/O_2 = 1/1$ and He, respectively. The sample loading was 20 mg. The temperature was raised at a rate of 5°C/min.

Figure 1 shows the weight loss in TGA experiments in He as a function of temperature for pure V_2O_5, MoO_3, and 80 mol% V_2O_5/MoO_3 mixture. It can be seen that no weight loss is observed for pure V_2O_5 and the weight loss is small for pure MoO_3 for temperatures up to about 620°C. The small amount of weight loss is probably due to the volatilization of MoO_3. However, for the 80 mol% V_2O_5/MoO_3 mixture, the weight loss arising from the evolution of lattice oxygen is obvious even at temperatures below 600°C in the TGA experiment. It is evident that the lattice oxygen evolution is promoted by the interaction between V_2O_5 and MoO_3.

In order to further understand the evolution process of lattice oxygen from the mixture and catalysts, the derivative curves of weight loss of the 60 mol% V_2O_5/MoO_3 mixture and catalyst as a function of temperature are shown in Fig. 2. It can be seen that the derivative curve is similar for the mixture and catalyst, and there are two peaks in the derivative curves of weight loss for the V_2O_5/MoO_3 mixture and catalyst, both curves have a peak at about 660°C and another peak at about 635°C for the mixture, but the latter is not obvious for the catalyst.

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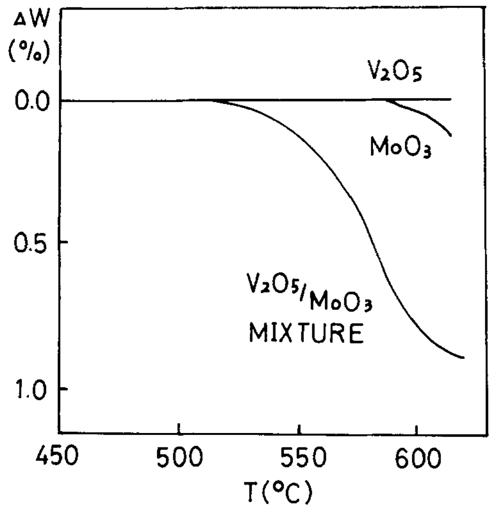

FIG. 1. Weight loss, $\Delta W(\%)$, in the TGA experiment in He as a function of temperature for pure V_2O_5, MoO_3, and 80 mol% V_2O_5/MoO_3 mixture.

We also noted that the low temperature peak is broad and may include more than one peak. This result indicates that there are at least two processes involved in the evolution of lattice oxygen either in a mixture or in a catalyst.

Figure 3 shows the weight change of 60 mol% V_2O_5/MoO_3 and 80 mol% V_2O_5/MoO_3 catalytic samples from a TGA experiment carried out in $He/O_2 = 1/1$ and subsequently in a He atmosphere. The weight change is caused by the oxygen absorption or evolution during the TGA experiments. The processes of oxygen absorption and evolution can be observed over and over again in this experimental temperature range, here only one circle is shown. From this figure, four points should be noted: (i) The V–Mo–O catalytic samples can absorb or evolve oxygen in a TGA experiment according to the oxygen partial pressure in the ambient atmosphere. If the partial pressure of oxygen in the ambient atmosphere is higher than that of the catalyst exposure, the catalyst can absorb oxygen from the gas phase and transform it into lattice oxygen; if this sample is put into an ambient atmosphere with a lower partial pressure of oxygen, the absorbed oxygen is evolved again. (ii) The amount of absorbing or evolving oxygen depends strongly on the V_2O_5 content. (iii) A considerable amount of oxygen vacancies exist in the starting V–Mo–O catalysts, which allowed the catalysts to absorb oxygen from the gas phase. (iv) All the pro-

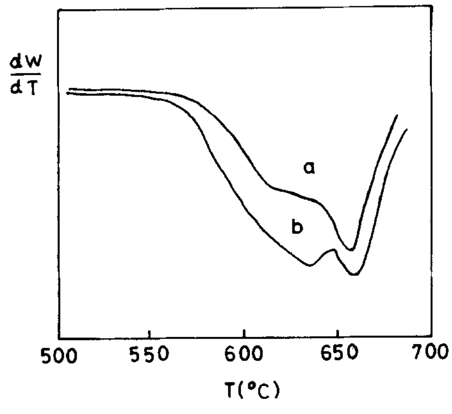

FIG. 2. Derivative curves of weight loss for the 60 mol% V_2O_5/MoO_3 mixture and catalyst as a function of temperature. (a) Catalyst, (b) mixture.

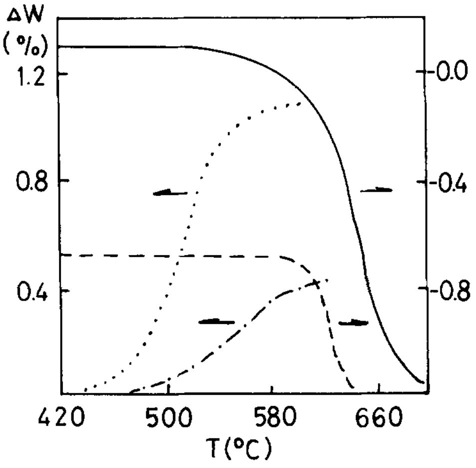

FIG. 3. Weight changes, $\Delta W(\%)$, as a function of temperature for (· · ·) the 60 mol% V_2O_5/MoO_3 catalyst in the TGA experiment in $He/O_2 = 1/1$ atmosphere; (—) above sample in a subsequent TGA experiment in He; (-····-) the 80 mol% V_2O_5/MoO_3 catalyst in the TGA experiment in $He/O_2 = 1/1$ atmosphere; (---) above sample in a subsequent TGA experiment in He.

cesses of oxygen absorption or evolution must occur at a certain temperature, e.g., oxygen absorption occurs at 450–550°C, while lattice oxygen evolution occurs at about 580–660°C. This suggests that a certain value of activation energy is required to induce the adsorption and evolution of oxygen, and the activation energy of lattice oxygen evolution is greater than that of oxygen absorption. This can be explained on the basis of a Lennard-Jones model (7). In adsorption, the activation energy for chemisorption, E_A, is required, which is the energy necessary to dissociate the molecule when it is physisorbed on the surface; in desorption process, the activation energy of desorption $E_D = E_A + Q$ is needed, in which Q is the heat of chemisorption. In addition, the evolution and absorption processes of lattice oxygen also involve the diffusion of lattice oxygen; however, the lattice oxygen diffuses easily in a V–Mo–O catalyst at temperatures above 400°C. Therefore, the temperature feature of evolving and absorbing lattice oxygen depends primarily on the activation energy for chemisorption and the heat of chemisorption in a V–Mo–O catalyst.

In summary, the interfacial interaction between V_2O_5 and MoO_3 can promote the evolution of lattice oxygen. The V–Mo–O catalyst behaves like a "reservoir of oxygen": When the oxygen partial pressure in the ambient atmosphere is higher than that of the previous catalyst exposure, the catalyst can absorb oxygen from the gas phase and "store" it in the lattice sites as lattice oxygen. If the partial pressure of oxygen is high enough, say in pure O_2, some absorbed oxygen may also be present as interstitial oxygen. When the oxygen partial pressure in the ambient atmosphere becomes lower than before, some lattice oxygen (or interstitial oxygen) can be evolved again. These processes of oxygen absorption and evolution can be reversible. There are at least two processes in the evolution of lattice oxygen from the V_2O_5/MoO_3 mixture and catalyst.

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