JOURNAL OF CATALYSIS **101**, 301–313 (1986)

Carbon and Oxygen Atom Mobility during Activation of Mo_2C Catalysts

KEVIN J. LEARY,*,† JAMES N. MICHAELS,*,†,[1] AND ANGELICA M. STACY*,‡,[1]

**Center for Advanced Materials, Lawrence Berkeley Laboratory, and* †*Department of Chemical Engineering and* ‡*Department of Chemistry, University of California, Berkeley, California 94720*

Received December 11, 1985; revised May 5, 1986

Temperature-programmed desorption (TPD) and reduction (TPR) were used to study the activation of Mo_2C for ethylene hydrogenation at 298 K. Mo_2C can incorporate large amounts of oxygen, and since oxygen is a poison for the reaction, it must be removed from the surface to activate the catalyst. As oxygen is removed from the surface by evacuation or reduction, it is replenished by diffusion of oxygen from the bulk. Therefore, the equivalent of several monolayers must be removed to obtain an oxygen-free surface, although it is not necessary to remove all the bulk oxygen. Furthermore, the oxygen cannot be removed by evacuation or reduction without also removing a significant amount of bulk carbon. Although the initial activity of the catalyst for ethylene hydrogenation is independent of the amount of carbon removed, the rate of deactivation of the Mo_2C strongly depends on the extent of carbon removal. As more carbon is removed, the rate of deactivation increases and the shape of the activity–time curve (deactivation curve) changes from an exponential decay to a sigmoidal shape. TPR spectra of oxygen chemisorbed on the surface after two different activation procedures showed that the surface of the catalyst depends on the extent of carbon removal. As more carbon is removed from the Mo_2C, the oxygen is bound more tightly to the surface. This suggests that ethylene also might be bound more tightly on the carbon-deficient catalyst, which is consistent with the higher rate of deactivation.

INTRODUCTION

There is a growing interest in the catalytic properties of transition metal carbides since several workers (*1–7*) reported that alloying carbon to these metals changes their catalytic properties. When transition metals are carbided, they form interstitial compounds in which the carbon atoms are located in the voids between the close-packed, or nearly close-packed, layers of metal atoms. The presence of the interstitial carbon significantly alters the bonding in these metals, causing marked changes in their physical and electrical properties (*8*). Moreover, the carbon also changes their catalytic properties, in some cases, conferring to them properties more typical of noble metals.

Most of the catalytic studies of carbides have focused on determining the activity of TaC, TiC, WC, and Mo_2C toward such reactions as ethylene hydrogenation, ethane hydrogenolysis, and CO hydrogenation. Prior to reaction, the catalysts were activated by evacuation between 1050 and 1300 K (*7, 9, 10*) or by reduction in flowing hydrogen between 600 and 1000 K (*4–6*). The purpose of the pretreatments was to remove oxygen which is often a poison and which readily dissolves in these materials at room temperature (*8, 11*). Following activation, the carbides exhibited activities for these reactions that were much higher than those of the parent metals and comparable to those of some noble metals (*3, 5, 6, 10*). However, the activities were still about an order of magnitude lower than the activity of the most active noble metal for each particular reaction (*12*).

While a number of studies have focused on the catalytic activity of the carbides after activation, there has been very little

---

[1] Authors to whom correspondence should be addressed.

0021-9517/86 $3.00

work directed at studying the nature of the activation process. Kojima *et al.* (*9*) found that the activities of WC, TaC, and TiC for ethylene hydrogenation varied strongly with evacuation temperature. Up to some critical evacuation temperature the catalysts were inactive. Then as the evacuation temperature was raised, the activity rose sharply, went through a maximum, and then decreased sharply. XPS studies revealed that the evacuation temperature at which the carbides became active corresponded to the temperature at which oxygen was removed from the surface. However, they were unable to explain the sharp decrease in activity caused by higher evacuation temperatures since their data showed that the loss of activity was not due to sintering. Also, they were unable to explain why the activity of TaC for ethylene hydrogenation was lower after reduction at 1270 K than after evacuation (*10*).

The goal of this study was to gain a better understanding of the activation process and the effect that different activation procedures have on the catalytic properties of the transition metal carbides, in particular, unsupported Mo_2C. The activation process was studied using temperature-programmed desorption (TPD) and reduction (TPR). By integrating the TPD and TPR peaks, the amount of carbon and oxygen removed from the Mo_2C was determined as a function of evacuation or reduction temperature. The effects of different activation procedures on the catalytic properties of Mo_2C were studied using ethylene hydrogenation as a probe reaction. Also, TPR of chemisorbed oxygen was used to probe changes in the catalyst surface resulting from different activation procedures.

EXPERIMENTAL

Apparatus. The reactor used in this study consisted of a 6-mm-o.d. quartz tube with a 9-mm-o.d. bulb-shaped middle in which a quartz frit used to support the catalyst was fused. The reactor was mounted inside a furnace made out of a 13-mm-o.d. quartz tube wrapped with nichrome wire. Power to the furnace was controlled by a programmable temperature controller (built in-house) capable of ramping the temperature linearly to 1200 K at rates ranging from 0.01 to 5 K/s. Feedback to the controller was provided by a sheathed thermocouple placed between the reactor and the inside wall of the furnace. The catalyst temperature was monitored with an exposed junction thermocouple placed in the catalyst bed.

The reactor inlet was connected to a gas manifold which allowed one gas, or any desired mixture of up to four gases, to flow continuously over the catalyst. Alternately, adsorbate pulses of known volume could be injected into a carrier gas stream which passed over the catalyst. The reactor effluent was analyzed with both a Finnegan Model 3300 mass spectrometer and a Varian Model 3760 gas chromatograph (GC), equipped with thermal conductivity and flame ionization detectors. During ethylene hydrogenation reaction studies, the product gases were separated in the GC with an activated alumina column. Data acquisition and experimental control were accomplished with an IBM PC; the system allowed up to 10 different masses to be sampled at a rate of 5 Hz.

Materials. All but one of the Mo_2C samples used in this study were taken from a single batch of catalyst prepared in a manner similar to that described by Boudart *et al.* (*6*); the details are given elsewhere (*13*). X-Ray diffraction results verified that the samples were predominantly hcp Mo_2C, but also contained some Mo (~13% by weight). Even though large amounts of oxygen were known to be present in the samples following exposure to air, no molybdenum oxides were seen in the X-ray diffraction patterns. The BET area of the catalyst was approximately 6 m^2/g, although it varied slightly after different activation treatments. An additional sample of 87 m^2/g fcc Mo_2C, prepared by another method outlined by Volpe and Boudart (*14*), also was used for one experiment.

Hydrogen (99.995%) was purified by passing it through a bed of 0.3% Pd/SiO_2 (heated to 450 K) to convert traces of O_2 to water, and the water was removed by molecular sieves cooled by a dry ice–ethanol bath. Traces of O_2 were removed from the helium (99.998%) by an "Oxisorb" cartridge (Alltech Associates), and then water was removed by cooled molecular sieves. Cooled molecular sieves also were used to remove water from the oxygen (Liquid Carbonic certified standard 20.6% O_2 in He). The ethylene (Matheson certified standard 2.15% C_2H_4 in He) was not purified further. No impurities were detected by the mass spectrometer in any of the gases.

Experimental procedure. Before each experiment, a fresh catalyst sample was placed in the reactor. Then the system was flushed with He and evacuated to below 10 mTorr for 1 h to remove air from the system. For all TPD and TPR experiments, the carrier gas (He or H_2) flow rate was set at 100 cm^3 (STP)/min, and the heating rate at 1 K/s. During a temperature ramp, the composition of the gas leaving the reactor was monitored by the mass spectrometer. For the reaction studies, the C_2H_4/He flow rate was set at 187 cm^3 (STP)/min (4 cm^3/min C_2H_4, 183 cm^3/min He), and the H_2 rate at 12 STP cm^3 (STP)/min, giving a total pressure of 830 Torr at 298 K.

RESULTS

TPD and TPR of Mo_2C

To gain insight into the nature of the activation process, samples of Mo_2C that had been exposed to air were heated in either flowing helium (TPD) or hydrogen (TPR) to 1173 K. In both cases, H_2O, CO, CO_2, and CH_4 were observed desorbing from the surface; in addition, C_2H_6 was observed in the TPR spectrum. The TPD and TPR spectra of each product were integrated to determine the amounts of carbon and oxygen removed from the catalyst so that changes in the bulk composition of the catalyst due to the activation process could be monitored.

Figures 1a and b present the results of a ramp in He from 298 to 1173 K for a 100-mg sample of Mo_2C, which was previously evacuated at 298 K for 1 h. An important feature of the TPD spectrum is that oxygen was not removed from the sample as molecular O_2. Instead, it combined with carbon in the sample and desorbed as CO and CO_2 in four distinct peaks at 583, 658, 918, and approximately 1068 K, with a fifth CO peak starting to rise at 1150 K. Water and methane peaks also were observed at 583 and 658 K. These peaks may have been due to reaction of oxygen and carbon with either residual hydrogen that might have dissolved in the sample during synthesis, or with hydrogen produced from the dissociation of strongly bound water. The water

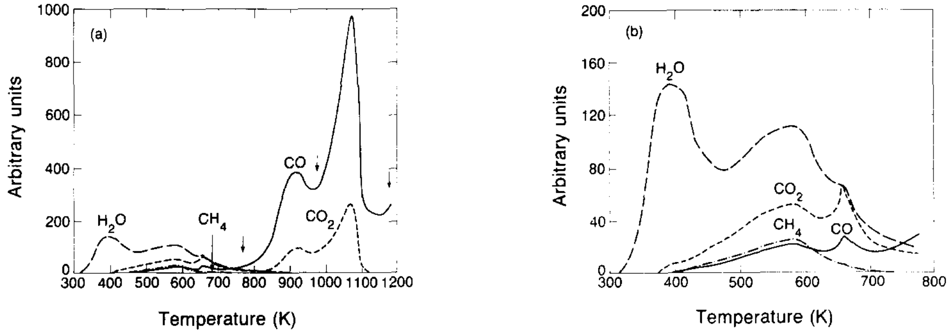

FIG. 1. (a) Desorption spectrum for a 1 K/s ramp in He to 1173 K for 100 mg of Mo_2C after evacuation for 1 h at 298 K. (b) First part of ramp expanded by a factor of 5.

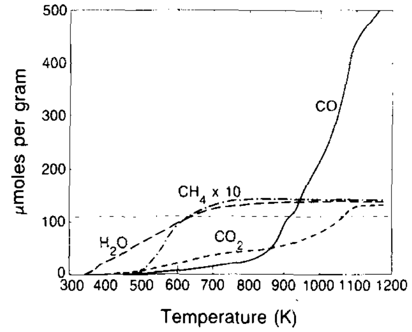

FIG. 2. Integrated area under desorption curves in Fig. 1 converted to micromoles of each gas desorbed per gram of catalyst as a function of temperature. The dashed horizontal line represents the number of surface sites per gram, assuming 1.1 × 10^{15} sites/cm^2 and a BET area of 6 m^2/g.

peak at 393 K probably resulted from water that was either strongly bound to the surface or trapped in the pores of the catalyst. It must be pointed out that the exact position and shape of each of the peaks in Fig. 1 (and in Fig. 3) varied slightly from sample to sample. This variation was most likely caused by a minor degree of inhomogeneity in the batch of catalyst from which they were taken. However, the general nature of the desorption spectrum did not change.

The spectra in Fig. 1 were integrated to determine the quantity of each product desorbed as a function of temperature; this is shown in Fig. 2. The horizontal dashed line in the figure represents the number of surface Mo atoms per gram, based on the BET area of 6 m^2/g and assuming 1.1 × 10^{15} sites/cm^2 (*14*). It is evident that the samples contained the equivalent of more than seven monolayers of oxygen (assuming one monolayer corresponds to one oxygen atom per surface Mo atom). In removing this oxygen, more than 650 μmole/g of carbon was removed simultaneously. This corresponds to 13% of the carbon originally contained in the sample. Even more carbon was removed for higher area samples. In fact, when the 87 m^2/g sample was subjected to the same temperature ramp, carbon was removed quantitatively. This was verified by X-ray diffraction which showed that the carbide had been converted completely to molybdenum metal. This proves that the carbon being removed as CO and CO_2 is predominantly coming from the carbide, and not from any carbonaceous surface species.

Figures 3a and b and 4 give the results of a TPR of a fresh sample from the same catalyst batch following evacuation at room temperature for 1 h. The major difference between the TPD and TPR spectra was the mechanism by which the oxygen was removed. In the TPD, the oxygen was removed by reaction with bulk carbon, whereas in the TPR, the oxygen reacted with hydrogen. This resulted in as many as five water peaks: a sharp peak at 518 K denoted α, two peaks at 598 and 658 K de-

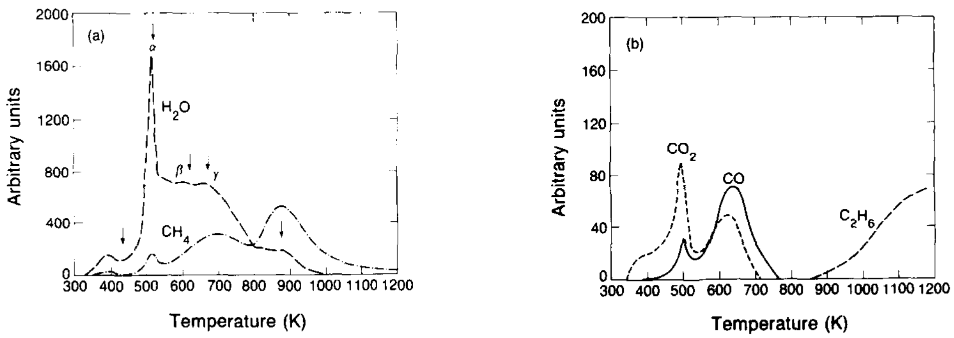

FIG. 3. (a) Desorption spectrum of water and methane for a 1 K/s ramp in H_2 to 1200 K for 100 mg of Mo_2C after evacuation for 1 h at 298 K. (b) CO and CO_2 desorption during the same ramp in H_2, magnified by a factor of 10.

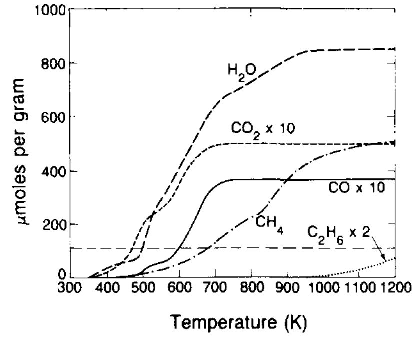

FIG. 4. Integrated area under desorption curves in Fig. 3 converted to micromoles of each gas removed per gram of catalyst as a function of temperature. The dashed horizontal line represents the number of surface sites per gram.

noted β and γ, respectively, which nearly merge into one very broad peak, and two smaller peaks at 818 and 878 K. Again, the water peak at 388 K probably was due to water tightly bound to the surface or trapped in the pores.

Although most of the oxygen was removed as water in the H_2 ramp, approximately 15% of it still reacted with carbon in the sample, desorbing in two small CO and CO_2 peaks at 500 and ~630 K. Furthermore, the carbon in the sample also reacted with the H_2 to form CH_4, and at higher temperatures C_2H_6. As shown in Fig. 4, the H_2 ramp removed close to 750 μmole of carbon per gram (~15% of the carbon originally in the sample), and still more could be removed at 1200 K. X-Ray diffraction analysis of samples heated to 1200 K in either He or H_2 showed that the removal of carbon resulted in an increase in the fraction of molybdenum metal mixed with the carbide.

To examine how fast the sample could incorporate oxygen during exposure to air at room temperature, reduced samples were removed from the reactor and exposed to air for various lengths of time ranging from a few minutes to several weeks. The exposed samples were placed back into the reactor, evacuated for 1 h, and ramped in H_2. It was found that after a few minutes of exposure, the catalyst contained between one and two monolayers of oxygen, as verified by TPR. Following this initial rapid uptake of oxygen, the samples continued to incorporate oxygen at a slower rate for several weeks as evidenced by increasing amounts of oxygen removed in the TPRs as a function of exposure time. The results of a TPR following exposure of the catalyst for 1 day are shown in Fig. 5. The amount of oxygen removed as water in Fig. 5 was equivalent to more than three monolayers, whereas over nine monolayers of oxygen were removed from a sample that had been exposed for over a month (Fig. 3a). This indicates that the rate of oxygen incorporation by Mo_2C is significant even at room temperature, and that the incorporation of oxygen into the bulk is not due to a rapid autothermal oxidation of the sample. It should also be emphasized that despite the large oxygen content of the exposed samples, no bulk oxides could be detected by X-ray diffraction. The spectrum in Fig. 5 also shows the clear distinction between the β and γ peaks that was not as obvious in Fig. 3.

The results of the ramps in He and H_2 indicate that oxygen is readily incorporated into Mo_2C, and that it is not possible to remove all the oxygen from the catalyst by evacuation or reduction without also removing a significant amount of bulk carbon. Moreover, the mechanism and rate of removal of the oxygen and carbon are not the same for evacuation and reduction, as evi-

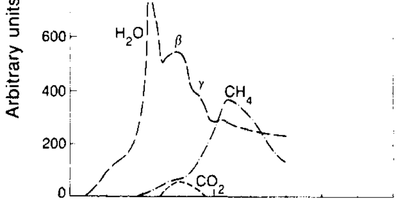

FIG. 5. TPR of an Mo_2C sample that was reduced at 1200 K, and subsequently exposed to the air for 24 h.

denced by the differences between the TPD and TPR spectra.

Activation of Mo_2C for Ethylene Hydrogenation

It was suggested by Kojima *et al.* (*9*), and verified in this laboratory, that surface oxygen poisons the activity of Mo_2C for ethylene hydrogenation at 298 K. Therefore, it was known that the pretreatment conditions required to fully activate the Mo_2C for this reaction would have to be sufficient to remove oxygen from the surface. However, the TPD and TPR results suggested that oxygen removed from the surface was replenished by oxygen from the bulk. As a result, it was not known whether all the oxygen in the sample would have to be removed to fully activate the catalyst for ethylene hydrogenation. For this reason, the activity of the catalyst for ethylene hydrogenation was compared after pretreatment conditions which removed different amounts of oxygen.

The TPD and TPR results showed that the pretreatment conditions required to remove oxygen simultaneously removed carbon from the sample. Since carbiding the Mo is known to change its catalytic properties, it was expected that removing carbon from the Mo_2C would affect its catalytic properties. Moreover, since the amount of carbon removed by activation in helium was not the same as in hydrogen, the catalytic properties were expected to change for different pretreatment methods. Therefore, the activity of Mo_2C for ethylene hydrogenation was measured after evacuation or reduction at several different temperatures.

The evacuation and reduction temperatures used were chosen based on the TPD and TPR spectra presented in Figs. 1 and 3. In both the helium and the hydrogen temperature ramps, oxygen was removed in several peaks. To determine the effect of removing the oxygen corresponding to each peak, the carbides were pretreated at temperatures slightly above each of the various peak temperatures in the TPD and TPR spectra. These temperatures are indicated by the arrows in Figs. 1 and 3.

The effect of the evacuation or reduction temperature on the activity of the catalyst for ethylene hydrogenation, as well as on the amount of carbon and oxygen removed from the sample and the BET area, is shown in Table 1. In each case, 14.7 mg of catalyst was heated to the designated activation temperature at 1 K/s in the gas listed, and held at that temperature for the time given in the table. The activities were normalized such that the maximum observed integral rate of 1.96×10^{-4} mole/g · s (97% conversion) corresponded to an activity of 100%. This initial rate corresponds

TABLE 1

Effect of Pretreatment Conditions on the Activity of Mo_2C for Ethylene Hydrogenation

Gas	Activation temperature (K)	Time (min)	$H_2O^{a,b}$ (μmole/g)	CO^a (μmole/g)	$CO_2{}^a$ (μmole/g)	$CH_4{}^a$ (μmole/g)	% Carbon removed	Initial activity (%)	Deactivation curve shape[c]	BET area (m^2/g)
He	773	10	135	50	50	14	2.3	0.3	—	5.0
He	973	10	135	350	80	14	9.0	93	3	—
He	1173	10	135	550	130	14	14.0	100	2	—
H_2	433	5	90	1	7	5	0.3	0	—	—
H_2	523	5	525	7	25	30	1.3	40	1	—
H_2	623	15	725	30	50	90	3.4	95	1	6.0
H_2	673	5	735	37	50	200	5.8	100	3	—
H_2	873	30	850	37	50	900	20.0	90	2	5.4

[a] Quantity desorbed during pretreatment.

[b] Includes contributions of adsorbed water plus water from reaction of oxygen and hydrogen.

[c] Shapes corresponding to each number are shown in Fig. 6.

to a turnover number of 1.79 s^{-1}, assuming 1.1×10^{15} sites/cm^2, which is slightly higher than the turnover number of 0.9 s^{-1} that can be calculated from the results of Kojima *et al.* (*9*) on tungsten carbide for $P_{C_2H_4} = 10$ Torr, $P_{H_2} = 20$ Torr, and $T = 273$ K.

As shown in Table 1, if changes in the surface area are accounted for, a 5-min reduction at 673 K gave the same initial activity as a 30-min reduction at 873 K. However, the 30-min reduction removed all the oxygen from the sample, and the 5-min reduction removed only 86%. Thus, it was not necessary to remove all the oxygen to fully activate the catalyst. However, it was necessary to remove more than the equivalent of one monolayer. A 10-min evacuation at 773 K gave an initial activity of only 0.3% of the full activity despite removing the equivalent of more than one monolayer of oxygen as CO and CO_2. Furthermore, a 5-min reduction at 523 K gave only a 40% initial activity, despite having removed the equivalent of about four monolayers of oxygen. This suggested that as oxygen was removed from the surface, oxygen from the bulk replenished it, leaving the surface partially covered with oxygen. This was supported by the fact that oxygen continued to react with the hydrogen and desorb as water even after 5 min at 523 K.

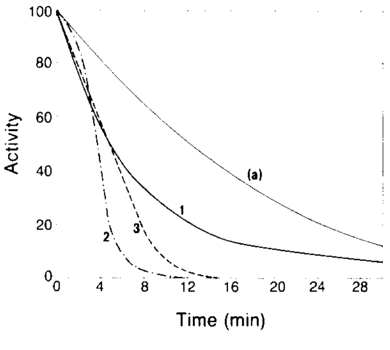

FIG. 6. Shapes of the three different deactivation curves for ethylene hydrogenation at 298 K after different activation treatments. All curves are normalized for an initial activity of 100%. Also shown is the deactivation curve expected for deactivation solely due to oxygen poisoning (curve a).

The results presented above demonstrate that it is not necessary to remove all the oxygen from the Mo_2C to activate it fully for ethylene hydrogenation. However, it is necessary to remove the equivalent of more than one monolayer since oxygen removed from the surface can be replenished by oxygen from the bulk. Furthermore, the initial activity does not depend on the amount of carbon removed by the activation process for the conditions considered. However, as shown below, the rate at which the catalyst deactivates depends strongly on the amount of carbon removed.

Deactivation of Mo_2C

Along with the initial activity of the catalyst, Table 1 also indicates the general shape of the activity vs time curve (deactivation curve) after each pretreatment. The three different shapes corresponding to the numbers 1 through 3 given in Table 1 are shown in Fig. 6. Each curve is normalized to give an initial activity of 100%. As shown in Table 1 and Fig. 6, the shape of the deactivation curve varied significantly depending on the amount of carbon removed by the pretreatment.

When the catalyst was activated by reduction below 623 K, less than 3.5% of the carbon was removed, and the activity appeared to decay exponentially with time, dropping three orders of magnitude after 1 h. However, if the activation removed between 6 and 9% of the carbon, as was the case for the 973 K evacuation and the 673 K reduction, the activity initially decreased almost linearly with time, before decreasing exponentially at longer times. In this case, the activity decreased by three orders of magnitude in just 15 min. Finally, if the activation removed between 14 and 20% of the carbon as in the 1173 K evacuation and 873 K reduction, the deactivation curve had a sigmoidal shape, and the activity decreased three orders of magnitude in just 12 min. Molybdenum metal that was reduced in H_2 at 1073 K for 30 min also followed a type 2 deactivation curve, although it deactivated slightly faster than Mo_2C that had been reduced at 873 K. Thus, the deactivation rate increased as carbon was removed by the pretreatment.

As shown above, the slowest deactivation rates were obtained for reductions below 623 K, but a 15-min reduction at 623 K was not sufficient to activate the catalyst fully. If, instead, the catalyst was reduced at 673 K for 5 min, an extra 1.4% of oxygen was removed and the catalyst was fully activated. However, as shown in Table 1, this pretreatment removed 70% more carbon than the 15-min reduction at 623 K. As a result, the catalyst deactivated almost four times faster after the 673 K reduction (type 3 deactivation curve) than after the 623 K reduction (type 1 deactivation curve). Therefore, a pretreatment method was devised which removed the extra 1.4% of oxygen while only removing 10% more carbon. This required reducing the catalyst in hydrogen according to the temperature schedule shown in Fig. 7. This "low-temperature reduction" resulted in an initial activity of 100% and a type 1 deactivation curve.

It must be emphasized that the only difference between activating the catalyst by a 5-min reduction at 673 K and activating it by the low-temperature reduction procedure was the amount of carbon removed from the sample; both pretreatments removed the same amount of oxygen. Therefore, the changes in the shape of the deactivation curve after different pretreatments only could have been caused by differences in the amount of carbon removed from the sample.

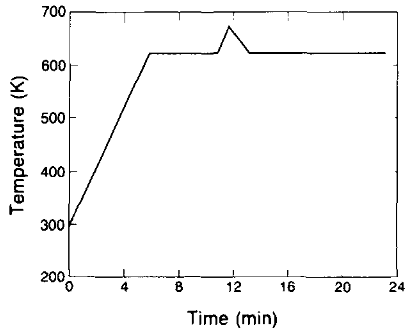

FIG. 7. Temperature schedule used during low-temperature reduction. H_2 flow rate = 100 cm^3/min (STP).

An interesting property of these catalysts is that even though they deactivated rather quickly, they could be reactivated completely by either a 10-min evacuation at 973 K or a 10-min reduction at 523 K. During either reactivation procedure no carbon species were observed to desorb from the catalyst surface. However, a small amount of water was detected when the catalyst was reactivated by reduction at 523 K. We believe that the source of this water was the residual oxygen in the system which slowly accumulated on the surface during ethylene hydrogenation. In separate experiments, the rate of oxygen accumulation on the surface due to residual oxygen was measured to be approximately 5×10^{-10} mole of O atoms/s, which corresponds to an oxygen concentration in the gas stream of 1.7 ppm.

To account for the deactivation due to poisoning by residual oxygen, experiments were performed in which varying amounts of oxygen were pulsed onto the surface, and the initial reaction rate was measured. It was found that inhibition of the hydrogenation rate by oxygen is third order in oxygen coverage ($r = r_0 (1 - \theta_O^3)$), assuming dissociative adsorption. This is consistent with the work of Kojima *et al.* (7) who found that poisoning of TaC for ethylene hydrogenation by CO was third order in CO coverage. From these data, the deactivation curve due solely to poisoning by residual oxygen was calculated for the sample sizes used, and is shown as curve (a) in Fig. 6. It is clear from Fig. 6 that the rate of deactivation due to residual oxygen is significantly smaller than the observed deactivation rates.

Another interesting property of these catalysts is that with each subsequent reactivation, the rate of deactivation decreased slightly. If the sample originally had a type 1 deactivation curve, three or more reactivations were sufficient to slow the deactivation to the point where its deactivation curve approached curve (a) in Fig. 6 (deactivation solely due to oxygen poisoning). Additional reactivations had no effect on subsequent deactivation curves.

The results presented show that although the initial activity of the catalyst does not depend strongly on the amount of carbon removed during the activation process, the rate of deactivation does. Moreover, the shape of the deactivation curve also varies with the amount of carbon removed.

TPR of Oxygen on Activated Mo_2C

The changes in the shapes of the deactivation curves after different activation treatments suggested that the pretreatment conditions in some way changed the surface of the catalyst. To explore this further, a sample of Mo_2C was activated in two ways: first by low-temperature reduction (LTR); and second, by a 15-minute reduction at 673 K (high-temperature reduction, HTR). Following each activation procedure, oxygen was pulsed onto the surface and the catalyst was heated in H_2. The differences in the resulting TPR spectra verified that the surface was not the same after the two different activation procedures.

As shown earlier, oxygen is readily incorporated into Mo_2C when it is exposed to air at room temperature. However, it was found that if the oxygen was pulsed onto the catalyst by injecting known quantities into a carrier gas (i.e., He), the catalyst became saturated after adsorbing the equivalent of one monolayer, suggesting that all of the adsorbed oxygen was on the surface. Monolayer coverage was taken as one oxygen atom per surface Mo atom, assuming dissociative adsorption (110 μmole O atoms/g, for a catalyst with a BET area of 6 m^2/g).

After a 15.3-mg sample was activated by low-temperature reduction (LTR), it was evacuated for 5 min at 623 K to remove any hydrogen that might be adsorbed on the surface and then cooled under He to 298 K. Then a monolayer of oxygen was pulsed onto the surface and the catalyst was heated in H_2 to 623 K at 1 K/s. The results of this TPR are shown in Fig. 8. The same sample was reduced subsequently at 873 K for 15 min (HTR) to remove the bulk oxygen that was not removed by the low-temperature reduction. This also removed an additional 550 μmole/g of carbon so that after the HTR, a total of 14.5% of the carbon originally contained in the sample had been removed. Then after evacuation at 623 K for 5 min, the sample was cooled to 298 K under He and a monolayer of oxygen was pulsed onto the surface. Finally, the temperature was ramped in H_2 to 873 K. The resulting TPR spectrum is presented in Fig. 8.

As shown in the figure, the TPR spectra were quite different for the two different reduction temperatures. In both cases, two peaks were observed, corresponding to the α and β peaks in Fig. 3. However, the position of the α peak shifted from 483 K after LTR up to 513 K after HTR, while the β peak shifted from 586 K after LTR down to 573 K after HTR. The relative intensities of the two peaks also changed after different pretreatments.

The two peaks in the TPR spectra may represent two different states of adsorbed oxygen on the surface, or the second peak may have been from surface oxygen that diffused into the bulk during the ramp and

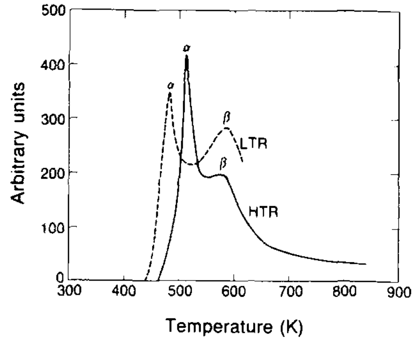

FIG. 8. TPR of oxygen chemisorbed on 15.3 mg of Mo_2C after activation by low-temperature reduction (LTR) compared to after high-temperature reduction (HTR).

then diffused back to the surface as the surface oxygen was depleted. In either case, the important point is that the differences in the TPR spectra of chemisorbed oxygen confirm that the catalyst surface was not the same after LTR as it was after HTR.

DISCUSSION

The results presented above reveal that carbon and oxygen are quite mobile in Mo_2C. In fact, oxygen is readily incorporated into this carbide even at room temperature. Since oxygen is a poison, it must be removed from the surface to activate Mo_2C for ethylene hydrogenation. However, the oxygen cannot be removed by evacuation or reduction without removing a significant amount of bulk carbon from the catalyst. When heated *in vacuo*, oxygen does not desorb molecularly, but instead reacts with carbidic carbon in the catalyst and desorbs as CO and CO_2. When the catalyst is reduced in hydrogen, on the other hand, oxygen is removed by reaction with the hydrogen to form water, and bulk carbon is removed by reaction with the hydrogen to form methane. By varying the pretreatment conditions, different amounts of carbon and oxygen can be removed. This allows investigation of the effects of bulk composition on surface chemistry and catalytic activity.

Because of the relative ease with which oxygen diffuses through Mo_2C, it is necessary to remove the equivalent of several monolayers of oxygen to obtain an oxygen-free surface and completely activate the catalyst. It is not sufficient to remove only one monolayer because as oxygen is removed from the surface during the pretreatment (evacuation or reduction), it can be replenished by oxygen from the bulk. The high mobility of oxygen also complicates interpretation of the TPD and TPR spectra, as evidenced by comparing Figs. 3, 5, and 8 (after HTR). In Fig. 8, oxygen initially was present only on the surface of the catalyst and two peaks (α and β) were observed in the TPR spectrum. As oxygen was added to the bulk in Fig. 5 (the catalyst contained the equivalent of three monolayers of oxygen) and 3 (the equivalent of more than seven monolayers of oxygen) the size of both the α and β peaks increased. Moreover, a third peak denoted γ appeared near 658 K, and two smaller peaks appeared at higher temperatures. Thus, when bulk oxygen is present the peak sizes increase and new peaks appear in the spectra.

Another possible explanation should be mentioned for the increase in the number of peaks in the TPR spectra when the catalyst is exposed to air as in Fig. 3a, compared to when oxygen is just pulsed onto the surface as in Fig. 5. As mentioned previously, when exposed to air, the samples rapidly incorporated between one and two monolayers of oxygen. If this oxygen uptake corresponded to a surface oxidation, it is possible that the surface was not oxidized homogeneously. This could result in multiple surface states which would produce extra peaks in the TPR spectra. However, if the extra peaks in the spectra were due to multiple surface states, then a greater number of surface sites should be exposed following activation by HTR than by LTR since the HTR procedure removes the higher temperature peaks while the LTR procedure does not. If this were the case, then both the initial activity of the catalyst for ethylene hydrogenation and the capacity of the surface for oxygen chemisorption (by pulsing) should be greater following HTR than after LTR. This was not the case. Therefore, these additional peaks are not due to inhomogeneous surface oxidation, but are due to oxygen in the bulk of the catalyst.

From the discussion above, it is evident that the γ peak and the other higher temperature peaks in the TPR spectra result from the presence of bulk oxygen. Furthermore, the sharpness and symmetry of the α peak suggest that this peak is produced by surface oxygen. At first glance, the presence of the β peak in the TPR spectra of Fig. 8, in which oxygen initially was present only on the surface of the Mo_2C, might suggest that this peak is produced by another surface state of adsorbed oxygen. While this cannot be ruled out, the broadness of the β peak and its long tail at higher temperatures suggest that it is produced by bulk oxygen. This may be explained as follows. During the temperature ramp, oxygen is removed from the surface by two processes: reaction with hydrogen to desorb as water, and diffusion into the bulk of the catalyst. As the temperature rises, the surface becomes depleted of oxygen, producing a concentration gradient which drives the oxygen diffusion from the bulk back to the surface. This oxygen reacts with hydrogen at the surface and desorbs as water at a rate equal to the diffusion rate. If the bulk diffusivity increases with increasing temperature, the diffusion rate will increase with temperature until the sample becomes depleted of oxygen, at which time the diffusion rate must decrease to zero. Thus, diffusion of oxygen between the bulk and the surface can produce higher temperature peaks in a TPR spectrum. Although this assignment of the β peak has not been proven as yet, the effect of diffusion between the surface and the bulk on TPD and TPR spectra is under further investigation.

One of the more surprising results of this study was that the initial activity of Mo_2C for ethylene hydrogenation did not depend on the amount of carbon removed by the activation process. Sinfelt and Yates (*3*) found that the activity of Mo for ethane hydrogenolysis changed by several orders of magnitude as it was carbided. Thus, it was expected that the activity of Mo_2C for ethylene hydrogenation would change as carbon was removed, but this was not the case. However, the rate of deactivation and the shape of the deactivation curve strongly depended on the extent of carbon removal.

The increase in the deactivation rate as more carbon was removed indicates that the bulk Mo : C ratio influences the surface chemistry. While the details of the deactivation mechanism are not understood, we believe that the deactivation is due to the accumulation of carbon on the surface which blocks the active sites. This carbon is produced by the slow cracking of ethylene which presumably occurs faster on a surface that binds ethylene more tightly. Therefore, the higher rate of deactivation of the carbon-deficient Mo_2C suggests that ethylene is bound more strongly to the surface as more carbon is removed from the bulk. Unfortunately, no direct measurement of the heat of adsorption of ethylene to the surface could be made using TPD or TPR because no desorption products were observed.

The assumption that ethylene adsorbs more strongly on the carbon-deficient catalyst is supported by the TPR spectra shown in Fig. 8. The shift in the position of the α peak from 483 to 513 K as more carbon was removed by the pretreatment indicates that oxygen is bound more tightly to the surface of the carbon-deficient catalyst. Thus, it seems reasonable that ethylene also would be bound more tightly to the carbon-deficient surface. This is also consistent with the work of Ko and Madix (*15*) who showed that ethylene adsorbs more strongly on a Mo(100) surface than on a carbided Mo(100)–C surface.

The change in shape of the deactivation curve may indicate that the deactivation mechanism changes as more carbon is removed, or it simply may indicate a change in the ability of carbon to diffuse into the bulk. The sigmoidal shape of the deactivation curve for the carbon-deficient sample suggests that as carbon is deposited on a surface which is not fully carbided, it can diffuse into the first few layers of the bulk. As a result, carbon does not build up on the surface and the rate of deactivation is slow initially. Eventually, the first few layers become saturated with carbon, and the rate of diffusion into the bulk decreases considerably; the deactivation then follows the exponential-type decay expected in the absence of diffusion into the bulk. This model of competition between diffusion into the bulk and deposition of surface carbon is similar to the competition model invoked in the Fischer–Tropsch literature (*16, 17*) to explain the time dependence of the activity of iron catalysts.

If the explanation given above for the change in shape of the deactivation curve is correct, one might have expected that once the first few layers were filled with carbon, the surface compositions of the catalysts would be identical, and therefore the rates of deactivation would be the same regardless of the amount of bulk carbon removed. However, this was not the case. After a short induction period in which the first few layers were filled, the catalyst activated by HTR deactivated more than five times faster than the catalyst activated by LTR. Thus, it appears that although the composition of the first few layers might have been the same, the surface structure was not.

Another interesting finding in this study was that even though Mo_2C deactivates quickly, it can be reactivated completely by either a 10-min evacuation at 973 K or a 10-min reduction at 523 K. Moreover, during reactivation no carbon species were observed desorbing from the surface. This suggests that during reactivation, the surface carbon simply diffuses into the bulk, unblocking the active sites. This is consistent with the TPD and TPR results which showed that carbon is mobile in Mo_2C under the conditions used for reactivation, and with the deactivation model discussed above.

This explanation is also consistent with the observation that following reactivation of the catalyst, the subsequent deactivation is slightly slower than before. During the reactivation, any carbon deposited on the surface dissolves into the catalyst, which results in a higher C : Mo ratio at the surface. Our results suggest that after multiple reactivations, the surface C : Mo ratio is sufficiently high that the deactivation can be attributed solely to oxygen poisoning. Thus, within the error of the experiment, it appears that ethylene does not crack on a fully carbided surface.

It is interesting to note that the catalyst can be reactivated in H_2 at only 523 K, whereas a temperature of 973 K is necessary for reactivation *in vacuo*. This suggests that hydrogen facilitates carbon transport in Mo_2C, perhaps by producing a mobile CH_x species. The details of the deactivation and reactivation mechanisms are under further investigation.

As a final note, we would like to mention how these results for Mo_2C might apply to other catalysts as well. It is possible that under reaction conditions, many catalysts including Pt, Pd, Ni, etc., dissolve carbon into the first few layers, especially in the case of supported catalysts since the small metal particles have many defects which aid the diffusion process. The mobility of carbon in these layers may have significant effects on the activity and selectivity of the catalysts. Also, the carbon might participate in the reaction mechanism in a manner analogous to metal oxide catalysis where oxygen from the catalyst is incorporated into the products and the catalyst is reoxidized by oxygen from the reactant stream. If bulk carbon in the catalyst does participate in the reaction mechanism, it might be possible to control the activity and selectivity of Fischer–Tropsch catalysts by varying the quantity and mobility of carbon in the catalysts. The fact that the activity and selectivity of iron catalysts in Fischer–Tropsch change as the iron is carburized (*18, 19*) suggests that this might be possible, although this is only one of many possible explanations for the changes in activity and selectivity.

ACKNOWLEDGMENTS

The authors thank G. S. Ranhotra for preparing the Mo_2C samples used in this study. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

REFERENCES

1. Muller, J. M., and Gault, F. G., *Bull. Soc. Chim. Fr.* **2**, 416 (1970).
2. Bohm, H., *Electrochim. Acta* **15**, 1273 (1970).

3. Sinfelt, J. H., and Yates, D. J. C., *Nature Phys. Sci.* **229,** 27 (1971).
4. Levy, R. B., and Boudart, M., *Science* **181,** 547 (1973).
5. Leclercq, L., Imura, K., Yoshida, S., Barbee, T., and Boudart, M., *in* "Preparation of Catalysts II," p. 627, Elsevier, Amsterdam/New York, 1979.
6. Boudart, M., Oyama, S. T., and Leclercq, L., *in* "Proceedings, 7th International Congress on Catalysis, 1980."
7. Kojima, I., Miyazaki, E., Inoue, Y., and Yasumori, I., *J. Catal.* **73,** 128 (1982).
8. Toth, L. E., "Transition Metal Carbides," Academic Press, New York, 1971.
9. Kojima, I., Miyazaki, E., Inoue, Y., and Yasumori, I., *J. Catal.* **59,** 472 (1979).
10. Kojima, I., Miyazaki, E., and Yasumori, I., *J. Chem. Soc. Chem. Commun.* 573 (1980).
11. Storms, E. K., "The Refractory Carbides." Academic Press, New York, 1967.
12. Oyama, S. T., and Haller, G. L., *in* "Catalysis" (G. C. Bond and G. Webb, Eds.), Specialist Periodical Reports, Vol. 5, p. 333. Chem. Soc., London, 1981.
13. Ranhotra, G. S., "Characterization of Molybdenum Carbide Catalysts." M.S. thesis, University of California, Berkeley, 1985.
14. Volpe, L., and Boudart, M., *J. Solid State Chem.* **59,** 348 (1985).
15. Ko, E. I., and Madix, R. J., *Surf. Sci.* **100,** L449 (1980).
16. Niemantsverdriet, J. W., and Van der Kraan, A. M., *J. Catal.* **72,** 385 (1981).
17. Niemantsverdriet, J. W., Van der Kraan, A. M., Van Dijk, W. L., and Van der Baan, H. S., *J. Phys. Chem.* **84,** 3363 (1980).
18. Amelse, J. A., Butt, J. B., and Schwartz, L. H., *J. Phys. Chem.* **82,** 558 (1978).
19. Raupp, G. B., and Delgass, W. N., *J. Catal.* **58,** 361 (1979).