

The Use of TPD and TPR to Study Subsurface Mobility: Diffusion of Oxygen in Mo₂C

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

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

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The application of temperature-programmed desorption (TPD) and reduction (TPR) to the study of subsurface diffusion in high surface area powders is considered. Although subsurface diffusion may be important in catalysis, relatively few techniques have been developed to study this process in high surface area materials. Since oxygen is very mobile in Mo₂C, we chose to study Mo₂C to illustrate how TPD and TPR can be used to study subsurface diffusion. In particular, the effect of the Mo : C ratio on the oxygen mobility is investigated. The TPR spectrum of oxygen adsorbed on Mo₂C contains two water peaks, a narrow one at 479 K, and a second much broader peak near 573 K. While the first peak is produced by surface oxygen, the second peak is caused by oxygen that diffuses into the subsurface region of the catalyst during the temperature ramp. As the surface becomes depleted at higher temperatures, this oxygen diffuses back to the surface, reacts with the gas-phase hydrogen, and desorbs as water. For carbon-deficient catalysts the two peaks merge into one asymmetric peak at 510 K with a tail extending to higher temperatures. A model is presented which gives a semiquantitative description of the effect of subsurface diffusion on TPD and TPR spectra. The model is able to explain the changes in the spectrum caused by varying the Mo : C ratio; the data cannot be explained by a model which assumes that the two peaks are due to two distinct adsorption sites on the surface. An important result of this work is that in cases in which a peak produced by subsurface diffusion is resolved, the activation energy for diffusion in the subsurface can be measured. © 1987 Academic Press, Inc.

INTRODUCTION

Temperature-programmed desorption (TPD) and related spectroscopies are useful tools for characterizing adsorption states on catalytic materials. A TPD spectrum contains one or more peaks which typically are produced by desorption of preadsorbed species from the surface. Multiple peaks may be produced by desorption from multiple adsorption states of different energies (surface heterogeneity) or they may be the result of lateral interactions between adsorbate molecules (induced heterogeneity) (1). Recently, low-temperature peaks in TPD spectra have been assigned to desorption of hydrogen absorbed in the subsurface or bulk regions of noble metals. For exam-

ple, Behm *et al.* (2) observed a desorption peak from Pd which was produced by hydrogen desorbing from subsurface adsorption sites. Also, Yates and co-workers (3) implanted hydrogen in Ni (111) and assigned low-temperature peaks in the TPD spectrum to desorption of hydrogen from the bulk. This paper investigates the effect of subsurface adsorption and diffusion on the temperature-programmed desorption and reduction (TPR) spectra from materials with high surface areas.

Since we have demonstrated that oxygen is mobile in Mo₂C (4), we chose to study Mo₂C to illustrate how TPD and TPR can be used to study subsurface diffusion. This system is particularly interesting because the oxygen mobility as well as the catalytic properties depend very strongly on the Mo : C ratio. Moreover, transition metal carbides in general have attracted a con-

¹ To whom correspondence should be addressed.

siderable amount of attention recently because they have shown promise as substitutes for noble metal catalysts. Most of the attention has focused on Mo_2C (5–17) and WC (7, 8, 14, 15, 17–23).

In a previous paper (4) we used TPR of oxygen adsorbed on Mo_2C to probe changes in the catalyst caused by different pretreatment conditions. We found that the spectrum contained two water peaks, a narrow one located between 483 and 513 K, and a second much broader peak between 573 and 586 K. The location of these peaks depended on the Mo:C ratio of the sample. In that paper (4), we suggested that the second peak was not the result of a second surface site, but instead might be caused by diffusion of oxygen into the subsurface layers of the carbide. This assignment was based on three pieces of information: (1) the extreme broadness of the peak, (2) the anomalous variations of the peak size and temperature with Mo:C ratio, and (3) the high mobility of oxygen in Mo_2C at room temperature and above. In this study, we present more definitive data which show that the second peak is indeed the result of oxygen diffusion between the surface and the subsurface. We also present a numerical model to account for the effect of subsurface diffusion on temperature-programmed desorption (TPD) and TPR spectra.

EXPERIMENTAL

Apparatus

The apparatus used for this study has been described previously (4). The catalyst was placed in a quartz microreactor which could be heated linearly to 1200 K at rates ranging from 0.01 to 5 K/s. The system is interfaced to an IBM PC which was used for data acquisition and control.

Materials

The Mo_2C catalysts used in this study were prepared according to the procedure described by Boudart *et al.* (9). X-ray dif-

fraction (XRD) patterns indicated that the catalyst was predominantly hcp Mo_2C and contained less than 5% Mo by weight. As before, there was no evidence in the XRD patterns of oxide formation despite the fact that the samples had been exposed to the air for several months and contained the equivalent of more than nine monolayers of oxygen. The BET area of the catalyst was approximately 4 m^2/g ; this varied only slightly after different pretreatments.

Hydrogen (99.995%) was purified by passing it through a bed of 0.3% Pd/SiO₂ (heated to 450 K) to convert traces of oxygen to water, and the water was removed by molecular sieves cooled by a dry ice-ethanol bath. Traces of oxygen 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 trap water in the oxygen (Liquid Carbonic certified standard 20.6% O₂ in He). Because of a relatively high water background in the mass spectrometer, deuterium (98.5% D) was used instead of hydrogen to obtain the TPR spectra of chemisorbed oxygen. The deuterium was purified by the same method as that used to purify the hydrogen.

Experimental Procedure

Before each TPR spectrum was measured, the catalyst was pretreated in one of three ways. By varying the pretreatment conditions, the Mo:C ratio of the catalyst could be varied, and thus it was possible to study the effect of this ratio on the TPR spectra. In each case, 100 mg of catalyst was placed in the reactor and evacuated at 0.1 Torr or less for at least 1 h. Then the catalyst was reduced by heating in 100 cm^3 (STP)/min of flowing deuterium according to one of three temperature schedules which will be described later. After reduction, the catalyst was evacuated for 5 min at the final temperature and then cooled under helium to 298 K.

Oxygen was adsorbed on the freshly pre-treated catalyst by injecting known quantities into a helium carrier gas which flowed over the sample. Following a 5-min evacuation at 298 K, deuterium was flowed over the catalyst and the temperature was raised linearly while monitoring the products with the mass spectrometer. Then the catalyst was reduced for 5 min at the final ramp temperature to completely remove all of the adsorbed oxygen. After a 5-min evacuation, the catalyst was cooled to room temperature and was ready for subsequent TPR experiments.

EXPERIMENTAL RESULTS

TPR of Air-Exposed Mo₂C

As discussed in our earlier paper (4), when Mo₂C is exposed to the air, it continues to incorporate oxygen over several months. This oxygen does not desorb as molecular oxygen, but can be removed from the sample by a reduction in hydrogen. However, the carbon in the catalyst also reacts with the hydrogen and is removed mainly as methane. The relative rates at which carbon and oxygen are removed from the sample as a function of temperature are shown in the temperature-programmed reduction spectrum in Fig. 1. For this experiment, hydrogen was used instead of deuterium so that methane could be easily distinguished from water in the

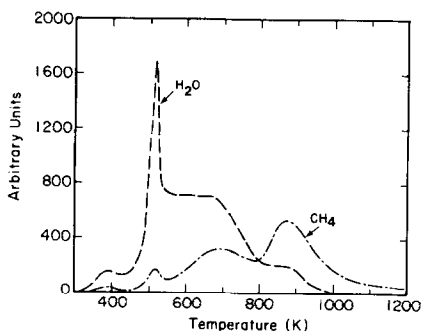


FIG. 1. TPR spectrum of Mo₂C after exposure to air for several months. H₂ flow rate = 100 cm³/min (STP), heating rate = 1 K/s.

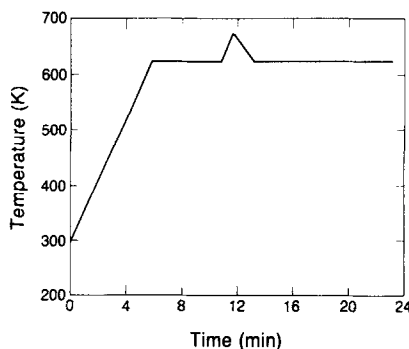


FIG. 2. Temperature schedule used during low-temperature reduction (LTR).

mass spectrometer. As discussed in our earlier paper, the first water peak is produced by water that was not removed by the evacuation. The other water peaks are attributed to the reaction of the hydrogen with oxygen in the sample. The amount of oxygen removed is the equivalent of over nine monolayers, assuming that one monolayer consists of one oxygen atom per surface Mo atom and that there are 1.1×10^{19} surface Mo atoms/m².

In our earlier paper (4), we also found that we could remove all the oxygen from the near surface region without removing much carbon. This was accomplished by reducing the catalyst in hydrogen while heating it according to the temperature schedule shown in Fig. 2. We referred to this pretreatment as "low-temperature reduction" (LTR). Conversely, if we reduced in hydrogen for 15 min at 873 K, we removed 14.5% of the carbon originally contained in the sample, and greatly increased the Mo:C ratio at the surface. This pretreatment was referred to as "high-temperature reduction" (HTR). Thus by varying the pretreatment conditions, we were able to vary the Mo:C ratio in the sample.

TPR Spectra of Oxygen after Low-Temperature Reduction

Figure 3 shows TPR spectra of oxygen adsorbed on an Mo₂C catalyst that was

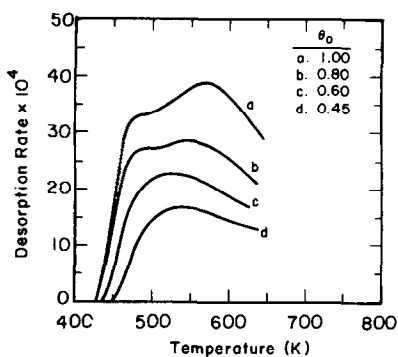


FIG. 3. TPR spectra of oxygen adsorbed on LTR-activated Mo_2C as a function of the initial surface coverage.

activated by low-temperature reduction. Before each spectrum was measured, the sample was dosed with differing amounts of oxygen corresponding to initial coverages between 0.45 and 1.0. In each case, the heating rate used was 1 K/s. At saturation ($\theta = 1$), one oxygen atom was adsorbed per surface Mo atom, assuming there are 1.1×10^{19} Mo atoms/ m^2 . From this we conclude that the oxygen is adsorbed dissociatively on the surface, and no surface oxide is formed.

As shown in the figure, the TPR spectrum contains two peaks when $\theta_0 = 1$, a relatively narrow peak at 479 K, and a second much broader peak at 570 K. These peak temperatures agree quite well with those obtained in the previous study (4) with a different Mo_2C catalyst, but the peaks are not as well resolved. The activation energies for each peak were measured by the heating rate variation method (24) and found to be 9.3 kcal/mole for the first peak and 18.0 kcal/mole for the second. For this measurement, the heating rate was varied from 0.3 to 3.0 K/s, and the results were quite reproducible.

The presence of two peaks in a TPD or TPR spectrum often indicates the existence of one or more surface states on the catalyst surface (1). Therefore, the results shown in Fig. 3 suggest that there are two distinct types of sites present for oxygen

chemisorption on the Mo_2C catalyst. However, it is difficult to explain the coverage dependence of these spectra in the context of a two-site model. The broadness of the second peak could be explained either by assuming that readsorption of water on this site is important, or by assuming that the activation energy is coverage-dependent for this site. However, in either case, the peak should shift to higher temperatures as the initial coverage decreases (25). As shown in Fig. 3, this peak shifts to lower temperatures with decreasing oxygen coverage.

This apparently anomalous shift in peak temperature could be explained by assuming that the rate of reaction of hydrogen with the oxygen follows a rate expression of the form

$$R_d = k_d \theta (1 - \theta)^n, \quad [1]$$

where θ is the oxygen coverage. However, this type of rate expression should produce a very narrow peak, in contrast to the observed broadness of the second peak. Furthermore, if the two peaks result from adsorption on two sites, then as the initial coverage decreases, the low-temperature peak should disappear before the high-temperature peak since the highest energy sites are expected to fill first. This type of behavior was not observed. Comparison of the spectra for $\theta_0 = 1.0$ and $\theta_0 = 0.8$ reveals that the sizes of *both* peaks decrease as the initial coverage decreases, and the second peak shrinks more than the first. Thus, we can conclude that the two peaks are not the manifestation of two distinct adsorption sites on the surface of the catalyst. We believe that the high-temperature peak is caused by oxygen that diffuses into the subsurface during heating and then back to the surface when the surface becomes depleted at higher temperatures.

To test whether oxygen diffused into the subsurface during the temperature ramp, we conducted the following experiment. The surface of the catalyst was saturated with oxygen at 298 K. Then the catalyst

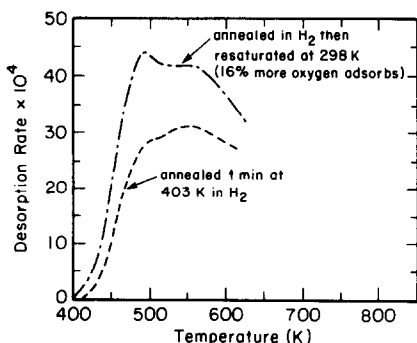


FIG. 4. TPR spectrum of oxygen on LTR-activated Mo_2C after saturating the surface at 298 K, annealing in deuterium for 1 min at 400 K (lower curve), and resaturating with oxygen at 298 K (upper curve).

was heated to 403 K at 1 K/s in flowing deuterium and annealed at this temperature for 1 min. Subsequently, the catalyst was evacuated for 5 min at 403 K and cooled to 298 K. During the anneal period less than 1% of the oxygen reacted with the deuterium and desorbed. However, upon cooling to 298 K, 16% more oxygen adsorbed on the catalyst surface. This strongly suggests that oxygen diffused into the subsurface during the anneal, and this has a significant effect on the TPR spectrum as shown in Fig. 4.

The upper curve in Fig. 4 shows the TPR spectrum obtained following saturation with oxygen at 298 K, a 1-min anneal in deuterium at 403 K, and subsequent resaturation with oxygen at 298 K. Also shown in the figure is the TPR spectrum for the case in which the catalyst was not resaturated with oxygen following the anneal in deuterium. The desorption rate from the resaturated sample is higher at all temperatures. Also the relative height of the first peak to the second peak is higher when the catalyst surface is resaturated than when it is not.

We also observed that shorter evacuation times at 403 K had a negligible effect on the amount of oxygen that could be read-sorbed. Thus oxygen diffusion is apparently much faster in the presence of deuterium than *in vacuo*. This is consistent with a

further observation that it was necessary to heat the catalyst in helium for 10 min at 573 K to allow the same amount of oxygen to diffuse into the subsurface as had diffused during the 1-min anneal in deuterium at 403 K.

The results presented above show that the two peaks in the TPR spectrum of the catalyst activated by LTR are not caused by two distinct surface sites. Moreover, the results strongly suggest that the second peak is produced by oxygen that diffused into the subsurface during the temperature ramp and then came back out when the surface became depleted. In our previous paper (4) we showed that the relative height of the second peak compared to the first decreased as the catalyst became more carbon deficient. If the second peak is due to diffusion as suggested, then this would indicate that less oxygen diffuses into the subsurface when the $\text{Mo}:\text{C}$ ratio is increased. Therefore, we need to check whether this is indeed the case.

TPR Spectra of Oxygen after High-Temperature Reduction

Figure 5 shows TPR spectra of an Mo_2C sample that was activated by high-temperature reduction and subsequently dosed with oxygen. The initial surface coverage was varied from 0.53 to 1.0. The spectra contain one narrow peak at 510 K with a long tail at

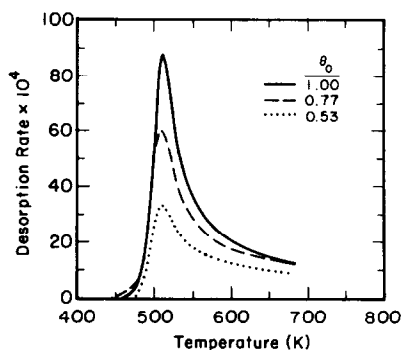


FIG. 5. TPR spectra of oxygen adsorbed on HTR-activated Mo_2C as a function of the initial surface coverage.

higher temperatures. This peak temperature is consistent with the results reported in our previous paper (4) for a different Mo_2C catalyst. Unlike the previous results, however, a second high-temperature peak is not resolved. Since the location of the sharp peak is independent of the initial oxygen coverage, we conclude that the reaction rate (or desorption rate) is first order in oxygen coverage. Also, water readsorption is negligible since this would cause the peak temperature to increase with decreasing coverage (25). Moreover, the activation energy must not be coverage dependent on the carbon-deficient surface since this would also cause a shift in the peak temperature with initial coverage. The activation energy of the narrow peak was measured as 15.2 kcal/mole by the heating rate variation method (24). This is significantly larger than 9.3 kcal/mole measured on the more carbon-rich catalyst activated by LTR, suggesting that oxygen is held more strongly on the carbon-deficient surface.

The fact that the high-temperature peak is unresolved in the TPR spectrum of the carbon-deficient catalyst suggests that less oxygen diffused into the subsurface during the temperature ramp. To test this hypothesis, we repeated the annealing experiment described above. During this annealing procedure, less than 0.5% of the oxygen reacted with the deuterium and desorbed; yet after it cooled to 298 K, we were able to readsorb an additional 3% of oxygen. Therefore, diffusion of oxygen into the subsurface does take place during the 1-min anneal in deuterium; however, the rate of diffusion is measurably lower for the highly carbon-deficient surface than for the relatively carbon-rich catalyst.

If we replaced the 1-min anneal in deuterium at 403 K with a 15-min anneal in helium at 773 K, we found that a significant amount of oxygen diffused into the subsurface of the carbon-deficient catalyst. In this experiment, the catalyst was saturated with oxygen at 298 K, and subsequently heated at 1

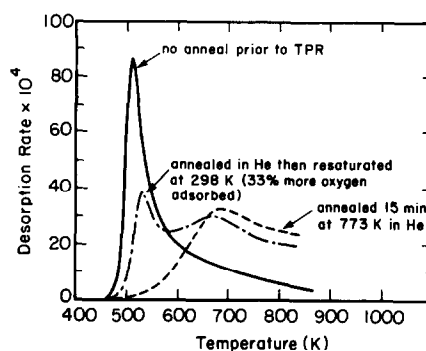


FIG. 6. TPR spectrum of oxygen on HTR-activated Mo_2C after saturating the surface at 298 K (bold curve), annealing in helium for 15 min at 773 K (dashed curve), and resaturating the surface at 298 K (dot-dashed curve).

K/s to 773 K in flowing helium and held there for 15 min. During this anneal in helium, nothing desorbed from the catalyst; yet after cooling to 298 K, 33% more oxygen could be readsorbed on the surface. This has a marked effect on the TPR spectrum as shown in Fig. 6.

Figure 6 shows three different TPR spectra of oxygen on the HTR-activated Mo_2C catalyst. The bold curve is the TPR spectrum shown in Fig. 5 for a saturated surface. The dashed curve is the TPR spectrum obtained after saturating the surface with oxygen at 298 K, and then annealing for 15 min in helium at 773 K. As seen in the figure, the narrow peak at 510 K is removed by the annealing process and is replaced by a second much broader peak at 690 K. If after annealing in helium, the catalyst is cooled to 298 K and resaturated with oxygen, the narrow peak reappears in the spectrum along with the second broader peak, as shown by the dot-dashed curve. The broadness of the peak produced by annealing the sample indicates that diffusion of oxygen into the subsurface produces a broad peak in the TPR spectrum. This is further evidence that the second peak in the TPR spectrum after LTR is due to oxygen that diffused into the subsurface during the temperature ramp.

TPR Spectra of Oxygen as a Function of Mo : C Ratio

The results presented above suggest that as the catalyst becomes more carbon deficient, the amount of oxygen that diffuses into the subsurface decreases. As a result, the relative height of the second peak compared to the first peak decreases. This trend is shown more clearly in Fig. 7a. This figure shows the TPR spectra from oxygen-saturated surfaces of Mo_2C samples which were activated by low- (dotted curve) and high- (solid curve) temperature reduction. Also shown are two additional spectra at intermediate levels of carbon deficiency. The dashed curve is the spectrum obtained after a 15-min reduction at 823 K. This does not remove quite as much carbon as the high-temperature reduction. The other curve is the spectrum obtained on a catalyst that was activated by low-temperature reduction and then subjected to several TPRs up to 650 K. During each TPR, a small amount of carbon was removed so that this catalyst became slightly more carbon deficient than the one activated by LTR.

It is clear from Fig. 7a that the relative size of the second peak decreases as the sample becomes more carbon deficient. Also, the temperature difference between the two peaks decreases. Eventually the second peak merges into the first, as shown

by the spectrum of the HTR-activated sample. The activation energy of the first peak was measured for each curve and increased from 9.3 to 12.1 to 15.0 to 15.2 kcal/mole as the sample became more carbon deficient. Thus it appears that oxygen is held more strongly as the sample becomes more carbon deficient, and that the rate of diffusion into the subsurface decreases.

Effect of Deuterium Flow Rate on the TPR Spectra

Before attempting to model the TPR spectra, we wanted to verify that the spectra were not affected either by readsorption of water or by slow diffusion in the pores of the catalyst. To do this, we examined how the TPR spectrum varied with deuterium flow rate. If flow rate has no effect on the TPR spectrum, then it can be concluded that readsorption is not important and that pore diffusion limitations do not affect the spectra. Figure 8 shows the effect of deuterium flow rate on the TPR spectrum of a moderately carbon-deficient Mo_2C sample. From this figure, we can conclude that readsorption and pore diffusion limitations are not significant.

The observed changes in the TPR spectrum when the deuterium flow rate is varied are also inconsistent with a model which

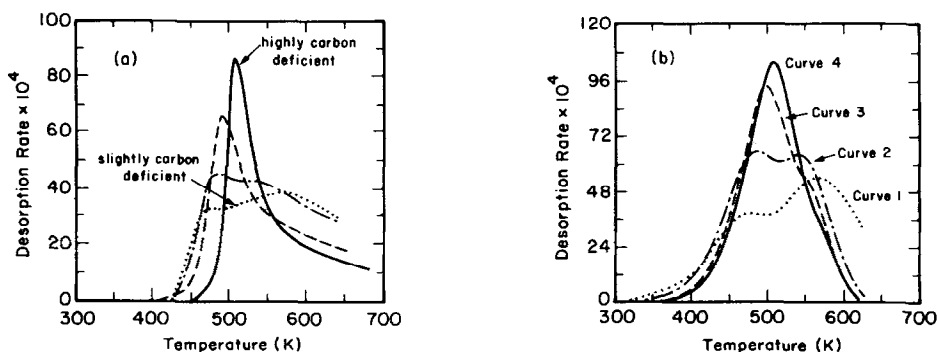


FIG. 7. (a) TPR spectra of oxygen adsorbed on Mo_2C as a function of the Mo : C ratio. After LTR, the catalyst is only slightly carbon deficient; after HTR, it is highly carbon deficient. Also shown are two intermediate cases described in the text. (b) Simulated TPR spectra for the four cases considered in Table 1.

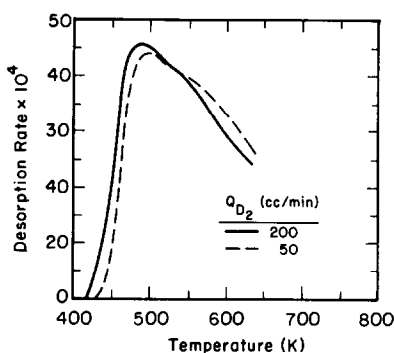


FIG. 8. Effect of D_2 flow rate on the TPR spectrum.

assumes that the two peaks are the result of two distinct adsorption sites. In such a model, the broadness normally would be attributed to readsorption, and the resolution between the peaks should increase with increasing flow rate. However, the opposite behavior is observed. This decrease in resolution is consistent with the subsurface-diffusion model. Since a slightly higher deuterium pressure is required for the higher flow rate, the rate of reaction (water desorption) is larger at the higher flow rate. The higher deuterium pressure does not affect the rate of diffusion into the subsurface; therefore, the rate of surface reaction increases relative to the rate of subsurface diffusion as the flow rate increases. As a result, less oxygen diffuses into the subsurface during the temperature ramp, and the relative size of the second peak decreases as seen in the figure.

The results presented above provide strong evidence that the second peak in the TPR spectrum of oxygen adsorbed on Mo_2C is caused by oxygen that diffuses into the subsurface during the temperature ramp. To aid in interpreting these results we now present a numerical model which accounts for the effect of subsurface diffusion on TPD and TPR spectra.

MODEL

Any quantitative model to describe TPD or TPR spectra in which subsurface diffu-

sion of adsorbates is significant would involve a large number of parameters. Since the values of many of the parameters cannot be measured independently, they would become adjustable parameters, and this would make discrimination between models difficult. Therefore, in the model presented below, we have not included many of the complexities required to model the system quantitatively. The purpose of this model is to demonstrate that subsurface diffusion of adsorbates can produce extra peaks in a TPD or TPR spectrum. We also hope to gain a semiquantitative understanding of how subsurface diffusion affects the TPD or TPR spectrum. Although the model is developed to describe TPR spectra of oxygen on Mo_2C , it can easily be adapted to any system in which subsurface diffusion is important.

The model is shown schematically in Fig. 9. The surface is assumed to be energetically homogeneous. A fraction of the surface sites, θ , is covered by preadsorbed oxygen. As the sample temperature is raised, this oxygen can either react with the gas-phase hydrogen and desorb as water with rate R_d , or penetrate into the subsurface layers of the catalyst with rate R_p . It is expected that the oxygen will penetrate only a small number of atomic layers during the temperature ramp; therefore, it is inap-

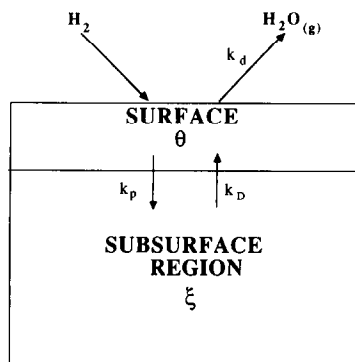


FIG. 9. Schematic of the model. Surface oxygen can react with gas-phase hydrogen and desorb as water, or diffuse into the subsurface during the temperature ramp.

appropriate to use a distributed model for diffusion such as Fick's law. For simplicity, we have chosen a lumped formulation for subsurface diffusion. Oxygen penetrates into a subsurface region of N atomic layers and distributes itself evenly in this region, filling a fraction, ξ , of the available subsurface sites. At higher temperatures, when the surface becomes depleted, the oxygen diffuses out of the subsurface back to the surface at a rate R_D .

Since the location of the first, narrow peak in the TPR spectrum of carbon-deficient Mo_2C showed no dependence on the initial oxygen coverage, we conclude that the reaction of adsorbed oxygen with hydrogen is first order in oxygen coverage. We also conclude that readsorption is not significant, and that the activation energy for desorption is not a strong function of coverage. These conclusions may not be valid for the relatively carbon-rich catalyst for which the location of the first peak did vary with the initial coverage. Nevertheless, to keep from adding additional parameters to the model, we make these assumptions for the carbon-rich catalyst as well. We also neglect diffusion limitations in the pores of the catalyst. With these assumptions, we can express the desorption rate simply as

$$R_d = \nu_d \exp(-E_d/RT)\theta, \quad [2]$$

where R_d is the desorption rate (s^{-1}), E_d is the desorption activation energy (kcal/mole), ν_d is the preexponential factor (s^{-1}) which is assumed to be independent of temperature and coverage, and θ is the surface coverage.

The rate of penetration of oxygen into the subsurface is assumed to be first order in the surface oxygen coverage, and first order in the fraction of subsurface sites available. Since this is an activated process, it is assumed to follow the Arrhenius expression given in Eq. [3],

$$R_p = \nu_p \exp(-E_p/RT)\theta(1 - \xi), \quad [3]$$

where R_p is the penetration rate (s^{-1}), E_p is

the activation energy for penetration, ν_p is the preexponential factor for penetration, and ξ is the fraction of filled subsurface sites. It is assumed that the preexponential factor and activation energy for diffusion are independent of coverage. In a similar manner, the rate of diffusion of oxygen from the subsurface back to the surface is assumed to be first order in the fraction of filled subsurface sites and available surface sites. This is expressed as

$$R_D = \nu_D \exp(-E_D/RT)(1 - \theta)\xi, \quad [4]$$

where R_D is the rate of diffusion, and ν_D and E_D are the preexponential factor and activation energy for diffusion, respectively.

These reaction and diffusion rate expressions can be combined with unsteady-state material balances on the surface and subsurface regions to describe the time evolution of the system,

$$d\theta/dt = -k_d\theta - k_p\theta(1 - \xi) + k_D(1 - \theta)\xi \quad [5]$$

$$d\xi/dt = (1/M)[k_p\theta(1 - \xi) - k_D(1 - \theta)\xi], \quad [6]$$

where

$$k_i = \nu_i \exp(-E_i/RT) \quad [7]$$

and M is the ratio of the total number of subsurface sites to the total number of surface sites. For TPD or TPR experiments, the temperature is varied in a linear fashion, so we can write

$$dT/dt = \beta. \quad [8]$$

We now have the equations which describe the system. Examination of Eqs. [5]–[7] reveals that there are seven parameters that must be set in the model: three preexponential factors (ν_d , ν_p , ν_D), three activation energies (E_d , E_p , E_D), and the relative capacity of the subsurface for oxygen (M). For each of the TPR spectra shown in Fig. 7a, the desorption activation energy, E_d , was measured by the heating rate variation method (24). For LTR-activated samples, it was possible also to

measure the activation energy for the second peak in a similar manner. If the spectrum is subsurface diffusion limited, this activation energy should correspond to E_D . This was verified by simulating a heating rate variation experiment and comparing the calculated value of E_D to the actual value input to the model. The value of E_D was not measurable for the other three spectra due to the poor resolution, and must therefore be left as an adjustable parameter. The remaining parameters are also unknown. However, we can estimate values for each of the parameters as a first guess, and then iterate on those estimates to obtain a best fit of the spectra.

It seems reasonable that the activation energy for penetration into the subsurface should not be very different from the activation energy for diffusion from the subsurface to the surface. Therefore, as a first guess, E_p was set equal to E_D . Then in the iteration procedure used to fit the spectra, the value of E_p was not allowed to vary from that of E_D by more than 1 kcal/mole. Since the system being modeled is TPR of adsorbed oxygen, we do not expect the preexponential factor for "desorption" (or reaction) to be the same as it would be for a simple first-order desorption process (10^{15} s^{-1}). In this case, the preexponential factor must incorporate the adsorption/desorption kinetics of hydrogen. However, it is possible to obtain a good estimate of ν_d from the desorption data. This is done by simulating a first-order desorption process with the measured value of E_d and determining the value of ν_d which yields the correct peak temperature. As seen in Table 1, the values of ν_d which best fit the data are many orders of magnitude lower than the values expected for a simple first-order desorption process.

For the LTR-activated sample, since E_D was measurable we used the same approach to obtain an estimate of ν_D . By assuming that ν_D is unaffected by the Mo:C ratio, this estimate of ν_D could be used for each spectrum in Fig. 7a. Furthermore, we

TABLE 1
Parameter Values Used to Simulate TPR Spectra

	Curve 1	Curve 2	Curve 3	Curve 4
ν_d (s^{-1})	130	3800	75,000	75,000
E_d (kcal/mole)	9.3	12.1	15.0	15.2
ν_p (s^{-1})	1.9×10^6	1.9×10^6	1.9×10^6	1.9×10^6
E_p (kcal/mole)	17.5	18.0	19.2	20.0
ν_D (s^{-1})	1.9×10^6	1.9×10^6	1.9×10^6	1.9×10^6
E_D (kcal/mole)	18.0	18.2	19.0	19.5
M	1.0	1.0	1.0	1.0

assume that the preexponential factor for diffusion between the surface and the subsurface is the same ($\nu_p = \nu_D$). Thus we have estimates for all three of the preexponential factors for each Mo:C ratio. The most difficult parameter to estimate is the value of M . Since we believe that the oxygen only penetrates a few layers into the subsurface during the ramp, we arbitrarily set the value of $M = 1$ (the subsurface capacity is the same as the surface oxygen capacity).

MODEL RESULTS

Figure 10 presents a simulation of the TPR spectrum for a Mo_2C catalyst activated by low-temperature reduction. For this simulation, the initial surface oxygen coverage was set equal to unity. This simulation can be compared to the experimental spectrum shown in Fig. 3 for $\theta_0 = 1$. The values of the parameters used in this simu-

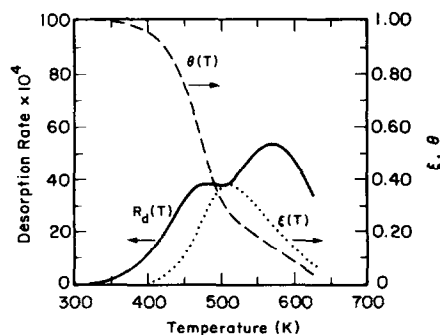


FIG. 10. Simulated TPR spectrum of oxygen adsorbed on LTR-activated Mo_2C . Changes in the surface and subsurface oxygen coverage as a function of temperature are also shown.

lation are listed in the first column of Table 1. Also shown in Fig. 10 are the surface and subsurface oxygen concentration profiles. From this figure we see that at lower temperatures, oxygen is removed from the surface by both desorption and diffusion into the subsurface. As the surface becomes depleted of oxygen, the desorption spectrum goes through a maximum and then decreases, producing the first peak. As the surface coverage approaches zero, oxygen starts diffusing from the subsurface back to the surface, and the TPR spectrum becomes diffusion limited. As the temperature increases, the rate of diffusion increases so the desorption rate increases. Eventually, the subsurface also becomes depleted, and the desorption goes through another maximum and decreases again, producing the second peak. Thus, it's clear from Fig. 10 that subsurface diffusion can lead to an extra peak in a TPD or TPR spectrum.

In a similar manner, simulations were made of each of the TPR spectra shown in Fig. 7a for various levels of carbon deficiency; the results are shown in Fig. 7b. The values of the parameters used to simulate each spectrum are listed in Table 1. As seen in Fig. 7b, the model reproduces the changes in the relative heights of the first and second peak as the sample becomes more carbon deficient. This variation is caused by a decrease in the rate of diffusion of oxygen into the subsurface relative to the rate of desorption, although both rates decreased with increasing carbon deficiency. This is consistent with the observation that less oxygen diffused into the subsurface region of HTR-activated Mo_2C than into LTR-activated Mo_2C during a 1-min anneal in deuterium at 403 K. The model also indicates why the peaks move closer together as the catalyst becomes more carbon deficient. This is caused by a larger increase in E_p than in E_D as the sample becomes more carbon deficient.

Comparison of the simulated spectra in Fig. 7b with the experimental spectra in

Fig. 7a reveals some interesting differences. The simulated values for the desorption rate at each temperature are slightly higher than the experimentally measured values. This suggests that a significant amount of the oxygen that diffuses into the subsurface does not desorb completely during the temperature ramp. This is consistent with the experimental results; examination of Fig. 7a reveals that a large amount of oxygen continues to desorb as water at the end of the temperature ramp. In fact, it was necessary to reduce the catalyst an additional 5 min at the final ramp temperature to remove all of the oxygen that was adsorbed originally. This was confirmed by integrating the area under the TPR spectrum. The probable reason why the model overestimates the desorption rate is that it does not account for the fact that the oxygen is inhomogeneously distributed over several subsurface layers.

The first peak in the simulated spectrum for each case is significantly broader than what is experimentally observed, and the second peak is slightly narrower. We believe that the reason the model predicts a broader first peak is because it oversimplifies the kinetics and the mechanism of the reaction of hydrogen with surface oxygen and the subsequent desorption of water. The probable reason why the second peak in the simulated spectra is slightly narrower than the experimental peak is because we have not accounted for the gradient in the subsurface oxygen concentration.

Despite the discrepancies between the simulated and experimental TPR spectra, we have been able to show with a simple model that subsurface diffusion can produce an extra peak in a TPD or TPR spectrum.

DISCUSSION

The results presented above have shown that the two peaks in the TPR spectrum of oxygen on Mo_2C are not caused by two distinct adsorption sites for oxygen on the surface of the catalyst. Such a model can-

not explain the broadness of the second peak and its shift to lower temperatures with decreasing initial coverage. It also cannot explain the observation that after saturating the surface of Mo_2C with oxygen at 298 K, annealing in deuterium at 403 K frees surface sites for the adsorption of additional oxygen despite the fact that nothing desorbs.

Instead, we have shown that the second peak is produced by initially adsorbed oxygen which diffused into the subsurface region during the temperature ramp. Such a diffusion-limited peak is expected to be very broad if the oxygen in the subsurface is distributed over several layers. As shown by the annealing experiments, the rate at which surface oxygen penetrates into the subsurface decreases as the catalyst becomes more carbon deficient. This change in oxygen mobility causes the observed change in the relative heights of the two peaks in the TPR spectrum. Furthermore, if the activation energy for penetration, E_p , increases more than the activation energy for diffusion from the subsurface to the surface, E_D , then the two peaks in the TPR spectrum should move closer together as the Mo:C ratio increases. This was observed experimentally.

Another possible explanation for the data presented above is that a second state of more strongly bound surface oxygen is created during the temperature ramp. However, this explanation is inconsistent with our previous observation that more than nine monolayers of oxygen could be removed from an air-exposed Mo_2C sample during activation. For this to occur, oxygen must be able to diffuse from the subsurface to the surface of the catalyst. Therefore, we conclude that this second peak is produced by diffusion between the surface and the subsurface region of the catalyst during the temperature ramp.

An interesting observation in this study is that a 10-min anneal in helium at 773 K is necessary to allow the same amount of oxygen to diffuse into the subsurface region

as diffuses during a 1-min anneal in deuterium at 403 K. This suggests that hydrogen (or deuterium) facilitates oxygen transport in Mo_2C , perhaps by producing a mobile OH species. This is consistent with an observation in our earlier paper (4) that carbon mobility in Mo_2C was higher in the presence of hydrogen than in helium.

It is important to note that the competition between desorption and diffusion of adsorbates into the subsurface layers of catalysts during TPD or TPR is not confined to oxygen on Mo_2C . This competition exists in any system in which adsorbed atoms or molecules are small enough to diffuse into the subsurface region. For example, we have also found that subsurface diffusion of hydrogen in Pd can lead to an extra peak in the TPD spectrum of hydrogen on Pd/ SiO_2 (26). Whether or not a diffusion-limited peak is seen in the spectrum and how far it is separated from the surface desorption peaks depends on the relative rates of desorption and subsurface diffusion. As a result, care should be taken when assigning TPD peaks to different sites on a catalyst surface.

An important result of this work is that when a peak due to subsurface diffusion is well resolved, it is possible to measure the activation energy for diffusion from the subsurface to the surface by the same technique used to measure desorption activation energies; namely, the heating rate variation method (24). This activation energy is not necessarily the same as the bulk diffusion activation energy which can be measured by other methods.

The observation that subsurface mobility has a pronounced effect on a TPD or TPR spectrum suggests that this technique might be useful in studying the role of carbon, oxygen, and hydrogen mobility in catalysts. It is interesting to note that one very good hydrogenation catalyst is palladium which absorbs hydrogen. One might speculate that subsurface mobility of hydrogen is important to the catalysis over this metal. This is under further investigation.

APPENDIX: NOMENCLATURE

E_d	Desorption activation energy (kcal/mole)
E_D	Activation energy for diffusion from the subsurface to the surface (kcal/mole)
E_p	Activation energy for penetration of surface oxygen into the subsurface region (kcal/mole)
k_d	Rate constant for desorption (s^{-1})
k_D	Rate constant for diffusion from the subsurface to the surface (s^{-1})
k_p	Rate constant for penetration of surface oxygen into the subsurface region (s^{-1})
M	Ratio of the number of subsurface sites available for oxygen to the number of available surface sites
n	Desorption order
N	Number of atomic layers over which subsurface oxygen diffusion occurs
R	Gas constant (kcal/mole K)
R_d	Desorption rate (s^{-1})
R_D	Rate of diffusion from the subsurface to the surface (s^{-1})
R_p	Rate of penetration of surface oxygen into the subsurface region (s^{-1})
t	Time (s)
T	Temperature (K)
β	Heating rate (K/s)
θ	Surface adsorbate coverage
θ_0	Initial surface coverage of adsorbate
ξ	Fraction of subsurface sites filled
ν_d	Preexponential factor for desorption (s^{-1})
ν_D	Preexponential factor for diffusion from the subsurface to the surface (s^{-1})
ν_p	Preexponential factor for penetration of surface oxygen into the subsurface region (s^{-1})

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