

Reactions of Acetaldehyde and Ethanol on W(100) and W(100)-(5 × 1)C Surfaces

E. I. KO¹ AND R. J. MADIX

Department of Chemical Engineering, Stanford University, Stanford, California 94305

Received February 9, 1981; revised September 9, 1981

The reactions of acetaldehyde and ethanol were studied on clean and carburized W(100) surfaces using temperature-programmed reaction spectroscopy (TPRS). On a clean tungsten surface the room-temperature adsorption of either molecule resulted in complete dissociation into adsorbed hydrogen, carbon, and oxygen atoms at low exposures. With increasing exposures acetaldehyde, ethanol, ethylene, and methane were observed to form as additional reaction products via an ethoxy surface intermediate. Passivation of the tungsten surface, either by the initial breakup of the parent molecule or by the deposit of carbon from cracking ethylene, resulted in markedly different product distributions. In particular, methane formation from C-C bond scission was eliminated by carbide formation, C-O bond rupture was reduced somewhat, and the reduction of surface oxygen to form water was enhanced. In the case of ethanol the dehydrogenation/dehydration selectivity was increased by a factor of 5 on the carbide surface. Formation of surface oxygen or surface alkoxide groups promoted a lower energy pathway for decomposition to all products.

1. INTRODUCTION

The high cost of precious metal catalysts (Pt, Rh, for example) provides a strong economic incentive for the search of their substitutes. The similarity in the chemical activities between platinum and tungsten carbide, first noted by Levy and Boudart (1) suggests transition metal carbides to be a viable alternative. Previous results from our laboratory on the chemisorption and surface reactions of simple molecules on W(100) have shown that surface composition significantly affects the reactivity of tungsten (2-4). Passivation of an otherwise very reactive tungsten surface was achieved by carburization, thus leading to an enhanced selectivity for hydrocarbon formation for the reactions of formaldehyde and methanol. In an attempt to further characterize and understand this general behavior and to assess the applicability of tungsten carbide as a catalytic material, we have extended the earlier investigation to

the C₂ compound of aldehyde and alcohol. In this paper the results for the decomposition of acetaldehyde and ethanol on clean and carburized W(100) surfaces will be presented.

2. EXPERIMENTAL

The experimental system and techniques employed in this study have been described in detail elsewhere (2, 3). All data were obtained in a conventional stainless-steel UHV chamber with LEED and AES capabilities. The system was also equipped with a quadrupole mass spectrometer to monitor reaction products. A linear heating rate of 30 K s⁻¹ was used in all temperature-programmed reaction spectroscopy (TPRS) experiments reported here. The cleaning and carburization of the W(100) sample followed the standard procedure outlined before (2).

Samples of acetaldehyde and ethanol were prepared and purified by methods previously reported (5, 6). Before use the reactant was immersed in a constant temperature bath (dry-ice-acetone for acetaldehyde, chlorobenzene-liquid nitrogen for

¹ Present Address: Department of Chemical Engineering, Carnegie-Mellon University, Pittsburgh, Pa 15213.

ethanol) and pumped on continuously until a constant vapor pressure was achieved. After this procedure the sample was admitted into the gas manifold just prior to dosing in order to minimize cracking in the line. Admission of the reactant onto the surface was done through a 22-gauge stainless-steel needle to provide a collimated beam onto the front face of the crystal. The formation of acetaldehyde, ethanol, ethylene, methane, water, carbon monoxide, carbon dioxide, and hydrogen was monitored by $m/e = 29, 31, 27, 16, 18, 28, 44,$ and $2,$ respectively. For each product other major mass cracking fractions were also checked for consistency, and corrections were made for contributions from other desorbing species with overlapping mass fragments. Quantitative yields were calculated using the procedure published elsewhere (3). The concentrations of adsorbed carbon and oxygen were determined by AES (2).

The reactions of acetaldehyde and ethanol led to carbon and oxygen deposits on an initially clean tungsten surface. This neces-

sitated cleaning the surface after each adsorption/desorption cycle by (i) heating the crystal to 1500 K to desorb CO (β) states, (ii) reacting the remaining carbon with oxygen, and (iii) annealing the crystal to 2300 K to desorb oxygen. This procedure was effective in restoring a clean surface as verified by AES. On the carbide surface the reactions led to oxygen buildup, which was reacted away with surface carbon by annealing the crystal to 1500 K. The thermal cracking of ethylene was then used to re-carburize the surface to give a distinct (5×1) LEED pattern.

3. RESULTS

3.1. Reactions of Acetaldehyde and Ethanol on W(100)

At low surface coverages of reactant the adsorption of acetaldehyde on W(100) at room temperature resulted in the complete dissociation of the parent molecule into atomic H, C, and O. Consequently hydrogen was the only flash desorption product

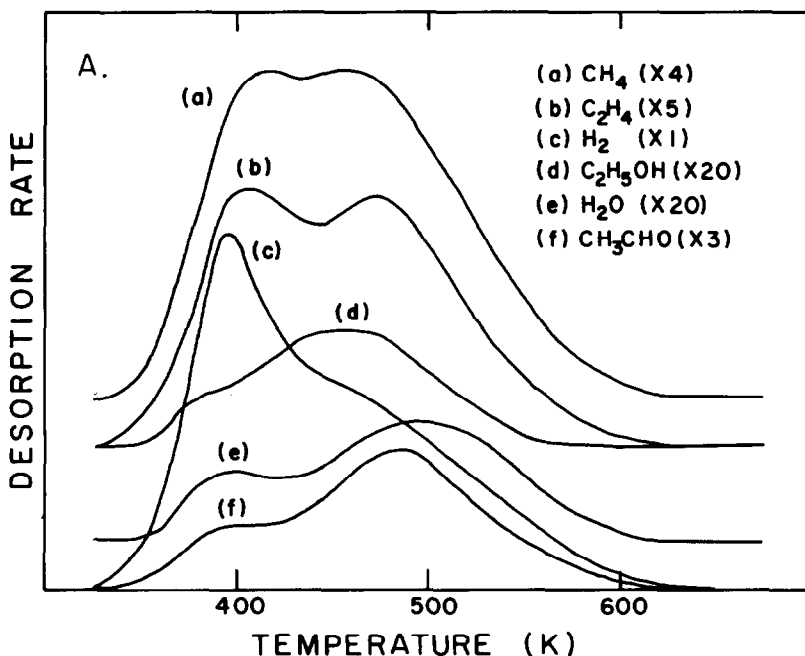


FIG. 1. Product distribution subsequent to saturation exposure of (A) CH₃CHO and (B) C₂H₅OH at room temperature on W(100).

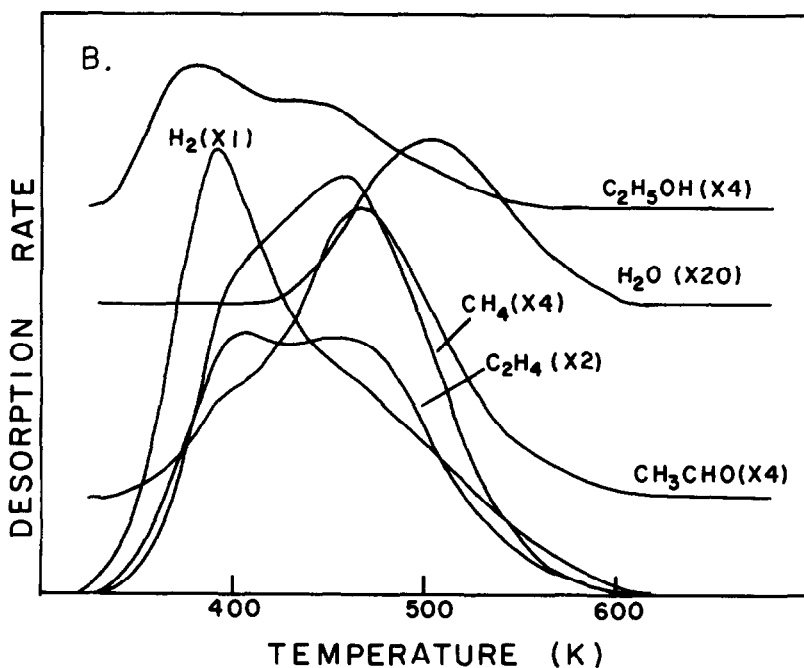


FIG. 1—Continued

detected below 700 K. Heating the surface with electron bombardment to 1500 K desorbed carbon monoxide from the surface, and, as to be expected from the stoichiometry, left behind residual carbon which was detected by AES. At higher exposures of acetaldehyde, additional products including ethylene, methane, small amounts of water, and ethanol ($m/e = 31$) were observed. As shown in Fig. 1A² all products desorbed in two peaks at 403 and 470 K, although the relative magnitude of the two peaks for each product differed. Coverage variation studies showed that the product peaks at 470 K developed first, followed by those at 403 K; both desorption peaks followed first-order kinetics, as the peak temperatures were found to be invariant with surface coverages. The product yields for the reactions of acetaldehyde on W(100) are summarized in Table I.

² In this and subsequent figures showing product distributions, the desorption peaks have been corrected for mass spectrometer sensitivities.

The decomposition of ethanol on W(100) was found to be very similar to that of acetaldehyde as evident in Fig. 1B and Table II. The clean tungsten surface had to be passivated by the initial decomposition of ethanol before products other than adsorbed H,

TABLE I
Product Yields for CH₃CHO Decomposition
(Saturation Exposure)

Product	Molecules/cm ²	
	W(100)	W(100)-(5 × 1)C
CH ₃ CHO	3.6×10^{13}	1.5×10^{14}
C ₂ H ₅ OH	5.2×10^{12}	2.5×10^{13}
CH ₄	1.0×10^{14}	—
C ₂ H ₄	7.7×10^{13}	1.8×10^{14}
H ₂ O	6.9×10^{12}	3.2×10^{13}
H ₂	3.3×10^{14}	6.0×10^{13}
CO	—	6.4×10^{12}
CO ₂	—	1.5×10^{12}
C(a) ^a	5.5×10^{14}	4×10^{13}
O(a) ^a	4.2×10^{14}	1.3×10^{14}

^a Detected by AES.

TABLE II
Product Yields for C₂H₅OH Decomposition
(Saturation Exposure)

Product	Molecules/cm ²	
	W(100)	W(100)-(5 × 1)C
CH ₃ CHO	6.0 × 10 ¹³	2.4 × 10 ¹⁴
C ₂ H ₅ OH	3.5 × 10 ¹³	8.6 × 10 ¹³
CH ₄	1.0 × 10 ¹⁴	—
C ₂ H ₄	1.5 × 10 ¹⁴	1.1 × 10 ¹⁴
H ₂ O	6.3 × 10 ¹²	4.2 × 10 ¹³
H ₂	4.0 × 10 ¹⁴	2.0 × 10 ¹⁴
CO	—	6.9 × 10 ¹²
CO ₂	—	1.8 × 10 ¹²
C(a) ^a	4.6 × 10 ¹⁴	—
O(a) ^a	4.3 × 10 ¹⁴	0.7 × 10 ¹⁴

^a Detected by AES.

C, and O were detected. At saturation exposure hydrogen, acetaldehyde, ethylene, methane, and ethanol desorbed coincidentally at 384 and 442 K; both peaks followed first-order kinetics, as the peak temperatures were invariant with exposure. Water, which was a minor product, desorbed as a single peak at 500 K.

The reactions of either acetaldehyde or ethanol led to carbon and oxygen deposits on W(100) as noted earlier (see Tables I and II). If the surface was not cleaned subsequent to a flash, a markedly different product distribution resulted from the ensuing decomposition of either reactant on the contaminated surface. Similar behavior was observed for acetaldehyde and ethanol; methane was *not* detected as a product, the ethylene yield dropped substantially, and the water formation was enhanced. The last observation suggested that an easily reduced state of oxygen existed on the contaminated surface that was not present on the clean surface. Another noteworthy point was that the high-temperature reaction pathway on the clean surface was suppressed after one flash, as the two-peak structure collapsed into a broad peak on the contaminated surface. These results

are shown for ethylene and water formation from acetaldehyde in Fig. 2.

3.2. Reactions of Acetaldehyde and Ethanol on W(100)-(5 × 1)C

The W(100)-(5 × 1)C surface was not sufficiently reactive to totally dissociate acetaldehyde into atomic species upon adsorption. In effect carbon passivated the surface in a manner similar to that of adsorbed carbon and oxygen from the initial decomposition on the clean surface. Subsequent to room-temperature adsorption, acetaldehyde decomposed to yield ethylene, hydrogen, and water. These products, together with unreacted acetaldehyde, desorbed coincidentally at 435 K, and were the only desorption peaks at low exposures. With increasing exposure product peaks started to grow in at 390 K with ethanol observed as an additional product. The coverage variation study of the ethylene product is shown in Fig. 3 to illustrate this trend. Moreover, small amounts of H₂, CO, CO₂, and H₂O desorbed at 550 K. The product distribution for the saturation exposure of acetaldehyde on W(100)-(5 × 1)C at room temperature is shown in Fig. 4A; the product yields are summarized in Table I. All desorption peaks were found to be first order from coverage variation studies. As ethanol only desorbed at 390 K, its separation from other desorption peaks allowed an accurate determination of kinetic parameters. The activation energy was determined from heating rate variation studies to be 22.9 kcal/mole, with a corresponding preexponential factor of 3.0 × 10¹³ s⁻¹. The activation energies for the decomposition steps at 435 and 550 K were calculated to be 24.9 and 31.8 kcal/mole, respectively, with a preexponential factor of 10¹³ s⁻¹ assumed.

The reaction of acetaldehyde on the carbide surface led to an oxygen buildup of ~0.13 monolayer as detected by AES. This was to be expected from the large amount of ethylene produced, a reaction which involved carbon-oxygen bond scission.

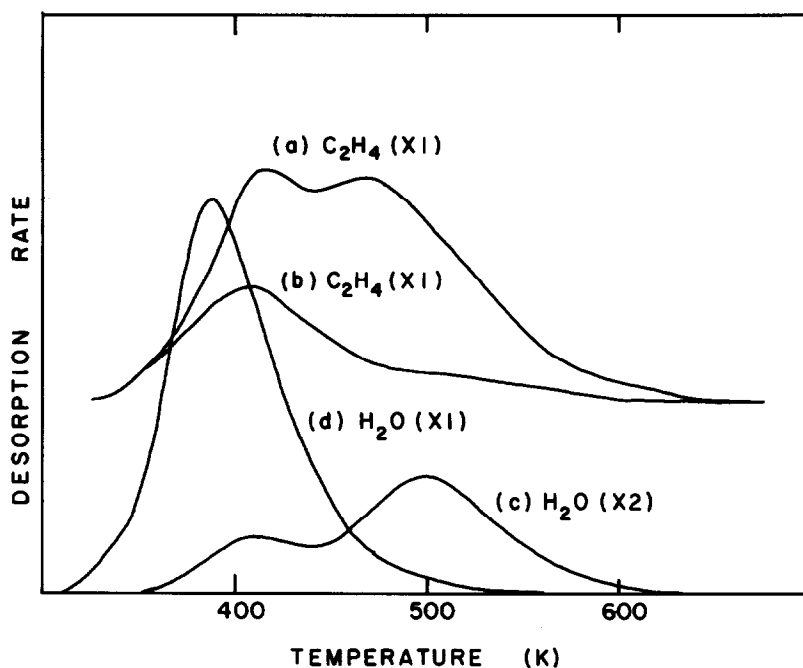


FIG. 2. (a) C_2H_4/CH_3CHO (300 K) on W(100). (b) C_2H_4/CH_3CHO (300 K) on W(100) after one flash without cleaning. (c) H_2O/CH_3CHO (300 K) on W(100). (d) H_2O/CH_3CHO (300 K) on W(100) after one flash without cleaning.

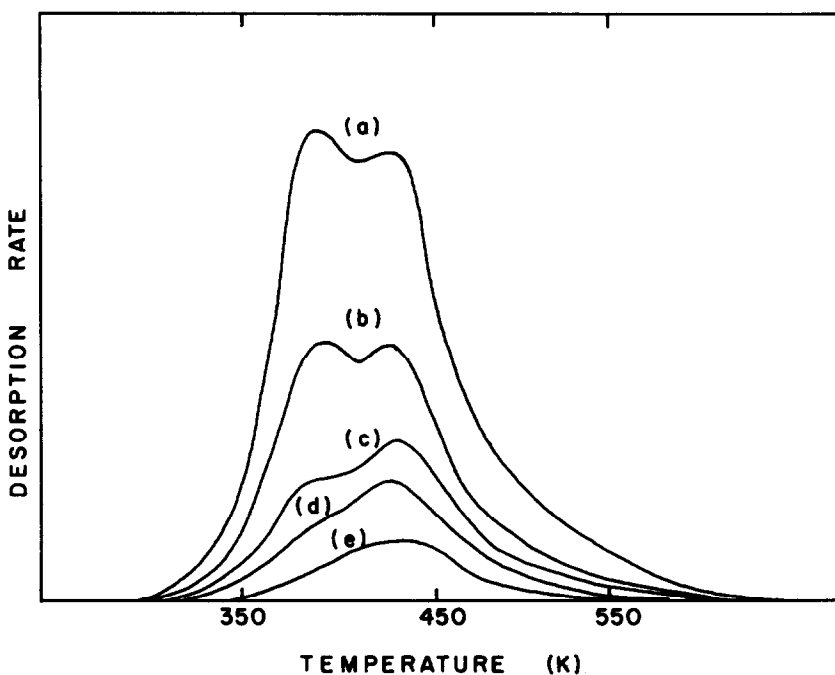


FIG. 3. Desorption spectra for C_2H_4/CH_3CHO (300 K) from W(100)-(5 × 1)C as a function of acetaldehyde exposure (1 $\mu\text{m-sec}$ denotes an exposure of 1 sec with the dosing line pressure at 1 μm): (a) 100 $\mu\text{m-sec}$. (b) 75 $\mu\text{m-sec}$. (c) 60 $\mu\text{m-sec}$. (d) 50 $\mu\text{m-sec}$. (e) 40 $\mu\text{m-sec}$.

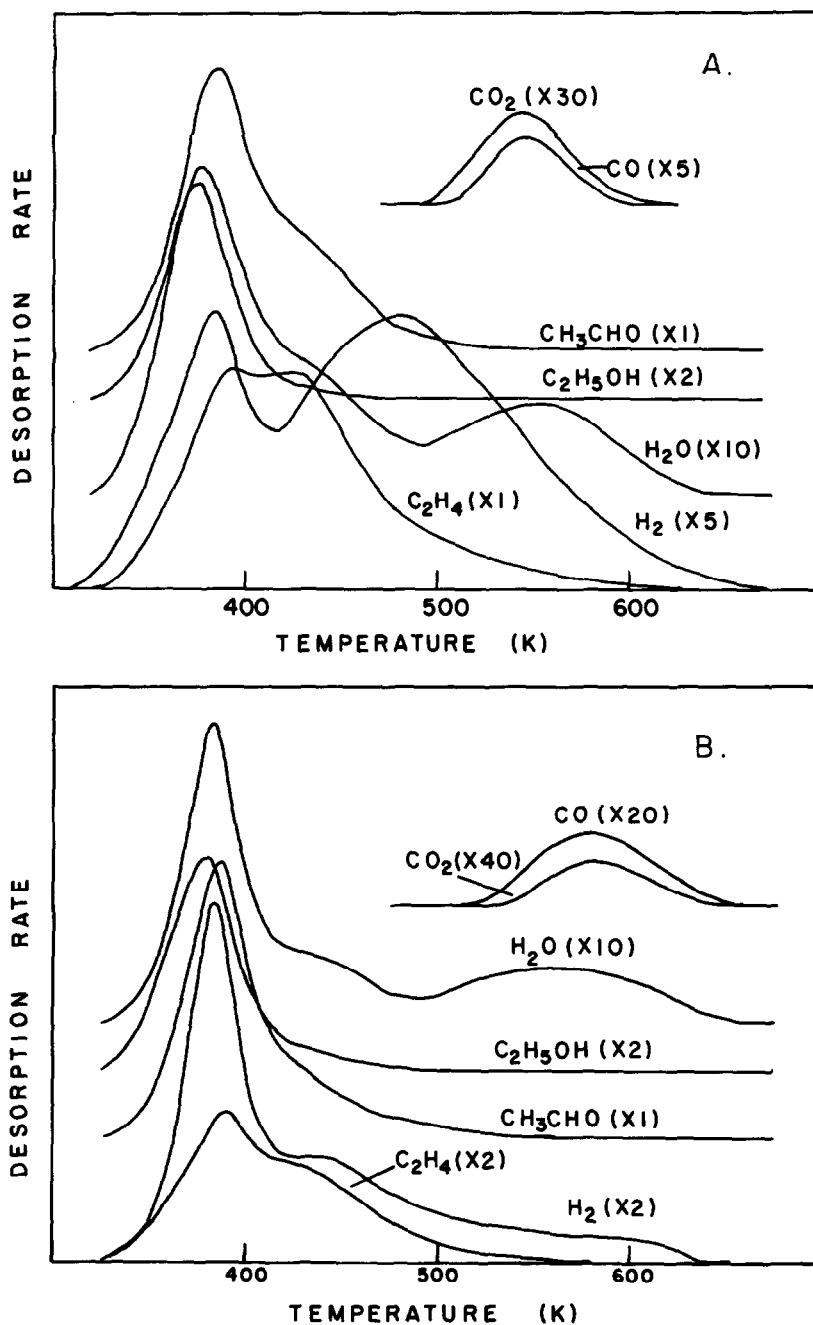


FIG. 4. Product distribution subsequent to saturation exposure of (A) CH_3CHO and (B) $\text{C}_2\text{H}_5\text{OH}$ at room temperature on $\text{W}(100)-(5 \times 1)\text{C}$.

There was also about 0.04 monolayer of carbon buildup from the reaction, indicating that the carbide surface dissociated a small amount of acetaldehyde and released

surface hydrogen atoms. This could account for the hydrogen product, and the formation of ethanol at high exposures.

The product distribution and yields for

ethanol decomposition on W(100)-(5 × 1)C subsequent to saturation exposure at room temperature are shown in Fig. 4B and Table II, respectively. Again many similarities existed between this reaction and that of acetaldehyde. At low exposures ethanol decomposed at 435 K to yield acetaldehyde, hydrogen, and ethylene. These products, together with water and unreacted ethanol, developed at 384 K with increasing exposures. H₂, CO, CO₂, and H₂O desorbed coincidentally at 580 K. AES showed that adsorbed oxygen was also a reaction product.

It was of interest to note that adsorbed oxygen also had an adverse effect on the reactivity of the W(100)-(5 × 1)C surface. In the case of acetaldehyde all product yields decreased if the oxygen was not removed after one flash; the decrease in ethylene product was most severe. The ethylene yield from ethanol showed a similar decline, so the ability of the carbide surface to break C-O bonds seemed to suffer the most from adsorbed oxygen.

4. DISCUSSION

Significantly different surface reactivities were observed in this work between clean and carburized tungsten surfaces for the reactions of acetaldehyde and ethanol. Coupled with earlier results for formaldehyde and methanol (3, 4), the following qualitative features are firmly established. A clean tungsten surface is highly reactive and dissociates reactants into atomic fragments. Passivation of the tungsten surface can be achieved by carburization. On the carbide surface the reactant does not completely dissociate, and a significant shift in the reaction selectivity toward hydrocarbon products away from C-C bond cleavage occurs. The carbide surface was still sufficiently reactive to produce a wide variety of products in significant amounts, as the adsorption of the parent molecule was not severely hindered. These results are clearly evident in Tables I and II. The formation of ethylene from ethoxy was a par-

ticularly nice example to illustrate the correlation between the binding strength of a surface intermediate and its reaction behavior. As noted earlier the initial decomposition of the parent molecule also passivated the W(100) surface as did carbon. However, the resulting surface produced considerably less ethylene from acetaldehyde and ethanol than the carbide surface. This difference can be accounted for by the weakening of the oxygen-metal bond due to the presence of oxygen, which in turn impedes the carbon-oxygen bond scission necessary to produce ethylene. In fact a W(100) surface predosed with one monolayer of oxygen was found to be extremely unreactive toward the adsorption and decomposition of acetaldehyde and ethanol (7). These results aptly show that the reactivity of tungsten can be modified by varying the relative carbon and oxygen surface concentrations, oxygen being more detrimental than carbon in passivating the surface.

The suppression of methane formation on the carbide surface further exemplified the sensitivity of reactivity to composition. The decomposition of adsorbed acetaldehyde and ethanol to produce methane requires the scission of both C-C and C-O bonds. Apparently on the carbide surface C-C bond scission was restricted since the surface was already saturated with carbon. Instead C-O bond scission occurred, leading to the production of ethylene as discussed above.

It should be pointed out that the high binding energy exhibited by tungsten for surface intermediates has been long realized. This characteristic has been used to explain the low catalytic activity for tungsten in the hydrogenation of ethylene (8) and the decomposition of formic acid (9). However, the surface cleanliness of the metal was not characterized in those studies. In view of the ease of a clean tungsten surface in dissociating adsorbed molecules as observed in the present work, one must be cautious in working with tungsten that

the measured rate indeed corresponds to the clean surface, and not to an initially clean surface contaminated (by carbon and oxygen, for example) during reaction conditions. In any event, the point remains that the reactivity of tungsten is sensitive to surface composition, as changing the binding strength of surface intermediates leads to significantly different product distributions.

There are several noteworthy points regarding the product distributions of acetaldehyde and ethanol. First the reducibility of surface oxygen was higher on the carbide surface than on the surface contaminated with adsorbed carbon and oxygen from the initial decomposition of the parent molecule. In a separate study hydrogen was found to be unable to reduce chemisorbed oxygen on clean tungsten (10). This indicated that oxygen was more weakly bonded on the carbide surface, in agreement with the findings of Levy and Boudart (1) that tungsten carbide catalyzes the formation of water from hydrogen and oxygen. Second, ethanol could dehydrogenate to yield acetaldehyde and hydrogen, or dehydrate to yield ethylene and water. The acetaldehyde/ethylene yields then provided a measure on the dehydrogenation/dehydration selectivity. It was found that the carbide surface favored a shift toward dehydrogenation by a factor of 5.5 (Tables II and III). The selectivity for dehydrogenation was even higher after one run since the oxygen buildup suppressed the ethylene production, whereas the acetaldehyde formation was *not* affected. This brings up the final point. As a consequence of the combination of the decreased ethylene production and the high reducibility of surface oxygen, there was a negligible compositional change of the carbide surface after several ethanol adsorption-desorption cycles. In other words, the carbide surface was not highly susceptible to poisoning by oxygen during the reaction, and this tolerance might be significant in the development of a practical catalyst. The results demonstrating this trend are shown

TABLE III

Comparison of the Reactions of Acetaldehyde and Ethanol

Product	W(100)	W(100)-(5 × 1)C
CH ₃ CHO adsorbed (molecules/cm ²)	4.4 × 10 ¹⁴	3.8 × 10 ¹⁴
CH ₃ CHO desorbed (molecules/cm ²)	3.6 × 10 ¹³	1.5 × 10 ¹⁴
CH ₃ CHO reacted (%)	91.8	60.5
Hydrocarbon yield (molecules/cm ²)	1.8 × 10 ¹⁴	2.1 × 10 ¹⁴
Selectivity for hydrocarbon formation	0.80	8.20
C ₂ H ₅ OH adsorbed (molecules/cm ²)	5.3 × 10 ¹⁴	4.4 × 10 ¹⁴
C ₂ H ₅ OH desorbed (molecules/cm ²)	3.5 × 10 ¹³	8.6 × 10 ¹³
C ₂ H ₅ OH reacted (%)	93.4	80.5
Hydrocarbon yield (molecules/cm ²)	3.1 × 10 ¹⁴	3.5 × 10 ¹⁴
Selectivity for dehydrogenation/dehydration	0.40	2.18

in Fig. 5b, and the corresponding results for clean W(100) in Fig. 5a. It is clearly evident that the product distribution changed drastically after just one adsorption-desorption cycle on the clean surface due to the buildup of adsorbed carbon and oxygen. The similar behavior between this contaminated surface and the carbide surface was also apparent.

As shown in Figs. 1 and 4, the products from the reactions of acetaldehyde and ethanol on clean and carburized tungsten surfaces desorbed in two peaks. The low-temperature state, indicative of a reaction channel of lower activation energy, emerged with increasing reactant coverage. This behavior suggests that at higher coverages binding of the adsorbed species was different from that at low coverage. Apparently, adsorbed oxygen produced the same effect, as the high-temperature path was eliminated when either of the surfaces was contaminated. These results suggest that adsorbed alkoxy intermediates and oxygen atoms force the reaction intermediates to bond differently, producing the low-temperature channel. It was pointed out earlier that methane and methanol also desorbed in two peaks following formaldehyde ad-

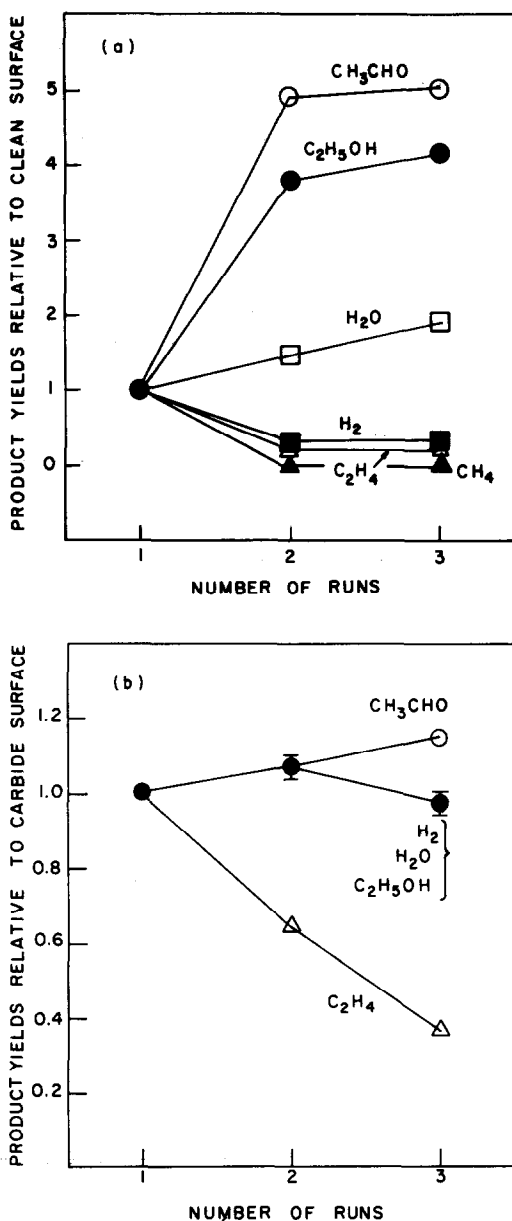


FIG. 5. Compositional effect on the product distribution from ethanol on: (a) W(100), (b) W(100)-(5 × 1)C. Each product yield was normalized with respect to its clean surface value.

sorption on W(100)-(5 × 1)C (4). However, it is important to note in that case the two peaks originated from attractive interactions between H₂CO molecules which predetermined the relative positions of the

methoxy intermediate. Consequently, two peaks were observed at all exposures including low coverages.

In TPRS experiments a temperature resolution of a few degrees K can be attained; in terms of energetics a 20 K difference in desorption temperature corresponds roughly to a 1-kcal/mole difference in activation energy. The striking similarities between the results of acetaldehyde and ethanol therefore strongly suggested a common surface intermediate for both reactions. Infrared spectroscopic studies of acetaldehyde adsorption on silica-supported nickel showed that the dominant surface species was of the alkoxide type (11). Ethoxy has also been identified as the surface intermediate for the decomposition of ethanol over a wide variety of surfaces (6, 12). The formation of ethoxy from ethanol requires only the loss of a hydrogen atom, and ethoxy can be easily produced from the reaction of acetaldehyde with surface hydrogen atoms, released from the initial dissociation step, in a manner similar to the formation of methoxy from formaldehyde (4).

The multiple desorption peaks in this study prevented a detailed kinetic analysis in most cases. However, it is of interest to note that over many different catalysts (12-14) the activation energy of decomposition of ethoxy ranges from 20-30 kcal/mole. If a first-order preexponential factor of 10¹⁸ s⁻¹ were assumed, then the corresponding desorption temperature would be expected to range from 350-500 K, the exact temperature region over which most desorption products were detected in this work. This agreement lends further support to the existence of an ethoxy intermediate.

5. SUMMARY

This study confirmed previous observations that the activity and selectivity of tungsten toward the decompositions of aldehydes and alcohols are very sensitive to surface composition. The carburized as well as the carbon, oxygen-contaminated surfaces displayed markedly different reac-

tivity from the clean surface; the carbon-to-oxygen ratio was critical to the product distribution. The many similarities between the reactions of aldehydes and alcohols suggested a common intermediate. The most abundant surface intermediate appears to be an alkoxy: methoxy in the case of formaldehyde and methanol, ethoxy in the case of acetaldehyde and ethanol. The present results further showed that adsorbed oxygen was more easily reduced from the carbide surface than the clean surface. In addition the carbide surface exhibited a high dehydrogenation/dehydration selectivity for ethanol decomposition. The stability of the carbide surface was demonstrated by its resistance to self-poisoning through many adsorption-desorption cycles.

ACKNOWLEDGMENTS

This work was supported by the NSF-MRL Program through the Center for Materials Research at Stanford University, Grant NSF-DMR-77-24222.

REFERENCES

1. Levy, R., and Boudart, M., *Science* **181**, 547 (1973).
2. Benziger, J. B., Ko, E. I., and Madix, R. J., *J. Catal.* **54**, 414 (1978).
3. Ko, E. I., Benziger, J. B., and Madix, R. J., *J. Catal.* **62**, 264 (1980).
4. Benziger, J. B., Ko, E. I., and Madix, R. J., *J. Catal.* **64**, 132 (1980).
5. Johnson, S. W., Ph.D. thesis, Stanford University, 1980.
6. Wachs, I. E., and Madix, R. J., *Appl. Surf. Sci.* **1**, 303 (1978).
7. Ko, E. I. and Madix, R. J., unpublished results.
8. Beeck, O., *Discuss. Faraday Soc.* **8**, 118 (1950).
9. Rootseart, W. J. M., and Sachtler, W. M. H., *Z. Phys. Chem.* **26**, 16 (1960).
10. Ko, E. I., and Madix, R. J., *J. Phys. Chem.*, in press.
11. Young, R. P., and Sheppard, N., *J. Catal.* **20**, 340 (1971).
12. Takezawa, N., Nahamaki, C., and Kobayashi, H., *J. Catal.* **38**, 101 (1975) and references therein.
13. Roca, F. F., Mourgues, L. D., and Trambouze, Y., *J. Catal.* **14**, 107 (1969).
14. Legendre, M., and Cornet, D., *J. Catal.* **25**, 194 (1975).