

Reactions of Formaldehyde on W(100) and W(100)-(5 × 1)C

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Received August 23, 1979; revised January 3, 1980

The reactions of formaldehyde on W(100) and W(100)-(5 × 1)C surfaces were studied by temperature-programmed reaction spectroscopy (TPRS). The clean W(100) surface was very reactive, completely decomposing formaldehyde upon adsorption at 300 K. The W(100) surface passivated by either adsorbed CO(β) or adsorbed carbon adsorbed formaldehyde nondissociately which reacted to form methane and methanol. Methane was formed from adsorbed methoxy groups complexed with hydrogen. The reactions of formaldehyde on W(100) and W(100)-(5 × 1)C were found to be very similar to the reactions of methanol. Two differences that were observed were (i) methyl formate was a major reaction product from the reactions of H₂CO on a carbide surface, but only a minor product from CH₃OH, and (ii) there was a second reaction pathway leading to methane formation from H₂CO that was not observed for CH₃OH. These differences have been attributed to lateral interactions among adsorbed species on the surface.

INTRODUCTION

It was previously shown that alloying tungsten with carbon conferred the tungsten with catalytic properties characteristic of noble metals. Surface carbon in carbidic form was shown to suppress the dissociative adsorption of both carbon monoxide and hydrogen (1). Furthermore it was shown that a clean W(100) surface displayed a much greater surface reactivity for methanol than a W(100)-(5 × 1)C surface; however, the carbide surface showed greater selectivity for the formation of hydrocarbons than the clean surface (2). These studies have been extended in order to compare the reactions of formaldehyde on W(100) and W(100)-(5 × 1)C with those of methanol.

The reactions of formaldehyde on tungsten have been previously studied by several different techniques. Yates *et al.* (3) followed the reactions of formaldehyde on W(100) and W(111) using flash desorption spectroscopy. They observed that for formaldehyde coverages of less than half a monolayer the formaldehyde decomposed to adsorbed hydrogen and CO, and as the

initial H₂CO coverage was increased, CH₄ and CO₂ were observed as additional products. The results of photoemission studies of Egelhoff *et al.* (4) agreed with these results. For low H₂CO exposures the uv photoelectron spectra from W(100) were a superposition of tungsten with adsorbed H atoms and dissociated CO. At higher coverages the spectra showed the existence of new surface intermediates which presumably gave rise to new reaction products. These results indicated that the clean tungsten surface was very reactive, completely decomposing formaldehyde to hydrogen, carbon, and oxygen atoms at 300 K. The carbon and oxygen atoms passivated the tungsten toward the decomposition of formaldehyde, allowing H₂CO to be associatively adsorbed to form new intermediates which gave rise to the formation of other products.

In this study temperature-programmed reaction spectroscopy (TPRS) was used to follow the reactions of formaldehyde on W(100) and W(100)-(5 × 1)C surfaces. Carburation of the W(100) surface produced a large increase in the selectivity for hydrocarbon formation from formaldehyde, simi-

lar to the effect observed with methanol (2). Furthermore, CH_4 and CH_3OH were formed by the same reaction from both CH_3OD and H_2CO . On the other hand, formaldehyde showed greater reactivity on the carbide surface than methanol, and methane and methanol reaction peaks were observed at two temperatures following formaldehyde adsorption, whereas only one peak was observed when methanol was the reactant. These differences in reaction mechanisms can be understood in terms of intermolecular interactions between intermediates on the surface.

EXPERIMENTAL

The experimental apparatus has been described in detail elsewhere (1). The system contained four-grid LEED optics, a double-pass cylindrical mirror analyzer for Auger electron spectroscopy (AES), and a quadrupole mass spectrometer. Oriented (100) tungsten crystals were cleaned by heating to 1500 K in 5×10^{-6} Torr oxygen for 2–3 hr and then flashing to 2500 K in vacuum. The W(100)-(5 × 1)C surface was prepared by cracking ethylene on the W(100) crystal at 1500 K as described previously (1). The structure and composition of both surfaces were verified by LEED and AES. The W(100) crystal was flashed to 2500 K before each experiment to restore surface cleanliness. Adsorbed oxygen was found to be a reaction product on both the clean and carbide surfaces. To maintain the W(100)-(5 × 1)C surface it was necessary to recarburize the surface after every adsorption-desorption cycle.

Formaldehyde was prepared by heating paraformaldehyde to 345 K while continuously pumping to maintain a pure sample. The resulting sample showed no impurities of trioxane or methyl formate; the fragmentation pattern for the H_2CO sample is given in Table 1. The gas manifold was filled with formaldehyde to 36 Pa (0.27 Torr), and then H_2CO was admitted into the vacuum system through a 22-gauge stainless-steel needle which provided a collimated beam to

TABLE 1
Fragmentation Pattern for H_2CO

Mass to charge ratio	Relative yield
30	85
29	100
28	40
14	5
13	3
12	2

the front face of the tungsten sample, which minimized adsorption on the backside of the crystal. Between doses the gas line was pumped down and refilled with formaldehyde to reduce problems of formaldehyde reacting in the gas lines.

The product desorption spectra were obtained by flashing the tungsten crystal directly into the ionizer of the mass spectrometer and monitoring the mass spectrometer signal as a function of crystal temperature up to 800 K. This procedure permitted the direct measurement of the desorption flux and suppressed the effect of different pumping speeds for different gases. Rates of desorption were calculated by correcting for ionization efficiency, mass spectrometer gain, transmission of mass fraction, and cracking fraction using the method outlined previously (2). Auger spectra were taken after each flash to determine coverages of adsorbed carbon and oxygen.

RESULTS

Reactions of Formaldehyde on W(100)

Formaldehyde was adsorbed on a clean W(100) surface at 300 K. At low exposures (less than 2 L) the only product observed to desorb below 800 K was hydrogen. Hydrogen desorption occurred between 300 and 600 K, desorbing as both $\text{H}_2(\beta)$ characteristic of clean tungsten (5, 6) and $\text{H}_2(\nu)$ characteristic of coadsorbed hydrogen and CO (7, 8). The Auger spectrum taken after heating the sample to 800 K showed $\text{CO}(\beta)$

also was a reaction product. No other products were observed until the coverage in the CO(β) state was greater than 80% saturation.

For H₂CO exposures greater than 2.5 L the CO(β) state was saturated (as determined by AES) and H₂, CH₄, CH₃OH, CO, CO₂, and H₂CO were all observed to desorb from the surface below 800 K. An Auger spectrum taken after heating the sample to 1500 K to desorb the CO(β) showed a net oxygen buildup on the surface, indicating the adsorbed oxygen was also a reaction product. The product desorption spectra for a 20 L exposure of formaldehyde, corresponding to saturation coverage, is shown in Fig. 1 and the product yields are summarized in Table 2. Hydrogen desorbed between 300 and 600 K in a multitude of peaks. Its origin was both desorption limited and reaction limited. Displacement of H₂ from the surface during adsorption was inferred from the stoichiometry of the products, which showed an overall H atom deficiency at high H₂CO exposure; after a 20-L exposure of H₂CO at 300 K there was a hydrogen atom deficiency of 15% (2×10^{14} atoms/cm²). Formaldehyde desorbed by itself in a desorption-limited peak at 350 K. Methane, methanol, and carbon monox-

TABLE 2
Product Yields for H₂CO Adsorption

Product	Yields (molecules/cm ²)			
	W(100)		W(100)-(5 × 1)C	
	20 L	0.2 L	0.9 L	20 L
H ₂	2.5×10^{14a}	0.29×10^{13}	5.6×10^{13}	1.2×10^{14}
CO(β)	4.2×10^{14}	—	—	—
CO(α)	6.0×10^{13}	3.9×10^{13}	1.3×10^{14}	2.6×10^{14}
H ₂ CO	5.0×10^{13}	0.2×10^{13}	0.8×10^{13}	2.0×10^{13}
CH ₃ OH	5.6×10^{13}	0.3×10^{13}	3.0×10^{13}	5.1×10^{13}
HCOOCH ₃	—	—	0.3×10^{13}	4.2×10^{13}
CH ₄	7.2×10^{13}	1.6×10^{13}	6.5×10^{13}	1.0×10^{14}
CO ₂	0.8×10^{13}	0.7×10^{13}	1.2×10^{13}	1.7×10^{13}
O (adsorbed)	5.0×10^{13}	0.8×10^{13}	4.5×10^{13}	8.0×10^{13}
H ₂ O	—	—	—	0.6×10^{13}
Overall stoichiometry (atoms/cm ²)				
C	7.4×10^{14}	6.7×10^{13}	2.5×10^{14}	5.3×10^{14}
O	7.2×10^{14}	6.6×10^{13}	2.4×10^{14}	5.3×10^{14}
H	11.1×10^{14}	13.8×10^{13}	5.2×10^{14}	10.6×10^{14}

^a This table includes only the H₂ desorbed during the flash and does not include H₂ displaced during adsorption.

ide all desorbed simultaneously in two peaks at 385 and 500 K, respectively. The CH₄ and CH₃OH product spectra from methanol showed only a single product peak at 500 K. Carbon dioxide desorbed in a single peak at 590 K. Formic acid decomposition on W(100) also led to H₂ and CO₂ desorption at 590 K (10), so the CO₂ product from H₂CO can be ascribed to the

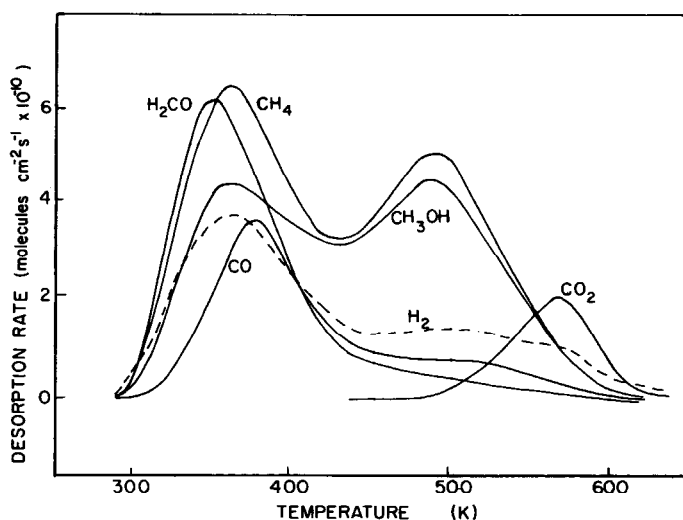


FIG. 1. Product desorption spectra for H₂CO adsorption on W(100), 20 L exposure.

decomposition of a surface formate. These results are qualitatively identical to those of Yates *et al.* (3), the only differences were that (i) surface oxygen was not previously identified as a product, and (ii) the methanol product was then thought to be ethane.

To help identify the intermediates involved in the formation of methanol and methane, D₂ and H₂CO were coadsorbed on the W(100) surface. The surface was first saturated with a 20 L exposure of D₂ at 300 K and subsequently exposed to 20 L of H₂CO. The reaction product spectra showed most of the deuterium to desorb in a desorption-limited fashion near 300 K. However, some D₂ and HD desorption was observed at all temperatures where H₂ desorption occurred in Fig. 1. Additionally both singly and doubly deuterated methanol and methane were observed as reaction products, but no products with more than two deuteriums were detected. This result indicated that adsorbed hydrogen atoms participated in the formation of both CH₄ and CH₃OH.

The role of surface hydrogen in the formation of methane was further examined by adsorbing formaldehyde on a surface presaturated with CO(β) with no adsorbed hydrogen atoms. The surface was saturated with CO(β) by exposing the W(100) surface to 5 L of CO at 300 K and then heating to 500 K to desorb the CO(α). After the surface was cooled to 300 K and exposed to 20 L of H₂CO, only small amounts of CH₃OH, H₂CO, H₂, and CO were found to desorb at 400 K (approximately 5–10% of the yield on an initially clean W(100) surface). No products were observed at 500 K, and no methane was observed. The absence of methane formation on this surface was also observed following methanol adsorption on a W(100)-CO(β) saturated surface (2). In addition, the product yields at 400 K from formaldehyde were much less than observed from methanol; the intermediates leading to products were clearly more easily formed from CH₃OD on this surface.

Product selectivity of the W(100) surface varied with formaldehyde exposure. The selectivity for hydrocarbon formation was defined as the total hydrocarbon yield (CH₄ + CH₃OH) divided by the total CO yield (CO(α) + CO(β)). It was found that for low exposures of H₂CO the selectivity was zero. The selectivity remained zero until the CO(β) state was more than 80% saturated at which point methane and methanol evolution was observed. Increasing the formaldehyde exposure resulted in an increase of the selectivity of 0.27 for saturation coverage of formaldehyde.

Discussion of Reactions of Formaldehyde on W(100)

The two reactions that produced methane and methanol from formaldehyde both involved intermediates that contained excess hydrogen with respect to either simple methoxy (OCH₃) or methyl (CH₃) intermediates, indicating that a surface complex was formed which stabilized hydrogen on the surface. The intermediate which decomposed at 510 K was previously identified in a study of the reaction of methanol and has been attributed to a methoxy complexed with surface hydrogen (2). The formation of singly and doubly deuterated methane and methanol from coadsorbed D₂ and H₂CO indicated that the methoxy-hydrogen complex was formed by the reaction of adsorbed H₂CO with adsorbed hydrogen atoms. The intermediate which decomposed at 385 K also appeared to be the result of a methoxy-hydrogen complex, as the reaction products and overall stoichiometric excess of hydrogen were the same.

The formation of methane from a methoxy intermediate required the methoxy to be complexed with hydrogen. When H₂CO or CH₃OD was adsorbed to saturation on a clean W(100) surface, the initial reactions produced a surface with coadsorbed hydrogen atoms and CO(β) as a result of the initial complete decomposition of either reactant. Further adsorption led to

the formation of the methoxy-hydrogen complex which reacted when heated to give methane and methanol at 510 K. When either CH_3OH or H_2CO was adsorbed on a surface presaturated with $\text{CO}(\beta)$ in the absence of coadsorbed hydrogen, CH_3OH , H_2CO , CO , and H_2 were found to desorb at 400 K. The overall stoichiometry of the reaction products evolved was approximately CH_3O , suggesting that the reaction step was the decomposition of a simple methoxy intermediate (2, 11); no methane was detected, and no products were detected at 510 K. It is interesting to note that much less product was observed at 400 K on the $\text{CO}(\beta)$ saturated surface from H_2CO than from methanol. This difference would be expected from the above mechanism, as CH_3OD can readily form a methoxy by losing the hydroxyl hydrogen, whereas the gain of a hydrogen by H_2CO to form a methoxy is restricted by the hydrogen deficiency of the surface.

The mechanism for the reactions of formaldehyde on an initially clean W(100) sur-

face are summarized in Table 3. Two reaction regimes can be distinguished for the clean W(100) surface and the W(100) surface with coadsorbed $\text{CO}(\beta)$ and hydrogen, respectively. On the clean W(100) surface H_2CO decomposed to adsorbed H, C, and O atoms. On the surface with coadsorbed hydrogen and $\text{CO}(\beta)$, formaldehyde was associatively adsorbed and subsequently reacted with surface hydrogen to form methoxy-hydrogen complexes, which in turn reacted to form methane and methanol. The formation and decomposition of the surface complexes have not been written as elementary steps as the exact nature of the complex is unknown. Formate formation probably occurred by the oxidation of adsorbed formaldehyde by surface oxygen as has been observed on Cu(110) and Ag(110) (11).

The results shown here help to clarify the mechanism suggested by Worley *et al.* (13, 14), where methyl formate was tentatively proposed as the intermediate involved in the formation of CH_4 and CO_2 .

TABLE 3
Reactions of H_2CO on W(100) and W(100)-(5 × 1)C

Temperature regime (K)		Reaction
W(100)	W(100)-(5 × 1)C	
300	NA ^a	$\text{H}_2\text{CO}(\text{g}) \rightarrow 2\text{H}(\text{a}) + \text{C}(\text{a}) + \text{O}(\text{a})$
300-600	350-600	$2\text{H}(\text{a}) \rightarrow \text{H}_2(\text{g})$
1000	NA	$\text{C}(\text{a}) + \text{O}(\text{a}) \rightarrow \text{CO}(\text{g})$
300 ^b	300	$\text{H}_2\text{CO}(\text{g}) \rightarrow \text{H}_2\text{CO}(\text{a})$
NA	300	$2\text{H}_2\text{CO}(\text{a}) \rightarrow \text{HCOOCH}_3(\text{a})$
NA	350	$\text{H}_2\text{CO}(\text{a}) \rightarrow 2\text{H}(\text{a}) + \text{CO}(\text{a})$
300	350	$\text{H}_2\text{CO}(\text{a}) + \text{H}(\text{a}) \rightarrow \text{H}_3\text{CO}(\text{a})$
300	350	$\text{H}_3\text{CO}(\text{a}) + \text{H}(\text{a}) \rightarrow \text{complex A}$
350	350	$\rightarrow \text{complex B}$
NA	350	$\text{H}_2\text{CO}(\text{a}) \rightarrow \text{H}_2\text{CO}(\text{g})$
385	410	$\text{HCOOCH}_3(\text{a}) \rightarrow \text{HCOOCH}_3(\text{g})$
510	500	$\text{complex A} \rightarrow \text{CH}_4(\text{g}) + \text{CH}_3\text{OH}(\text{g})$
300-500	410-500	$+ \text{H}_2(\text{g}) + \text{O}(\text{a}) + \text{H}_2\text{CO}(\text{g})$
590	545	$\text{complex B} \rightarrow \text{CH}_4(\text{g}) + \text{CH}_3\text{OH}(\text{g})$
		$+ \text{H}_2(\text{g}) + \text{O}(\text{a}) + \text{H}_2\text{CO}(\text{g})$
		$\text{H}_2\text{CO}(\text{a}) + \text{O}(\text{a}) \rightarrow \text{HCOO}(\text{a}) + \text{H}(\text{a})$
		$\text{HCOO}(\text{a}) \rightarrow \text{H}(\text{a}) + \text{CO}_2(\text{g})$

^a NA, not applicable.

^b Only after the $\text{CO}(\beta)$ state is saturated.

Methyl formate was shown to desorb at 350 K (15), well below the temperature at which methane was formed. Additionally, the stoichiometry of the products formed were not consistent with methyl formate as the intermediate leading to methane formation.

Reactions of Formaldehyde on W(100)-(5 × 1)C

The reactions of formaldehyde on the W(100)-(5 × 1)C surface were analogous to those observed for the W(100) surface saturated with H₂CO. Carbon passivated the tungsten, significantly reducing the activity for the complete decomposition of H₂CO, so that at 300 K formaldehyde was associatively adsorbed. For H₂CO exposures between 0.2 and 20 L the products observed were H₂, CO, CH₃OH, CH₄, and CO₂. Adsorbed oxygen detected by AES after heating to 800 K was also identified as a reaction product. Following exposures of formaldehyde greater than 0.8 L, methyl formate (HCOOCH₃) and water were also observed as reaction products. Product distributions as a function of H₂CO exposure are shown in Fig. 2; the product yields are summarized in Table 2. Nearly equal amounts of molecular CO and (CH₄ + CH₃OH) were formed on the W(100)-(5 × 1)C surface, independent of H₂CO exposure.

The results shown in Fig. 2 indicate that the reaction progressed through a series of intermediates. Unreacted formaldehyde desorbed at 350 K, and at higher coverages of H₂CO, methyl formate was also observed to desorb at 350 K. The desorption of CO and H₂ at 350 K indicated that formaldehyde decomposed at that temperature. The CO and H₂ peaks from the formaldehyde decomposition shifted from 350 K at low coverages of H₂CO to 395 K at high coverages, indicative of increased stability of the adsorbed formaldehyde with increasing coverage. The relative yield of CO to H₂ in the initial decomposition step was approxi-

mately 4 to 1, showing little variation for initial coverages of formaldehyde of 7×10^{12} molecules/cm² to 6.6×10^{14} molecules/cm². The overall stoichiometry of H₂CO was recovered when all of the reaction products at all temperatures were summed; the hydrogen deficiency in the products at 395 K indicated that most of the hydrogen evolved by the initial decomposition reaction remained on the surface to higher temperatures.

This hydrogen on the surface reacted to form new intermediates which yielded CH₄, CH₃OH, and H₂ in two reaction steps, evidenced by the two peaks at 390 and 500 K. The stoichiometry of these intermediates at and above 390 K was estimated from the product yields to be approximately CH_{4.5}O. The high-temperature product peaks shifted with coverage from 515 K after a 0.2 L exposure of H₂CO to 470 K after a 20 L exposure. The shift of the product peaks near 500 K with formaldehyde coverage and the reaction product distribution at 500 K from formaldehyde adsorption were the same as those observed for methanol, indicating both methanol and formaldehyde gave rise to the same intermediate. Isothermal analysis of the peak at 500 K showed the apparent reaction order decreased from 1.7 to 1 with decreasing coverage (1, 9), suggesting the reaction step was first order with repulsive interactions. Evolution of methane and methanol at 400 K was observed from H₂CO but not from CH₃OH. The product peaks at 400 K did not shift with coverage, indicating the rate-limiting step was a first-order process. The product yields at 400 K were estimated by subtracting the product yields at 500 K from the overall product yields. The reaction step at 400 K also involved a hydrogen-rich intermediate with a stoichiometry of approximately CH_{4.5}O.

The third reaction intermediate was a surface formate which decomposed to H₂ and CO₂ at 545 K, the same temperature at which formic acid decomposed to yield H₂ and CO₂ on the carbide surface.

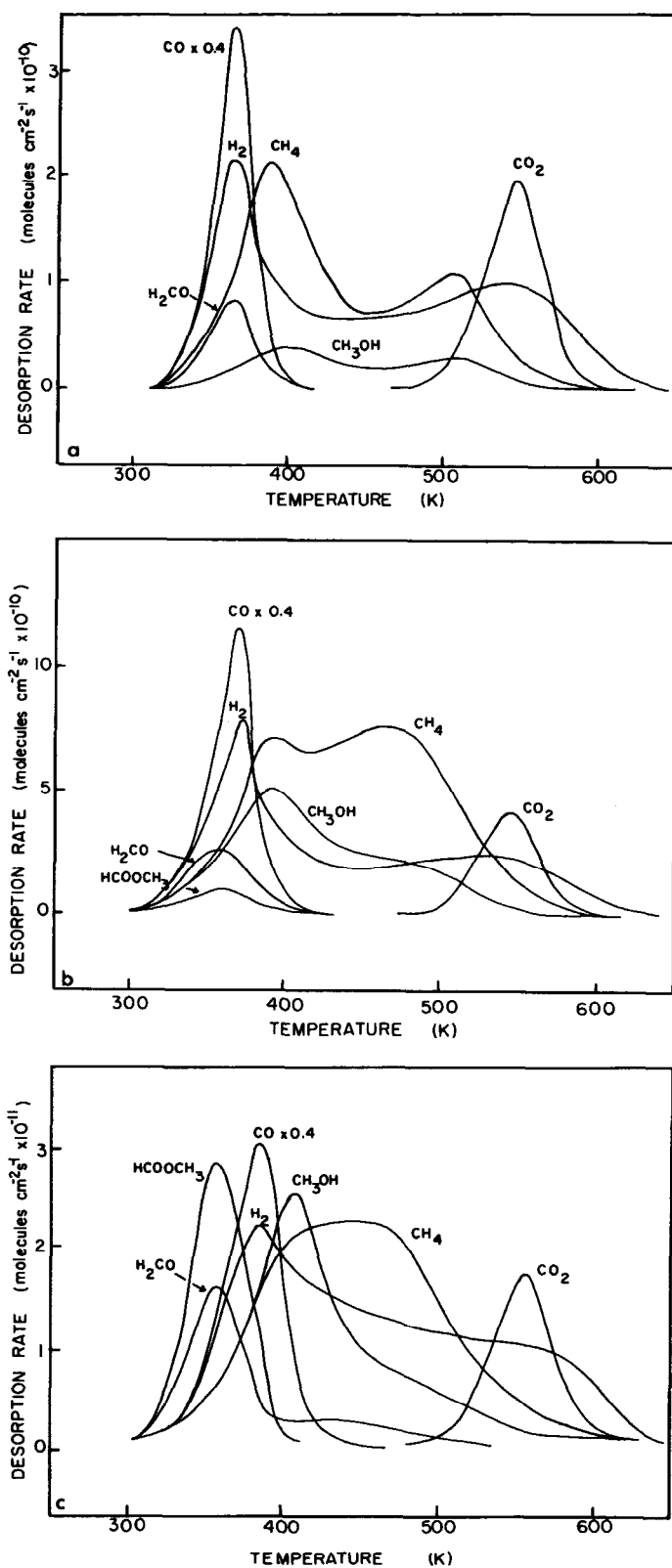


FIG. 2. Product desorption spectra for H_2CO adsorption on $\text{W}(100)-(5 \times 1)\text{C}$. (a) 0.2 L exposure; (b) 0.9 L exposure; (c) 20 L exposure.

Discussion of Reactions of Formaldehyde on W(100)-(5 × 1)C

The initial interaction of H_2CO with the W(100)-(5 × 1)C surface obviously differed from W(100) by its high selectivity for hydrocarbon formation. Even at low exposures of formaldehyde, methane and methanol were formed on the carbide surface, whereas only the complete dissociation of formaldehyde was observed on clean tungsten. The role of surface carbon was to passivate the tungsten, facilitating the associative adsorption of formaldehyde. Molecularly adsorbed formaldehyde then reacted with hydrogen to form methoxy intermediates, which reacted to form methane and methanol. The simultaneous desorption of CO, H_2 , and H_2CO at 350 K shown in Fig. 2a was the result of competitive decomposition and desorption of the adsorbed formaldehyde. Following their adsorption on W(100)-(5 × 1)C, methanol (2), methyl formate (15), and formaldehyde also decomposed and/or desorbed near 350 K. This result indicated that all three species were bound to the surface in similar fashion, presumably through the lone-pair electrons on the oxygen as has been suggested for other systems, including CH_3OH on Ni(111) (16) and Ru(110) (17), and CH_3OH , $(\text{CH}_3)_2\text{O}$, CH_3CHO , and $(\text{CH}_3)_2\text{CO}$ on polycrystalline Pd (18).

The decomposition of H_2CO at 350 K was also accompanied by the reaction of adsorbed H_2CO with hydrogen atoms to form methoxy-hydrogen complexes on the surface. As mentioned above, only 25% of the hydrogen formed in the decomposition of H_2CO desorbed at 350 K, and the remaining 75% reacted with adsorbed formaldehyde to form more stable intermediates which decomposed at higher temperatures. In addition, both CH_3OH (2) and H_2CO gave rise to CH_4 and CH_3OH formation at 470 K on the carbide surface, which was suggestive of a common intermediate. These facts indicated that methoxys complexed with hydrogen were the important

intermediates which decomposed at 470 K. The similarity of both the reaction products at 400 K and their stoichiometries to those at 470 K suggested that the products formed at 400 K were also derived from a methoxy-hydrogen complex. The reaction products formed, namely, CH_4 , CH_3OH , H_2 , adsorbed oxygen, and small amounts of CO and H_2CO , indicated that the complex followed three reaction pathways: (i) loss of hydrogen to yield H_2CO or CO and hydrogen, (ii) addition of hydrogen to form CH_3OH , or (iii) hydrogenation of the methyl group to yield CH_4 and surface oxygen. Complexing the methoxy with hydrogen caused the latter two options to be favored.

The adsorbed oxygen formed by the reaction remained on the surface above 800 K after all of the other products had desorbed. The formate, which decomposed at 540 K, was probably formed by the oxidation of formaldehyde by the surface oxygen—similar to the mechanism proposed previously (11). The water which desorbed at the same temperatures as that for reaction of the methoxy-hydrogen complex probably resulted from hydrogen reacting with surface oxygen.

Two major differences existed between the reactions of formaldehyde and those of methanol on the W(100)-(5 × 1)C surface. First, methyl formate was a major reaction product subsequent to formaldehyde adsorption, whereas the reactions of methanol produced only a minor amount of methyl formate. Second, formaldehyde adsorption and reaction resulted in two distinct methane and methanol reaction peaks in contrast to only one peak for methanol. Both of these differences may be the consequences of lateral interactions between adsorbed species.

The appearance of methyl formate was coverage dependent and was only observed for initial formaldehyde coverages greater than 0.6 monolayer. The methyl formate product desorbed at 350 K, the same temperature at which desorption occurred after

methyl formate adsorption (15), indicating that methyl formate was formed near 300 K—at lower temperatures than H_2CO decomposed. These results indicated that methyl formate was formed by an intermolecular hydrogen transfer between adjacent formaldehyde molecules as shown in Fig. 3 (19). This configuration for adsorbed formaldehyde would be favored by a near head to tail alignment of the dipoles of the formaldehyde molecules due to attractive interactions.

The reaction step that formed methane and methanol at 400 K can be attributed to repulsive dipole interactions between methoxys in adjacent sites on the surface, which only occurred when H_2CO was the reactant. The effects of the dipole interactions are best understood by considering the binding energy of the adsorbed intermediates as consisting of the unperturbed binding energy of an individual surface intermediate and the configurational contribution due to dipole–dipole interactions:

$$E_B = E_{B_0} + E_{\text{config}}$$

If formaldehyde were associatively adsorbed at 300 K, bonded through the lone-pair electrons on the oxygen, as shown in Fig. 4, the dipole of formaldehyde would make an angle of approximately 30° with the surface. If the molecular dipoles aligned due to attractive interactions the binding energy of adsorbed formaldehyde would increase (20). An increase in binding energy was in fact observed with increasing H_2CO coverage, as the H_2 and CO desorp-

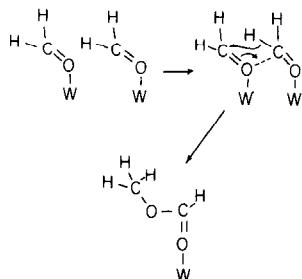
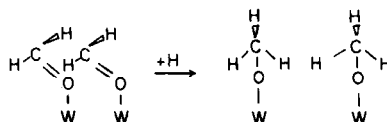


FIG. 3. Mechanism for methyl formate formation from formaldehyde.

MOLECULAR CONFIGURATION



DIPOLE CONFIGURATION



FIG. 4. Configuration of adsorbed surface intermediates.

tion peaks from H_2CO decomposition shifted from 350 to 395 K with increasing H_2CO coverage. This shift amounts to a net attractive interaction of about 3 kcal mol^{-1} . The appearance of the two peaks at 400 and 470 K may also have its origin in attractive interactions between H_2CO molecules. The reaction of adsorbed H_2CO with surface hydrogen would then result in methoxy groups in nearest-neighbor positions. The hydrogenation of formaldehyde to methoxy would change the bonding configuration from planar to tetrahedral. Whereas the bonding geometry of formaldehyde to the surface via the lone-pair electrons would favor alignment of the dipoles, the methoxy group would be nearly normal to the surface. The dipoles of the methoxys would then be in a repulsive configuration, which would reduce the binding energy and therefore cause the methoxy–hydrogen complexes to decompose at lower temperatures than in the absence of such interactions. The net result is that there would be two peaks for methane and methanol formation—a low-temperature peak where the decomposition rate was enhanced by repulsive dipole interactions with a high-temperature peak from the decomposition of isolated methoxy–hydrogen complexes. The repulsive interaction between methoxys can be estimated by approximating the dipole moment by that for methanol (1.7 D)

(21). Assuming a nearest-neighbor distance of 3.2 Å, the repulsive energy was calculated to be 11 kJ/mol, which would cause a difference in peak position of approximately 60 K, compared to the 55 K shift observed.

It is extremely important to note two features of the above model. First, if the two peaks for methane and methanol actually originated from nearest-neighbor H₂CO packing due to attractive dipole interactions, then the two peaks should occur even at low coverages, as the attractive interactions would cause condensation of H₂CO into nearest-neighbor configurations. Condensation will occur for all coverages greater than a critical coverage, which is typically quite small for attractive interactions (20). This feature was observed. Second, repulsive dipole interactions would inhibit adsorption of methanol to nearest-neighbor positions, and the low-temperature methane and methanol peaks due to the repulsive interactions were not observed following methanol adsorption (2).

Summary of Reactions of Methanol and Formaldehyde

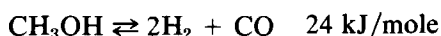
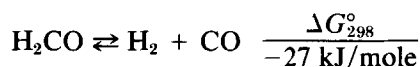
The reactions of methanol and formaldehyde on W(100) and W(100)-(5 × 1)C are summarized and compared in Tables 3 and 4. It is evident that there was a large increase in the selectivity for hydrocarbon formation on the carbide surface for both reactants. There were two substantial differences between the reactions of methanol and formaldehyde on the carbide surface. More H₂CO than CH₃OH could be adsorbed on the surface, possibly due to the attractive dipole interactions which allowed for closer packing. It was also observed that methanol was less reactive than formaldehyde. The reactivity was defined as the total amount of reactant that gave rise to products divided by the total amount of reactant adsorbed. The difference in reactivity may have been the result of the relative thermodynamic stabilities of the

TABLE 4

Comparison of the Reactions of CH₃OD and H₂CO

	W(100)	W(100)-(5 × 1)C
CH ₃ OD adsorbed (molecules/cm ²)	5.4 × 10 ¹⁴	2.7 × 10 ¹⁴
CH ₃ OD desorbed (molecules/cm ²)	1.5 × 10 ¹³	1.5 × 10 ¹⁴
% CH ₃ OD reacted	97.3	44.4
CO product yield (molecules/cm ²)	4.6 × 10 ¹⁴	3.7 × 10 ¹³
Hydrocarbon yield (molecules/cm ²)	9 × 10 ¹³	8.4 × 10 ¹³
Selectivity for hydrocarbon formation	0.20	2.27
H ₂ CO adsorbed (molecules/cm ²)	6.6 × 10 ¹⁴	5.5 × 10 ¹⁴
H ₂ CO desorbed (molecules/cm ²)	5.0 × 10 ¹³	2.0 × 10 ¹³
% H ₂ CO reacted	92.4	96.5
CO product yield (molecules/cm ²)	4.8 × 10 ¹⁴	2.6 × 10 ¹⁴
Hydrocarbon yield (molecules/cm ²)	1.3 × 10 ¹⁴	2.4 × 10 ¹⁴
Selectivity for hydrocarbon formation	0.27	0.92

two reactants. At 298 K the following equilibria can be considered:



The thermodynamic driving forces favor formaldehyde decomposition but oppose methanol decomposition, so that the relative reactivity of methanol and formaldehyde followed their relative thermodynamic driving forces.

CONCLUSIONS

Carbon has been shown to passivate tungsten for the total decomposition of formaldehyde, resulting in the formation of methane, methanol, methyl formate, carbon monoxide, and hydrogen from formaldehyde. Both a surface carbide and a surface with dissociated CO(β) and adsorbed hydrogen atoms displayed much greater selectivities for hydrocarbon formation than clean tungsten. Methane and methanol were both evolved from the decomposition

of methoxy-hydrogen surface complexes. The reactions of formaldehyde differed from those of methanol, as methane and methanol were produced in two reaction steps when formaldehyde was the initial reactant. Additionally methyl formate was a major product from formaldehyde on a carbide surface, whereas it was a minor product from methanol. These differences between methanol and formaldehyde have been suggested to arise from lateral attractive/repulsive interactions between adsorbed species.

ACKNOWLEDGMENT

This work was supported by the NSF-MRL Program through the Center for Materials Research at Stanford University under the NSF-MRL Program.

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