

Temperature-Programmed Studies of the Adsorption of Synthesis Gas on Zirconium Dioxide

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Received June 20, 1983; revised December 6, 1983

The adsorption and reaction of CO and H₂ on ZrO₂ were studied by the temperature-programmed desorption (TPD) and decomposition (TPDE) techniques. A distinctive temperature distribution pattern was found for multiple TPD and TPDE products of the CO/H₂/ZrO₂ system. Carbonate, bicarbonate, formate, and methoxide intermediates were postulated to form from CO and H₂. Carbon dioxide, HCOOH, and CH₃OH were also used as chemical probes in TPD/TPDE studies to verify both the temperature distribution patterns and the decomposition patterns of surface intermediates. Labeling experiments were conducted to reveal the role of surface OH groups on ZrO₂. A mechanism for CO/H₂ interaction on the surface of ZrO₂ is proposed.

I. INTRODUCTION

Certain metal oxides are capable of selective conversion of synthesis gas into methanol and branched aliphatics. The former process, as discussed in a recent review (1), is generally conducted over ZnO and Zn-Cu-O systems. The latter process is referred to as isosynthesis in which branched C₄ to C₈ hydrocarbons are produced, with isobutane as the major product. Zirconia and thoria are the most active isosynthesis catalysts (2). Both methanol synthesis and isosynthesis require high pressures, typically 40-300 atm (1 atm equals 101.3 KPa). Methanol synthesis is conducted at temperatures on the order of 250°C (1); whereas isosynthesis is conducted at temperatures on the order of 400°C (2). A unique characteristic of the isosynthesis catalysts is their extremely high sulfur tolerance (3, 4) which, on a practical basis, may compensate for the high pressure and temperature requirements.

Little information is available on the isosynthesis reaction mechanism. The effects of oxide composition and synthesis conditions on rate and selectivity are reported (2, 3, 5, 6). Mechanisms have been proposed in which intermediate ethers or alco-

hols are produced (2, 3, 6); however, the details of the mechanism are not reported, merely the stoichiometry of the proposed reactions. The research reported herein was directed toward an understanding of the interaction of synthesis gas with ZrO₂ and in turn the catalytic processes which may initiate isosynthesis.

Infrared studies have established that the zirconia surface contains two types of hydroxyl groups (7-10), which are attributed to bridged and terminal species (8, 9). These hydroxyl groups were found to exchange with hydrogens on acetone and 2-propanol (7, 8); the terminal hydroxyl was more active. This exchange indicates that the hydroxyl hydrogens are labile and may be expected to interact with CO. Additional studies have revealed that these hydroxyl groups are neither strongly acidic nor basic (8, 10, 11).

The possible species which may form upon adsorption of CO onto ZrO₂ include carbonates, bicarbonates, and formates. Precedence for these come from adsorption studies of CO₂ onto ZrO₂ where carbonates and a bicarbonate were reported (10), and from CO/H₂ exposure to ThO₂ where a formate was observed (12). Carbon dioxide formed both carbonates and formate on

ThO₂; the monodentate carbonate reacted with hydrogen to produce a formate (12). Zirconia and thoria are catalytically similar for isosynthesis and the unrelated alcohol dehydration reaction (13, 14) implying that the species observed on ThO₂ may also be expected over ZrO₂.

The presence of these species and possible surface reactions were studied at 1 atm using temperature-programmed techniques. Surface species desorbed intact or underwent some form of surface reaction during the desorption process giving rise to the terminology, temperature-programmed desorption/temperature-programmed decomposition (TPD/TPDE). The stable hydrocarbon products formed at this pressure differ from those observed at isosynthesis pressures (2, 4-6); however, the C₁ intermediates formed on the ZrO₂ surface can be expected to be the same at both pressures, their relative abundances may differ with pressure.

II. METHODS

The apparatus used for these studies was typical of those used for temperature-programmed studies over supported catalysts. Zirconia was placed in a 12.70-mm-o.d. quartz tube fitted with a quartz frit. The tube was positioned in a furnace which was heated linearly at 1°C/sec; the catalyst temperature increased linearly between 100 and 550°C. Gas at 1 atm flowed through the ZrO₂ bed at a rate of 30 SCCM. A small portion of the effluent gas was admitted to a UTI 100C quadrupole mass spectrometer (MS) through a series of two 0.07-mm orifices. The leak rate into the MS was controlled by adjusting a metering valve upstream of the first orifice and by adjusting the mechanical pump pressure between the two orifices. The leak rate was set such that the quadrupole pressure was always maintained at 2×10^{-6} Torr. The MS was driven by a UTI Programmable Peak Selector which was capable of monitoring nine mass channels as a function of time.

Two grams of ZrO₂ were used in these

studies. A fresh loading was used for each experiment unless noted in the text. The large loading was used to enhance the MS signal intensities, which was necessitated by the low surface area of the ZrO₂, 5.8 m²/g BET area. With this loading and at the low gas flow it is reasonable to assume that readsorption of desorbed species can occur.

The normal procedure involved heating the ZrO₂ to 620°C in flowing oxygen and maintaining it at 620°C for 0.5 hr (O₂, 620°C), followed by flushing with helium at 620°C for 0.25 hr and exposure to flowing hydrogen at 620°C for 0.5 hr (H₂, 620°C). Hydrogen was then flushed from the tube with helium. The catalyst was either cooled to 25°C in helium or in the gas to be adsorbed. If the catalyst was cooled in helium the adsorbate gas was admitted at 25°C and continued to flow while the temperature was raised to 620°C and lowered back to 25°C. This adsorption procedure was followed to give ample opportunity for the different structures, which may only form at elevated temperatures, to form. The carrier gas, referred to as the flushing gas in the tabulated data, was changed to the desired mixture and the temperature was subsequently ramped at the constant rate of 1°C/sec.

Mass signals were measured for nine masses. The signal for the flushing gas was not monitored. The MS was calibrated according to the procedure of Ko *et al.* (15). Pulses of known amounts of CO were directed to the MS and the corresponding signal was related to the number of molecules in each pulse. The relative amounts of all other species were related to the intensity of the CO signal (15) and the integrated areas of all species were related to the area of the CO calibration. The areas were divided by the BET area to produce the values reported as molecules/nm². These values should not be interpreted as absolute, rather as representative of the relative amounts of each species.

The zirconia (Alfa-Ventron) was 99%

pure. It was supplied as a powder (1–3 μm) and was loaded into the reactor without pretreatment. The hydrogen (Matheson UHP, 99.999%) was passed through a Dextro cylinder and a bed of 4- \AA molecular sieves to remove oxygen and water. Carbon monoxide (Matheson UHP, 99.8%) was heated to 180°C over molecular sieves to decompose metal carbonyls. Helium had a minimum purity of 99.995% and was passed through a bed of 4- \AA molecular sieves to remove water.

III. RESULTS

The heating rate and carrier flow were held constant for all experiments, as was the adsorption procedure for CO, CO₂, and H₂. Desorbed species were observed at five distinct temperature regions for all the experiments. These were α —40 to 60°C, molecular CO; β —120 to 180°C, carbonate; γ —380 to 420°C, bicarbonate; δ —460 to 510°C, methoxide; ϵ —580 to 620°C, formate. The species desorbing and/or react-

ing at the higher temperatures involve processes with higher activation energies than those species observed at lower temperatures. Due to the complications introduced by possible readsorption of desorbed species and an undetermined initial concentration of adsorbed species (16, 17), it was not possible to determine kinetic parameters.

This section describes a large number of different experiments directed toward identifying surface species and their reactions. The species assignments are indicated above without justification to facilitate following the presentation of our results. We also present the proposed mechanism for the interaction between CO and H₂ in Fig. 1 at this time. Justification for these assignments and for the mechanism are presented in the next section.

TPD/TPDE of CO and H₂

Untreated ZrO₂, as supplied by the manufacturer, was positioned in the reactor and heated in flowing He without any pretreat-

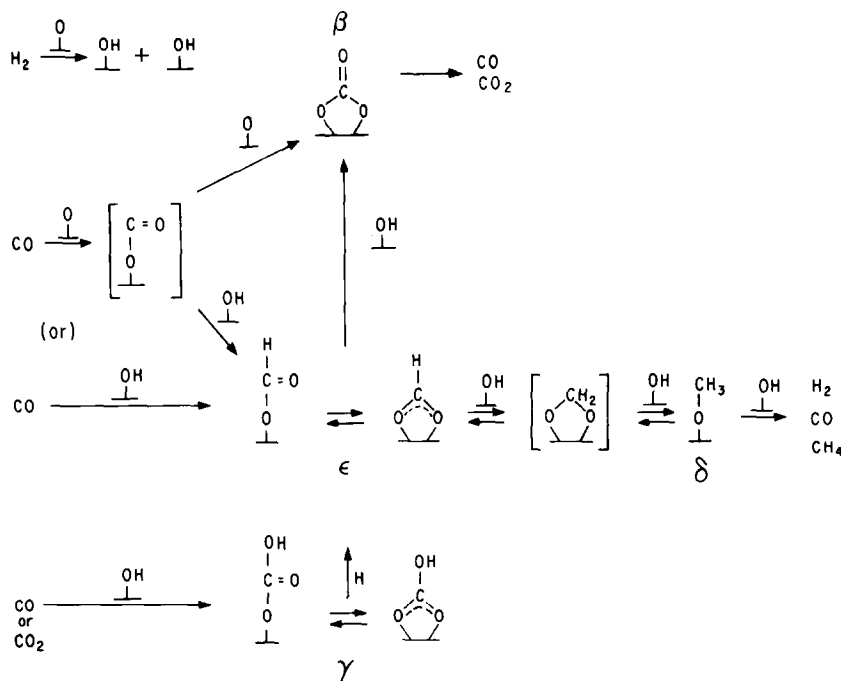


FIG. 1. Tentative mechanism for the interaction of CO and H₂ over ZrO₂.

ment or preadsorption. The MS response is shown in Fig. 2 and the results are tabulated in Table 1 (No. I). A large amount of adsorbed water evolved from the surface, with the maximum amount detected at 590°C. This water was associated with adsorbed molecular water and did not result from dehydroxylation of the surface which requires temperatures near 750°C (10). Treatment of the surface under O₂ at 620°C was found to dehydrate the surface. In addition to molecular water, species were present on the untreated surface which gave rise to CO and CO₂ peaks at the γ and ϵ temperatures, and H₂ at the ϵ temperature.

Zirconia was oxygen-treated at 620°C and cooled to 25°C in He. Oxygen treatment was performed to remove any residual carbon species from the surface (9). During subsequent heating of the ZrO₂ in He no species were detected. Oxygen-treated zirconia was also heated in CO. The results shown in Fig. 3 and Table 1 (No. II) reveal that CH₄, H₂, and CO₂ were formed

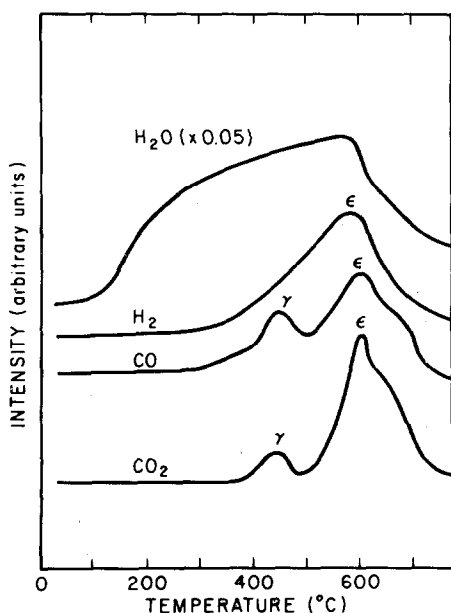


FIG. 2. Mass signals characteristic of the indicated molecules during the TPD/TPDE of untreated ZrO₂ into He.

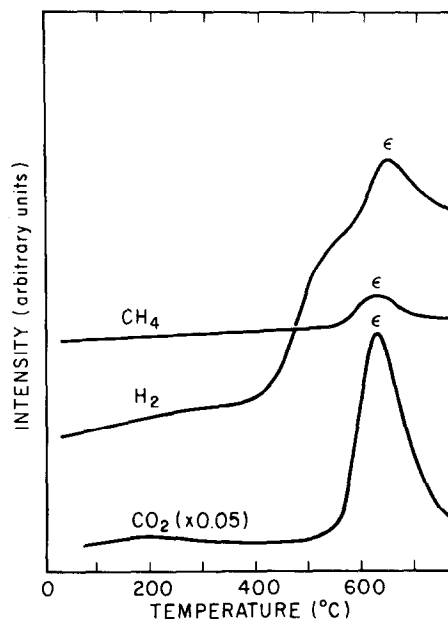


FIG. 3. Mass signals characteristic of the indicated molecules during the TPD/TPDE of oxygen-treated ZrO₂, without preadsorption into CO.

at the ϵ temperature. Additional studies were performed in which ZrO₂ was treated with O₂ and H₂ at 620°C and cooled to 25°C in He. Subsequent temperature-programmed heating in He produced a CO₂ signal at the β temperature which was too weak to quantify. These studies suggest that the surface species giving rise to CH₄, CO₂, and H₂ were formed during the TPD/TPDE cycle between the hydroxylated ZrO₂ surface and the CO flushing gas.

Oxygen and hydrogen treatment at 620°C followed by adsorption of H₂ produced a different result from that observed without H₂ adsorption. As shown in Table 1 (No. III), H₂ was detected at the ϵ temperature (the maximum appeared at 600°C) when this surface was heated linearly in He. This demonstrates that H₂ interacted with ZrO₂ during adsorption in a manner which was different than that during hydrogen treatment at 620°C for 30 min.

Adsorption of CO and subsequent TPD/TPDE in He resulted in the desorption of CO and CO₂ as shown in Fig. 4 and Table 1

TABLE 1
 TPD/TPDE of CO, H₂, and CO/H₂

No.	ZrO ₂ treatment	Preadsorbate (25–620°C, 620–25°C)	Flushing gas	Product	Molecules/nm ²				
					α	β	γ	δ	ϵ
I	None	Exposure to air	He	CO			0.03		0.08
				CO ₂			0.02		0.23
				H ₂					0.08
				H ₂ O					9.90 ^a
II	O ₂ , 620°C	None	CO	CO ₂					5.26
				CH ₄					0.08
				H ₂					0.48
				H ₂					0.26
III	O ₂ , 620°C H ₂ , 620°C	H ₂	He	H ₂					0.26
IV	O ₂ , 620°C H ₂ , 620°C	CO ^b	He	CO	0.31		0.04		
				CO ₂		1.56			
V	O ₂ , 620°C	CO	He	CO	0.18				
				CO ₂		1.47			
VI	O ₂ , 620°C H ₂ , 620°C	CO	H ₂	CO	0.15		0.17	0.08	
				CO ₂		0.99			
				CH ₄				0.21	
VII	O ₂ , 620°C H ₂ , 620°C	H ₂	CO	CO ₂		0.47		0.45	
				H ₂				0.41	
VIII	O ₂ , 620°C H ₂ , 620°C	CO/H ₂ ^b	He	CO	0.07	0.01	0.51	0.20	
				CO ₂		0.82			
				CH ₄				0.10	
				H ₂				0.26	0.20
IX	O ₂ , 620°C H ₂ , 620°C	CO/H ₂	CO/H ₂	CO ₂		0.53		3.13	
				CH ₄				0.27	
X	O ₂ , 620°C H ₂ , 620°C	None	CO/H ₂	CO ₂		0.39		0.82	
				CH ₄				0.05	

^a Broad peak, covered the range of γ to ϵ .

^b Adsorbed as the temperature was lowered from 620 to 25°C.

(Nos. IV and V). Carbon dioxide was observed at the β temperature for both the oxygen only and oxygen/hydrogen-treated surfaces. Carbon monoxide was observed at the α temperature for both treatments and at the γ temperature when the ZrO₂ was treated with H₂. The total amount of CO and CO₂ observed was approximately the same for both treatments suggesting that hydrogen treatment does not significantly change the surface generated during oxygen treatment.

A series of ZrO₂ samples was examined by X-ray diffraction. Oxygen, oxygen/hydrogen, untreated ZrO₂, and a sample of ZrO₂ with a purity of 99.9975% all displayed a pattern characterized by the

monoclinic form of ZrO₂. No other diffraction peaks were observed. These observations demonstrate that, at the temperatures employed, only one bulk phase was present.

Figure 5 and Table 1 (No. VI) represent TPD/TPDE of adsorbed CO in flowing H₂. In this case methane was detected at the δ temperature. Carbon monoxide was detected at the α , γ , and δ temperatures, and the amount detected at the γ temperature was significantly greater than the amount detected for CO TPD/TPDE into He. Carbon dioxide was detected at the β temperature; the amount was less than TPD/TPDE into He. The total amount of carbon-containing species was approximately the same

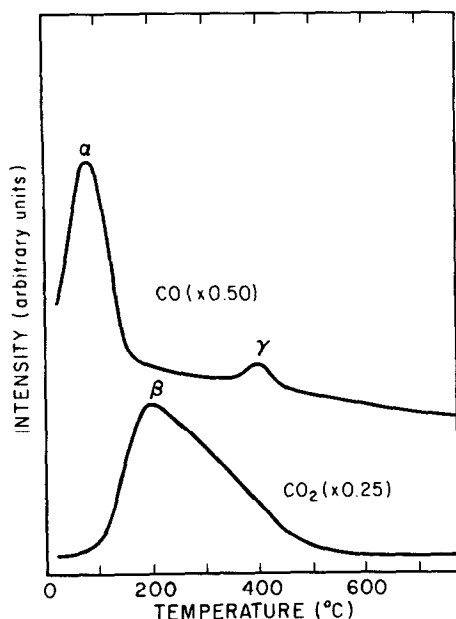


FIG. 4. Mass signals characteristic of the indicated molecules during the TPD/TPDE of oxygen/hydrogen-treated ZrO_2 , with CO preadsorption into He.

as that generated during TPD/TPDE into He suggesting that the same amount of CO adsorbed on the surface but underwent different reactions in the presence of H_2 .

Adsorption of H_2 and TPD/TPDE in CO is shown in Fig. 6 and Table 1 (No. VII). Hydrogen was detected at the ϵ temperature. Carbon dioxide was detected at the β and ϵ temperatures. Methane was not detected.

A series of experiments was performed in which a 1/1 mixture of CO/H_2 was either adsorbed or used as the flushing gas. The results are presented in Table 1 (Nos. VIII-X). The MS response for TPD/TPDE into He is shown in Fig. 7. The results for CO_2 were consistent with the observations made earlier; CO_2 was detected at the β temperature when CO was preadsorbed, (Nos. VIII and IX), or when CO interacted with H_2 (No. X), and at the ϵ temperature when CO was present in the flushing gas (Nos. IX and X). Co-adsorption of hydrogen resulted in a CO signal which displayed similar peaks to those observed when CO underwent TPD/TPDE in H_2 (Nos. VIII and VI, respec-

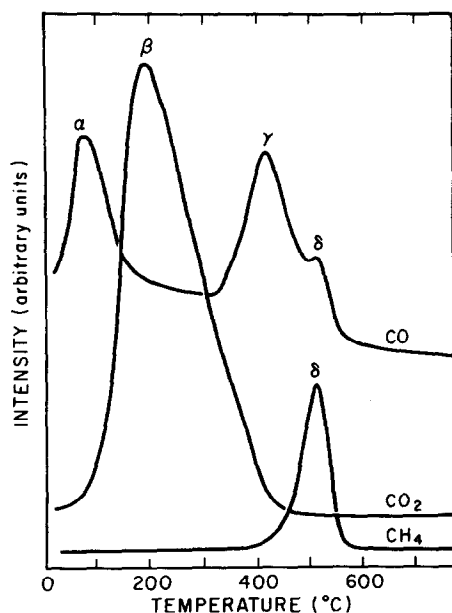


FIG. 5. Mass signals characteristic of the indicated molecules during the TPD/TPDE of oxygen/hydrogen-treated ZrO_2 , with CO preadsorption into H_2 .

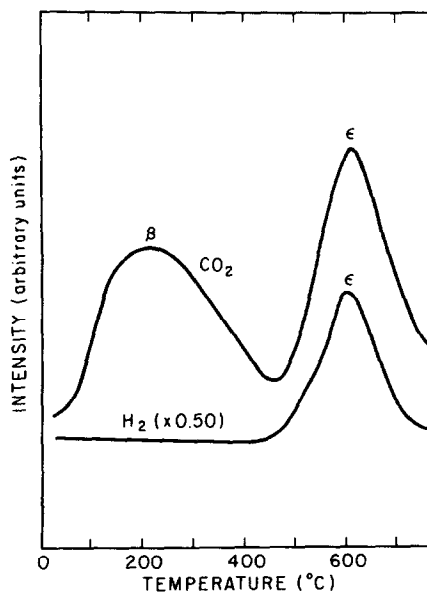


FIG. 6. Mass signals characteristic of the indicated molecules during the TPD/TPDE of oxygen/hydrogen-treated ZrO_2 , with H_2 preadsorption into CO.

tively). Coadsorption also resulted in a H₂ signal at the δ temperature. Methane was observed at the δ temperature when CO was preadsorbed and caused to interact with H₂ added to the system. Heating the treated surface in the presence of CO/H₂ (No. X) resulted in methane at the ε temperature.

The studies between CO and the hydroxylated surface demonstrated that CO interacted with the ZrO₂ to produce CO₂ and CH₄. The production of CH₄ from CO and added H₂ depended upon the manner in which adsorption and TPD/TPDE were performed. Preadsorbed CO reacted with hydrogen to give CH₄ at the δ temperature. The hydrogen could be added during TPD/TPDE or during adsorption. However,

TPD/TPDE of the hydroxylated surface in CO/H₂ resulted in CH₄ at the ε temperature, the same temperature at which TPD/TPDE of the oxygen-treated surface in CO alone generated CH₄. Unexpectedly, TPD/TPDE of adsorbed H₂ into CO did not generate CH₄.

TPD/TPDE of CO₂, H₂, HCOOH, and CH₃OH

A series of studies were performed with CO₂ as an adsorbate or flushing gas to determine if it was interconvertible with CO. The results are shown in Table 2 (Nos. I to V). Heating the oxygen treated surface in CO₂ did not produce any products. The TPD/TPDE of adsorbed CO₂ into flowing He resulted in CO at the β and γ tempera-

TABLE 2
TPD/TPDE of CO₂, H₂, HCOOH, and CH₃OH

No.	ZrO ₂ treatment	Preadsorbate (25–620°C, 620–25°C)	Flushing gas	Product	Molecules/nm ²				
					α	β	γ	δ	ε
I	O ₂ , 620°C	None	CO ₂	None					
II	O ₂ , 620°C	CO ₂	He	CO	0.04	0.18			
				CO ₂	0.51	0.03			
III	O ₂ , 620°C H ₂ , 620°C	CO ₂ ^a	He	CO	0.10	0.12			
				CO ₂	0.57				
IV	O ₂ , 620°C H ₂ , 620°C	None	CO ₂ /H ₂	CO				2.56	
				CH ₄				0.06	
V	O ₂ , 620°C H ₂ , 620°C	CO ₂ /H ₂	H ₂	CO	0.06	0.06			
				CO ₂	0.36				
VI	O ₂ , 620°C	HCOOH ^b	He	CH ₄			0.05		
				CO		6.54		0.26	
				CO ₂		1.35		0.32	
				CH ₄		0.02		0.15	
				H ₂		0.17		0.07	
				H ₂ O		3.17			
VII	O ₂ , 620°C	CH ₃ OH ^b	He	H ₂ CO			0.03		
				CO	0.44		0.21	0.38	
				CO ₂			0.10	0.53	
				CH ₄	3.50		2.21		
				H ₂			(Overscale)		
				H ₂ O			^c		
				CH ₃ OH	4.22				
H ₂ CO	1.62								

^a Adsorbed as the temperature was lowered from 620 to 25°C.

^b Adsorbed at 25°C.

^c Broad peak, covered the δ and ε regimes.

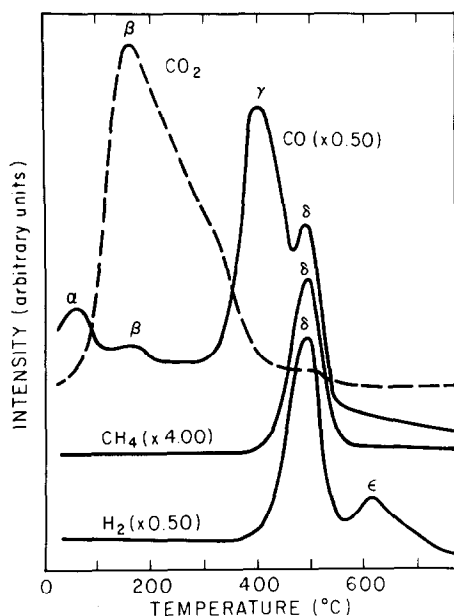


Fig. 7. Mass signals characteristic of the indicated molecules during the TPD/TPDE of oxygen/hydrogen-treated ZrO_2 , with CO/H_2 preadsorption into He.

tures for both oxygen- and oxygen/hydrogen-treated ZrO_2 . Oxygen-treated ZrO_2 produced CO_2 at the β and γ temperature; whereas, oxygen/hydrogen-treated ZrO_2 produced CO_2 at the β temperature. The β signal was the major CO_2 signal. The total amount of all desorbed species were reasonably close when CO_2 was adsorbed and nearly half of all desorbed species detected when CO was adsorbed.

The presence of H_2 in the flushing gas resulted in methane formation. Methane and CO were detected at the ϵ temperature when an oxygen/hydrogen-treated surface was heated in 1/1 CO_2/H_2 . Methane was observed at the δ temperature when 1/1 CO_2/H_2 were adsorbed and subjected to TPD/TPDE in flowing H_2 . These results were similar to those observed with CO ; methane was formed at the δ temperature when CO and CO_2 were adsorbed and methane was formed at the ϵ temperature when CO or CO_2 were a component of the flushing gas.

As discussed in the Introduction, formate

may be present on ZrO_2 following adsorption of CO or CO/H_2 . Formate and/or the formate ion have been observed upon contacting metal oxides such as Al_2O_3 (18), ZnO , MgO (19), Fe_2O_3 (20), and TiO_2 (21) with formic acid. Formic acid was adsorbed on oxygen-treated ZrO_2 in an attempt to generate adsorbed formate or the formate ion. The adsorption was conducted at $25^\circ C$ by bubbling helium through formic acid at $25^\circ C$ and contacting the ZrO_2 with the vapor for 1 h. The ZrO_2 was then flushed with pure helium for 1 hr to remove weakly adsorbed formic acid.

Formate decomposition occurs via dehydrogenation to H_2 and CO_2 or dehydration to H_2O and CO . The selectivity of the decomposition cannot be predicted a priori (22); therefore, if formate is generated over ZrO_2 either path could occur. Furthermore, the decomposition of formate may be different in the presence of gaseous formic acid (18, 21, 22) which may evolve undissociated from the ZrO_2 surface as the temperature is increased.

The TPD/TPDE results for adsorbed formic acid are shown in Fig. 8 and Table 2 (No. VI). Signals were detected at the γ and ϵ temperatures. Water and carbon monoxide were the major products at the γ temperature. Carbon dioxide was the major species at the ϵ temperature. A significant amount of methane was also detected at ϵ temperature.

Methanol has been shown to form methoxide over Fe_2O_3 (20), ZnO (23), Al_2O_3 (24), and MgO (25). 2-Hexanol formed an alkoxide over ThO_2 (26). These observations suggested that methanol may form methoxide over ZrO_2 . Methanol was adsorbed on ZrO_2 using the same procedure used for formic acid. Subsequent TPD/TPDE of the ZrO_2 produced the results shown in Fig. 9 and Table 2 (No. VII). Carbon monoxide, methane, methanol, and formaldehyde were detected at the β temperature. Carbon monoxide, carbon dioxide, methane, hydrogen, and water were observed at the δ temperature. In addition,

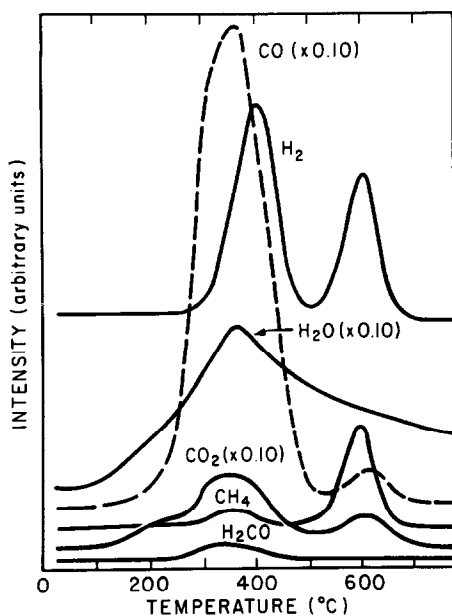


FIG. 8. Mass signals characteristic of the indicated molecules during the TPD/TPDE of oxygen-treated ZrO_2 , with $HCOOH$ preadsorption into He.

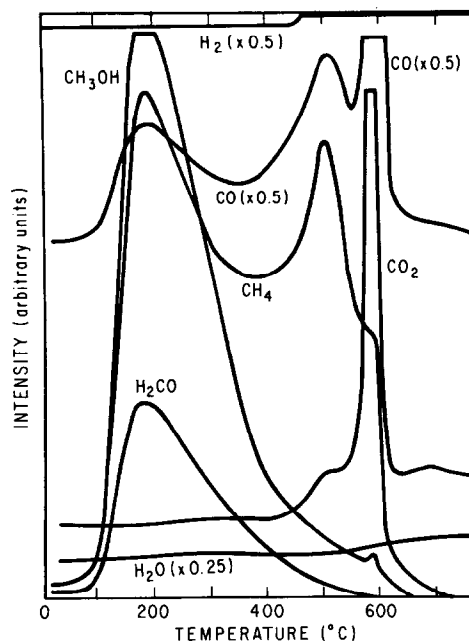


FIG. 9. Mass signals characteristic of the indicated molecules during the TPD/TPDE of oxygen-treated ZrO_2 , with CH_3OH preadsorption into He.

carbon monoxide and carbon dioxide were observed at the ϵ temperature. The major species at the δ temperature were H_2 , CO , and CH_4 .

Pulse Adsorption of CO and H_2

Pulse adsorption at certain temperatures was used to determine the effect of adsorp-

tion temperature upon the TPD/TPDE products. The results are listed in Table 3. Zirconia was oxygen- and hydrogen-treated at $620^\circ C$ and cooled to the adsorption temperature in He. Five pulses containing $87 \mu mole$ of gas were injected into helium and directed through the catalyst bed. This was estimated at 0.5 to 4.0 times the number of

TABLE 3
TPD/TPDE of CO and H_2 after Pulse Injection

No.	ZrO_2 treatment	Preadsorbate	Flushing gas	Product	Molecules/ nm^2					
					α	β	γ	δ	ϵ	
I	$O_2, 620^\circ C$	CO	He	CO	0.03					
	$H_2, 620^\circ C$	$320^\circ C$		CO_2	0.05					
II	$O_2, 620^\circ C$	CO/H_2	He	CO	0.41					
	$H_2, 620^\circ C$	$320^\circ C$		CO_2	0.07	0.20				
III	$O_2, 620^\circ C$	CO/H_2	He	CH_4	0.17					
	CO			0.26						
	CO_2			0.10						
	H_2			0.37						
	$620^\circ C$	$520^\circ C$					0.22	0.26	0.23	0.74

total surface sites for each pulse. The ZrO_2 bed was flushed with He for 30 min at the adsorption temperature and cooled to 25°C in flowing He.

Only CO and CO_2 were observed at the γ temperature during the TPD/TPDE of CO adsorbed at 320°C. The temperature of 320°C is between the β and γ regimes. These results suggest that the surface species which decomposed at the α and β temperature in Table 1 (No. IV), were not formed at 320°C and/or by surface reactions which may occur during cooling the adsorbed species to 25°C. (The results presented in Table 1 were arrived at by cooling the ZrO_2 in the presence of gas phase CO.)

Pulse adsorption of CO/H_2 at 320°C resulted in CO, CO_2 , and CH_4 at both the δ and ϵ temperatures. Pulse adsorption of CO/H_2 at 520°C, intermediate between the δ and ϵ regimes, resulted in CO, CH_4 , and H_2 at the δ and ϵ temperatures and CO_2 at the ϵ temperature. Formation of H_2 suggests that different or additional species formed at 520°C or that the ZrO_2 surface was affected differently at 520 versus 320°C; both adsorption temperatures resulted in methane at the δ and ϵ temperatures.

Deuterioxide Studies

The OH groups of ZrO_2 have been converted into OD groups by contacting dehydrated ZrO_2 with D_2O at 25°C (8) and at 300°C (9). The role of hydroxyl groups in the formation of surface intermediates was examined by contacting the deuterium exchanged surface with CO. The exchange conditions and TPD/TPDE results are listed in Table 4. Deuterium oxide exposure at the indicated temperatures lasted 30 min. The formation of HD in experiment II-1 indicates that OD groups were present and that deuteration of the original hydroxyl groups was incomplete.

When preadsorbed CO was subjected to TPD/TPDE in H_2 (No. I), HD and D_2 appeared near 300°C and the only hydrocarbon detected was CH_4 . The CO and CO_2 signals were similar to those reported in Ta-

ble 1 (No. VI). Infrared studies have revealed that OD groups are rapidly converted into OH groups at 200°C by exposing the deuterioxide surface to flowing H_2 (27). The appearance of HD and D_2 support this observation. Furthermore, CH_4 formation suggests that H-D exchange with both surface OD groups and partially deuterated C_1 species was complete by the time the δ temperature was reached.

Numbers II-1 to II-4 correspond to sequential experiments in which the ZrO_2 was contacted with D_2O vapor and oxygen-treated for the first experiment (No. II-1). The subsequent experiments were carried out by cooling in CO without additional ZrO_2 conditioning. The results for the first experiment were similar to those shown in Table 1 (No. II). All the products appeared at the ϵ temperature. Oxygen treatment at 620°C for 30 min is sufficient to remove molecular water (10). The deuterium in HD, D_2 , CD_4 , and CHD_3 was clearly from the OD groups of ZrO_2 . The TPD/TPDE process was repeated three more times in an

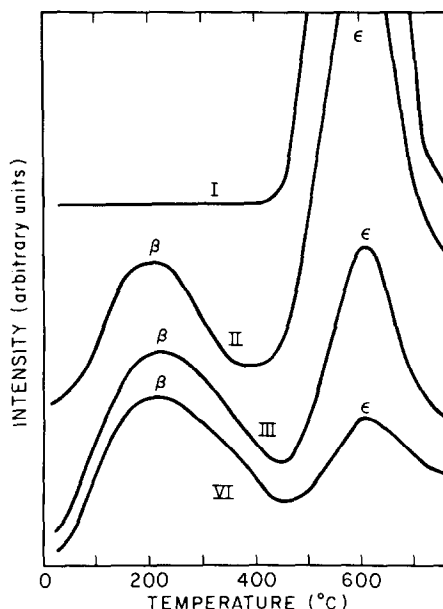


FIG. 10. Signal intensity of CO_2 for a sequence of TPD/TPDE cycles in which CO was the flushing gas and no preadsorption was used for curve I, and CO preadsorption was used for all other curves.

TABLE 4
TPD/TPDE of CO and Surface OD Groups

No.	ZrO ₂ treatment	Preadsorbate	Flushing gas	Product	Molecules/nm ²				
					α	β	γ	δ	ϵ
I	O ₂ , 620°C D ₂ O, 25°C O ₂ , 620°C	CO ^a	H ₂	HD		0.16 ^b			
				D ₂		0.01 ^{b,c}			
				CO	0.09		0.08		
				CO ₂		0.36			
				CH ₄			0.07		
II-1	O ₂ , 620°C D ₂ O, 25°C O ₂ , 620°C	None	CO	HD				0.12	
				D ₂				0.21	
				CO ₂				5.66	
				CD ₄				0.22	
				CHD ₃				0.14	
II-2	II-1	CO ^d	CO	HD				0.14	
				D ₂				0.30	
				CO ₂		0.28		0.94	
				CD ₄			0.01		
				CHD ₃			0.11		
II-3	II-2	CO ^d	CO	HD				0.09	
				D ₂				0.15	
				CO ₂		0.49		0.39	
II-4	II-3	CO ^d	CO	HD				0.05	
				D ₂				0.06	
				CO ₂		0.52		0.12	
II-5	II-4 D ₂ O, 320°C He, 320°C	None	CO	HD				0.10	
				D ₂				0.34	
				CO ₂		0.12		2.34	
				CD ₄				0.36	
				CHD ₃				0.51	
II-6	II-5 O ₂ , 620°C D ₂ O, 320°C He, 320°C	CO ^a	H ₂	HD		0.22 ^b			
				D ₂		0.01 ^{b,c}			
				CO	0.08		0.10		
				CO ₂		0.39			
				CH ₄			0.08		

^a Adsorbed as the temperature was raised from 25 to 620°C and lowered back to 25°C.

^b Temperature maximum of the peak was 302°C.

^c The signal extended into the δ regime.

^d The ZrO₂ was cooled to 25°C in CO after the preceding experiment.

attempt to consume surface OD groups. As shown in Fig. 10, the CO₂ peak appeared at the β and ϵ temperatures; the intensity of the β signal increased and that of the ϵ signal decreased with each experiment. Methane, CD₄, and CHD₃, were observed at the δ temperature for the first TPD/TPDE cycle of adsorbed CO (No. II-2). The total amount of HD plus D₂ decreased with each cycle.

The zirconia used in No. II-4 was con-

tacted with D₂O, flushed with He at 320°C and cooled to 25°C in flowing He. This was done to restore some of the OD groups. The TPD/TPDE of the treated surface in CO produced results which were similar to those for No. II-1 with the exception that CO₂ appeared at the β temperature. The differences between II-1 and II-5 could be due to the different ZrO₂ treatment temperatures.

As a final experiment, the zirconia used

in II-5 was oxygen treated at 620°C cooled in He to 320°C and treated as in No. II-5. Carbon monoxide was adsorbed and subjected to TPD/TPDE in H₂. The results are nearly identical to those shown for a fresh loading of ZrO₂ (Table 4 (No. I)). This demonstrates that deuteration at 25 or 320°C produced similar surfaces and that the ZrO₂ can be restored to the fresh state by oxygen treatment at 620°C.

IV. DISCUSSION

All the products of the TPD/TPDE process appeared at certain temperatures which were denoted as α , β , γ , δ , and ϵ . These products were formed by desorption or decomposition of surface species. The discussion addresses the surface species expected at each temperature regime and the interconversion of surface species. These observations are then combined to propose a mechanism for synthesis gas conversion over ZrO₂ at 1 atm.

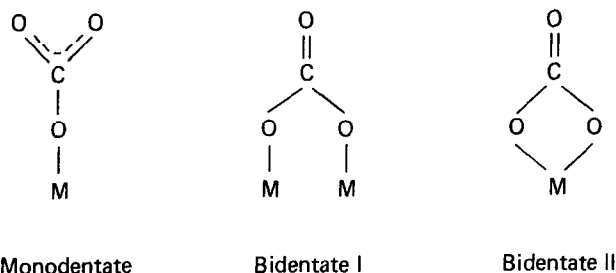
Surface Species Assignments

The α temperature was the lowest at 40 to 60°C. Carbon monoxide was the only product detected at this temperature and it was only observed when CO was adsorbed at temperatures between 320 and 25°C. The

low desorption/decomposition temperature implies that the species giving rise to α -CO was weakly adsorbed molecular CO. Support for this interpretation comes from observations over ThO₂ where an infrared band for weakly adsorbed molecular CO was observed following adsorption at 200°C. This molecular CO could be pumped off under vacuum at 25°C (28).

Carbon monoxide and CO₂ were the only products observed at the β temperature and carbon dioxide was always the major component. The β species was formed by adsorption of CO below 320°C, adsorption of CO₂, TPD/TPDE of adsorbed H₂ in CO and CO/H₂, and during the TPD/TPDE of an oxygen-treated surface in CO/H₂. This surface species was converted to CO₂ and/or CO and was formed by either CO₂ or CO. The β species is thought to be a bidentate carbonate.

Infrared studies of CO₂ adsorption on ZrO₂ (10) and CO₂ and CO adsorption on ThO₂ (12, 28) reveal that carbonates form over these oxides upon adsorption of CO₂. (Carbon monoxide formed a structure on ThO₂ which had bands similar to a formate or a carboxylate; the structure was assigned to the formate (28).) The carbonate structures are



The formation of monodentate and bidentate II from CO₂ has been investigated over ThO₂ where it was shown that the monodentate structure was more stable, decomposing at temperatures near 350°C while bidentate II decomposed near 150°C (28). Both of these structures involve a surface oxygen of the metal oxide. Tret'yakov *et*

al. (10) noted the bands formed upon adsorption of CO₂ onto ZrO₂. They inferred that bidentates I and II formed but did not compare the spectra against known zirconium compounds as was done over ThO₂ (28). This makes their assignments less definitive. The two carbonate species had different stabilities, bidentate I was removed

by evacuation at 150°C while bidentate II was removed by evacuation at 300°C.

The preceding observations demonstrate that carbonates are present over ZrO₂. The β carbonate decomposed in the temperature range of 120–180°C suggesting either bidentate I (10) or bidentate II (28). It is not possible to assign the structure over ZrO₂ without additional infrared data.

Adsorption of CO and CO₂ resulted in the formation of CO at the γ temperature during TPD/TPDE into H₂ or He. Carbon dioxide was observed when CO₂ was adsorbed on the oxygen-treated surface, when untreated catalyst was subjected to TPD/TPDE, and when CO was adsorbed at 320°C. The untreated results (Table I, No. I), imply that CO₂ adsorbed on the surface during storage of the ZrO₂ in a manner similar to that reported over ThO₂ (12, 28). The γ species is assigned to a bicarbonate. The assignment of the γ species could not be made solely from the TPD/TPDE studies reported herein; it was also based on infrared studies reported in a future paper (27).

Tret'yakov *et al.* (10) reported infrared bands following CO₂ adsorption which they tentatively assigned to a bicarbonate species. Tanaka and White (29, 30) found that when CO₂ or CO were adsorbed on TiO₂ a bidentate carbonate formed via a bicarbonate species. A bicarbonate species has also been observed via infrared (27) upon adsorption of CO₂ or CO over ZrO₂. The thermal decomposition of bicarbonate should give rise to CO and/or CO₂ and H₂O and/or H₂. Water and H₂ were never observed at the γ temperature for the experiments listed in Tables 1–3. This H₂O or H₂ may have reacted with the ZrO₂ surface into surface hydroxyl species.

Several products appeared at the δ temperature during the TPD/TPDE process, CO, CH₄, H₂, and in one instance CO₂. Peaks appeared at the δ position only when CO or CO₂ were preadsorbed and underwent TPD/TPDE in H₂ or in the presence of preadsorbed H₂. Aside from the formic acid experiments, which will be discussed later,

the δ temperature was the lowest temperature at which methane formed.

As discussed in the Results section, a methoxide species was expected upon adsorption of CH₃OH. Infrared studies in our laboratory have shown that methanol does form a methoxide over ZrO₂ at 25°C (27). The decomposition of methoxide on metal oxides gives rise to H₂, CO, and CH₄ at high temperatures, e.g., above 420°C for Al₂O₃ (24) and above 450°C for MgO (25). The methanol induced methoxide most likely decomposed at the δ temperature because the δ temperature gave rise to methane whereas the ε temperature did not. It seems reasonable to suggest that the CO/H₂ induced surface species which decomposed at the δ temperature was a methoxide.

Formic acid was expected to produce formate or formate ion upon adsorption on ZrO₂. Infrared results confirm the presence of formate upon formic acid adsorption but do not indicate the temperature at which decomposition occurs or the mechanism by which decomposition occurs (27). We propose that the formic acid induced formate probably decomposed at both temperatures shown in Table 2 (No. VI). At the γ temperature, surface formate decomposition was probably accompanied by an Eley-Rideal process in which gas-phase formic acid reacted with surface formate (19) or with surface OH (18). At the ε temperature, the remaining formate underwent decomposition. The decomposition products at the ε temperature were CO, CO₂, CH₄, and H₂.

The species decomposing at the ε temperature gave rise to CO, CO₂, CH₄, and H₂. Preadsorbed H₂ also evolved H₂ at this temperature. Gas-phase products were observed at this temperature when CO, CO/H₂, and CO₂/H₂ were present in the flushing gas or when CO/H₂ were adsorbed above 320°C. The γ species is associated with a bicarbonate. Formic acid resulted in products at the γ and ε temperatures and the ε products were assigned to formate decomposition. The similar nature of the products derived from CO/H₂ and formic acid at the

ϵ temperature suggest that the ϵ species is a formate.

Interconversion of Surface Species

Methane was formed at both the δ and ϵ temperatures. Methoxide is proposed to be the immediate precursor to methane and the formate is proposed to be the intermediate species from which methoxide forms. This requires that CO interact with the surface to form a formate. Experimental evidence supporting this postulate is discussed below.

Adsorption of CO by continuous contact either from 620 to 25°C (a process requiring 60 min) or from 25 to 620 to 25°C (a process requiring 75 min) provided sufficient opportunity for formate to form and interact with surface hydroxyl and/or added hydrogen to generate some methoxide. (This is supported by infrared studies which have revealed that adsorption of CO and CO/H₂ from 25 to 540 to 25°C resulted in formate and methoxide species (27).) Temperature-programmed heating in H₂ of a surface containing formate and methoxide species resulted in CH₄ at the δ temperature. During this TPD/TPDE process in H₂ any remaining formate was converted to methoxide (represented as $\epsilon \rightarrow \delta$) by the time the temperature had increased to 510°C, the end of the δ temperature regime. Methoxide decomposition at the δ temperature was also accompanied by the appearance of CO and H₂; methane was the major carbon-containing product. This CO and H₂ may have formed by some of the methoxide decomposing along the reverse path of its formation, as shown in Fig. 1, or by some additional route which was not revealed in these studies.

Desorption/decomposition of methanol induced methoxide resulted in products at the δ and ϵ temperatures (Table 2, No. VII). The major product was methane at the δ temperature. The CO, CO₂, H₂, and H₂O observed at the ϵ temperature are consistent with formate decomposition (22). This formate could have formed at the δ

temperature as methoxide decomposed in the reverse direction shown in Fig. 1. Alternately some of the methanol generated at the β temperature may have served as an oxygen source (31, 32) for the oxidation of methoxide to formate prior to the δ temperature. The means by which methanol induced methoxide converted into formate were not investigated.

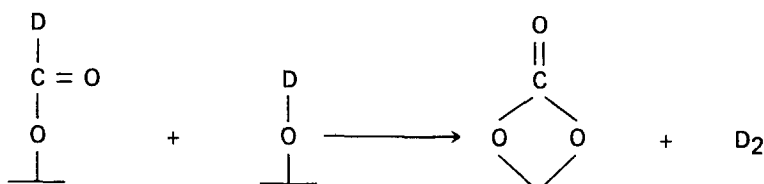
Methane was observed at the ϵ temperature when a treated surface was heated in flowing CO (Table 1, Nos. II and X). Carbon dioxide was the major component observed at the ϵ temperature in these experiments. The formate species formed during this heating in CO. There may not have been sufficient time for a detectable amount of the formate to convert into methoxide after the formate was generated and before the δ temperature regime was reached. This would explain the absence of any gas-phase products at the δ temperature. Methane, CO₂, and H₂ were detected at the ϵ temperature. The methane may have formed by some of the formate decomposing via the methoxide species as shown in Fig. 1. Carbon dioxide and H₂ are expected during formate decomposition (22).

The cause for the absence of methane during the TPD/TPDE of adsorbed H₂ into flowing CO was not revealed in these studies. Methane was expected at the ϵ temperature in accordance with the reasoning given above. Hydrogen preadsorption did lead to a hydrogen signal during TPD/TPDE into He suggesting the surface had been altered by hydrogen adsorption versus hydrogen treatment. This may suggest that the oxygen atom concentration, which could have been reduced by hydrogen adsorption, is an important variable for CO interaction with the surface.

The sequential experiments listed in Table 4, Nos. II-1 and II-2 further demonstrate the $\epsilon \rightarrow \delta$ conversion. Both involved TPD/TPDE in flowing CO where only ϵ products were expected based on the results in Table 1. The results for II-1 were obtained without preadsorption and agree

with the similar experiment in Table 1. The TPD/TPDE process for No. II-1 served as the preadsorption procedure for No. II-2. This contact time was sufficient for $\varepsilon \rightarrow \delta$ conversion, leading to the methane observed for No. II-2. The OD groups were removed with each successive experiment. The failure to observe methane for Nos. II-3 and II-4 implies that OD groups were involved in the $\varepsilon \rightarrow \delta$ conversion and that their concentration was too low or the type, bridged versus linear, was wrong for methoxide formation.

Final evidence for the interconversion of methoxide and formate species is found in the isothermal CO/H₂ adsorption experiments listed in Table 3. Adsorption at 320 and 520°C resulted in the production of



Alternately, repeated removal of D from the surface OD groups could increase the concentration of surface oxygen which may facilitate formation of the β species upon exposure of ZrO₂ to gas-phase CO.

Methanation of CO₂

The methanation of CO₂ on ThO₂ was reported recently (12). We have also found that CO₂ reacts with hydrogen on ZrO₂ to yield methane. Comparison of Table 1 (No. II) and Table 2 (No. I) reveals that CO and CO₂ interact differently with surface OH groups. These results indicate that CO₂ did not form a formate directly as did CO. Carbon dioxide resulted in a bicarbonate. The isothermal adsorption of CO at 320°C resulted in the appearance of CO and CO₂ at the γ temperature implying that a bicarbonate had formed. Coadsorption of H₂/CO at the same temperature resulted in methoxide and formate species. These observations suggest that the bicarbonate can be

methane at both the δ and ε temperatures. Methoxide was found to decompose during TPD/TPDE at the δ temperature, 460–510°C. The observation that methoxide was formed during adsorption in H₂/CO at 520°C or during the time required to cool the ZrO₂ to 25°C in He demonstrates that formate can be converted into the methoxide.

The β and ε species, carbonate and formate, respectively, also appear to be related. As demonstrated in Table 4, formate formation involved surface OD groups. The generation of CO₂ at the ε temperature decreased while that at the β temperature increased with sequential experiments. A possible reaction for the $\varepsilon \rightarrow \beta$ conversion could be

reduced to formate over a ZrO₂ surface. (Infrared results over ZrO₂ demonstrate that the bicarbonate can be reduced to the formate (27).) Coudurier *et al.* (12) proposed that CO₂ hydrogenation proceeded through a monodentate carbonate that converted into CO; the CO manifested itself on the surface of ThO₂ as a formate. Our results suggest that methanation of CO₂ over ZrO₂ may proceed via a bicarbonate which directly forms the formate in the presence of hydrogen. This is shown as the last reaction in Fig. 1.

Tentative Mechanism for the Interaction of CO and H₂

Surface OH groups have been shown to be important for CO conversion into formate and methoxide. The results in Table 4 demonstrated that OD groups underwent rapid exchange with gas-phase H₂. Holm and Blue (33) also observed H–D exchange over ZrO₂ at 300°C. Evolution of H₂ at the ε

temperature following H₂ adsorption and the H–D exchange results suggest the presence of atomic hydrogen which is strongly bonded to the surface. (Tret'yakov *et al.* have shown that the OH groups decompose under vacuum at 750°C.) The nature of this atomic hydrogen was not revealed in these studies. A tentative mechanism for CO and H₂ conversion is presented in Fig. 1 where the hydrogen source is OH. Our results suggest this but do not rule out interaction with atomic hydrogen. The role of gas phase H₂ in the proposed mechanism is to replenish OH groups which was demonstrated.

The results shown in Table 1 (Nos. IV and V) and Table 3 (No. I) suggest that CO interacts with surface oxygen to form a carbonate and bicarbonate. Infrared studies reveal that CO forms a formate on ZrO₂ (27). Two possible CO surface reactions are presented for formate formation. Carbon monoxide may react with metal oxide oxygen to form a [COO] intermediate which reacts further to the carbonate or formate. Alternatively, CO may react directly with OH to form the formate. Studies are in progress to help establish this initial interaction.

The formate interacts with OH groups to form the carbonate or is reduced to the methoxide. The structure intermediate between the formate and methoxide is merely meant to represent the stoichiometry of this intermediate. This mechanism incorporates the $\epsilon \rightarrow \delta$ and $\epsilon \rightarrow \beta$ conversion suggested by the TPD/TPDE studies. Infrared evidence which supports this tentative mechanism is presented in a future paper (27).

V. CONCLUSIONS

Carbon monoxide and hydrogen were shown to interact with the surface of ZrO₂ to give five distinct surface species. Each species decomposed at different temperatures. The use of labeling, methanol, and formic acid facilitated identification of the species. They are α —molecular carbon monoxide, β —a bidentate carbonate, γ —bicarbonate, δ —methoxide, ϵ —formate.

The methoxide was argued to be the immediate precursor to methane. This methoxide was formed via a formate which either reacted to a carbonate or the methoxide. These conversions were postulated to involve the surface OH groups.

Carbon dioxide was shown to be methanated over ZrO₂. The yields were much lower than those observed using CO under identical conditions. The reaction was proposed to involve a CO₂ \rightarrow bicarbonate \rightarrow formate route. Once the formate formed the reaction was similar to that proposed for CO/H₂.

ACKNOWLEDGMENTS

The authors acknowledge the many productive discussions of these results with Dr. J. M. White of the University of Texas. M.-Y. H. thanks the Research Institute of Petroleum Processing (Beijing PRC) for a leave of absence. This work was supported in part by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract DE-AS05-80ER1072 and the University of Texas Center for Energy Studies.

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