Oxidation of C₂ Hydrocarbon Products during the Oxidative Coupling of Methane over a Li/MgO Catalyst

Peter F. Nelson*

CSIRO Division of Coal Technology, P.O. Box 136, North Ryde 2113, Australia

and Noel W. Cant

School of Chemistry, Macquarie University, Sydney, NSW 2109, Australia (Received: August 21, 1989)

The contribution of oxidation of C2 hydrocarbons to carbon oxide formation during the oxidative coupling of methane over a Li/MgO catalyst has been investigated. Small quantities of ${}^{13}C_2H_6$ and ${}^{13}C_2H_4$ were added to CH_4/O_2 in a recycle reactor and the ${}^{12}C$ and ${}^{13}C$ contents of C_2H_6 , C_2H_4 , CO, and CO₂ were determined by mass spectrometry and Fourier transform infrared spectroscopy. At temperatures greater than 740 °C, C_2 oxidation was responsible for the formation of 30–80% of the carbon oxides. However at lower temperatures (<700 °C) C_2 oxidation accounted for less than 10% of the carbon oxides. Possible mechanisms for C_2 oxidation are competition with CH₄ for O_2 in a surface-promoted reaction and/or a purely homogeneous process involving competitive reactions of the methyl radical. Calculations based on known rate constants and experimental observations of increased C_3H_6 formation when ${}^{13}C_2H_4$ is added to the CH_4/O_2 mixture show that the abstraction and combination reactions, $CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$ (6), $CH_3 + C_2H_4 \rightarrow CH_4 + C_2H_3$ (7), and $CH_3 + C_2H_4 \rightarrow C_3H_7 \rightarrow C_3H_6 + H$ (8), compete effectively with the methyl coupling reaction. The ${}^{13}C$ content of C_2H_6 and C_2H_4 confirms that secondary reactions of C_2H_6 are responsible for C_2H_4 formation. Results for the ¹³C content of CO and CO₂ are consistent with CO oxidation being the source of CO_2 but are not precise enough for this conclusion to be definitive. The experiments also show that there is an exchangeable pool of CO₂ on the catalyst, and the formation of Li₂CO₃ under reaction conditions is probably responsible.

Introduction

The direct catalytic conversion of methane to higher hydrocarbon products has attracted considerable research attention recently, since it provides a possible method for more efficient use of abundant natural gas reserves. Of particular interest is the oxidative coupling route, which entails the conversion of methane to C_2 hydrocarbons and has been demonstrated for a wide range of materials; catalysts based on PbO,¹ Na-promoted Mn supported on SiO₂ and MgO,² alkaline³ and rare earth⁴ oxides, and Li-promoted magnesia (Li/MgO)^{5,6} have been reported, inter alia, to give significant methane conversions and high selectivities to hydrocarbon products.

It is clear from previous studies that the only significant primary source of higher hydrocarbons in this reaction is coupling of methyl radicals to form ethane. Evidence for the role of CH₃, and for the importance of a purely gas phase coupling process, is provided by matrix isolation electron spin resonance measurements $(MIESR)^7$ and by isotopic studies using CH_4/CD_4 mixtures.^{8,9} Secondary reactions of C_2H_6 are responsible for the formation of other higher hydrocarbons, principally ethylene.¹⁰

Every catalyst system so far reported also produces significant yields of carbon oxides, both CO and CO₂. In a practical application of the oxidative coupling process, excessive formation of CO_x is undesirable since it leads to inefficient use of the

(4) Otsuka, K.; Junsold, J. H.S. Chem. Soc., Chem. Commun. 1560, 1210.
(4) Otsuka, K.; Jinno, K.; Morikawa, A. J. Catal. 1986, 100, 353.
(5) Ito, T.; Lunsford, J. H. Nature 1985, 314, 721.
(6) Ito, T.; Wang, J.-X.; Lin, C.-H.; Lunsford, J. H. J. Am. Chem. Soc. 1985, 107, 5062.

feedstock and creates engineering difficulties because of the large exothermicities of the total oxidation reactions.¹¹

The mechanism for the formation of carbon oxides is not as well understood as that for the coupling reaction. Lunsford and co-workers^{6,12} have proposed that an important source of carbon oxides is the methylperoxy radical, CH₃O₂. This radical is produced by an addition reaction:

$$CH_3 + O_2 \rightarrow CH_3O_2 \tag{1}$$

Recent measurements^{13,14} of the equilibrium constant for (1) show that significant amounts of CH₃O₂ would be present under the experimental conditions of temperature, CH_4/O_2 ratios, and pressure used for oxidative coupling reactions. This species has also been detected by ESR,¹⁵ albeit at somewhat lower temperatures than usually employed for this reaction. In the scheme of Lunsford^{6,12} carbon oxides are produced by subsequent reactions of CH₃O₂:

$$CH_3O_2 + C_2H_6 \rightarrow CH_3O_2H + C_2H_5$$
(2)

$$CH_3O_2 + CH_3O_2 \rightarrow CH_2O + CH_3OH + O_2 \qquad (3)$$

$$CH_2O, CH_3OH \rightarrow CO, CO_2$$
 (4)

However, recent measurements9 of selectivity changes observed when CH₄ is substituted by CD₄ and the flow rate is reduced to compensate for the lower rates of conversion with CD₄ are inconsistent with a mechanism involving purely homogeneous reactions of CH_3O_2 . Thus the participation of the surface in formation of CO_x is probably indicated.

Another possible source of carbon oxide formation in this reaction is oxidation of the C_2 hydrocarbons. Although these are present in low concentration relative to CH₄, they are considerably more reactive to oxygen. They have already been shown to be responsible for significant CO_x formation over a Sm₂O₃ catalyst.¹⁶

- (11) Edwards, J. H.; Tyler, R. J. Catal. Today 1989, 4, 345.
 (12) Lin, C.-H.; Wang, J.-X.; Lunsford, J. H. J. Catal. 1988, 111, 302.
 (13) Khachatryan, L. A.; Niazyan, O. M.; Mantashyan, A. A.; Vedeneev, V. I.; Teitel'boim, M. A. Int. J. Chem. Kinet. 1982, 14, 1231.
 (14) Elschel L. G. Corrector D. L. C. Corrector and Construction of the construction of the construction of the construction.
- (14) Slagle, I. R.; Gutman, D. J. Am. Chem. Soc. 1985, 107, 5342.
 (15) Driscoll, D. J.; Martir, W.; Wang, J.-X.; Lunsford, J. H. J. Am.

⁽¹⁾ Hinsen, W.; Bytyn, W.; Baerns, M. Proc. Int. Congr. Catal. 1984, 8(2), 581

 ⁽²⁾ Sofranko, J. A.; Leonard, J. J.; Jones, C. A. J. Catal. 1987, 103, 302.
 (3) Aika, K.; Lunsford, J. H. J. Chem. Soc., Chem. Commun. 1986, 1210.

⁽⁷⁾ Campbell, K. D.; Morales, E.; Lunsford, J. H. J. Am. Chem. Soc. 1987, 109. 7900.

^{(8) (}a) Nelson, P. F.; Lukey, C. A.; Cant, N. W. J. Phys. Chem. 1988, 92, 6176. (b) Mims, C. A.; Hale, R. B.; Rose, K. D.; Meyers, G. R. Catal. Lett. 1989, 2, 361

⁽⁹⁾ Nelson, P. F.; Lukey, C. A.; Cant, N. W. J. Catal. 1989, 120, 216. (10) Tyler, R. J.; Lukey, C. A. Prepr.—Am. Chem. Soc., Div. Fuel Chem. 1987, 32(3), 249.

Chem. Soc. 1985, 107, 58.

TABLE I: Conditions for ¹³C₂H₆ Runs^a

temp.	CH ₁ /O	flow rate.	recirculn rate.	O ₂ conversion, %		C ₂ selectivity, %		C_2H_4/C_2H_6	
°C	(% of flow)	mL/min	mL/min	loop off	loop on	loop off	loop on	loop off	loop on
740	90/10	40	400	43	27	78	73.5	0.48	0.40
680	90/10	15	400	23	18	66	63	0.19	0.23
740	90 /10	25	400	56	34	76	70	1.49	1.87
780	21/11 ^b	20	400	34	20	54	52	1.03	1.03

^a Loop off refers to reactor operating in single-pass mode; loop on in recycle mode with no ${}^{13}C_2H_6$ addition. ^b Balance helium.

TABLE II: Conditions for ¹³C₂H₄ Runs^a

temp	CH_{1}/O_{2}	flow rate.	recirculn rate.	O_2 conversion, %		C ₂ selectivity, %		$C_{2}H_{4}/C_{2}H_{6}$	
°C	(% of flow)	mL/min	mL/min	loop off	loop on	loop off	loop on	loop off	loop on
740	90/10	25	400	60	35	78.3	72.5	0.71	0.55
780	20/10	20	400	78	47	53.4	52.6	2.10	0.99
740	90/10	40	400	45	27	80.5	75.4	0.50	0.40
672	90/10	16	400	19	13	65	59	0.21	0.20

^a Loop off refers to reactor operating in single-pass mode; loop on in recycle mode with no ${}^{13}C_2H_4$ addition. ^b Balance helium.

In this study, oxidation of C₂ hydrocarbons as a source of carbon oxides is further evaluated by using a Li/MgO catalyst similar to that originally reported⁵ by Ito and Lunsford. Small amounts of ${}^{13}C_2H_6$ or ${}^{13}C_2H_4$ were added to CH₄/O₂ mixtures in a recycle reactor and the ${}^{13}C$ contents of ethane, ethylene, CO, and CO₂ were determined by mass spectrometry (MS) and Fourier transform infrared (FTIR) spectroscopy.

Experimental Section

The Li/MgO catalyst was similar to that used previously.^{8a} It had an Li content of 0.77% w/w after firing at 850 °C in air and 0.095% w/w after these experiments. The surface area of this catalyst was $0.45 \text{ m}^2/\text{g}$ after these experiments. Experiments were performed at atmospheric pressure using a flow system and a recycle reactor constructed from fused alumina tubing (4 mm i.d., Alsint 99.7) which was mounted vertically and heated by a tube furnace. The catalyst bed was supported on a bed of crushed alumina which was held in place by the tip of an alumina thermocouple sheath, inserted into the bottom of the reactor. A second thermocouple, also sheathed in alumina, was located just above the catalyst bed. Bed size was 0.200 g.

Recycling of the gases was achieved with a stainless steel bellows circulating pump (Metal Bellows Corp.), a needle valve to control the recirculation rate, and a pressure transducer to monitor the pressure at the entrance to the bed.

The use of a recycle reactor for this experiment was essential, since a single-pass system would lead to different concentration profiles in labeled and unlabeled species along the reactor. Thus the labeled and unlabeled C_2 hydrocarbons would not be exposed to the same catalyst at the same concentrations and there could be no guarantee they would react in the same way.

The recycle pump ensures that the profiles for labeled and unlabeled C_2 species are almost constant along the catalyst bed. A recycle rate of about 10 times the input and output flows from the loop was used and is sufficient to ensure the above condition is satisfied.

Pretreatment of the Li/MgO comprised heating the sample to reaction temperature in flowing helium over a period of 1 h. The reaction mixture, with preset composition and flow rate, was then introduced and the system run until stable activity was reached (2-5 h). The catalyst remained usable for a further 30 h before a steep increase in carbon monoxide production, and loss of hydrocarbon selectivity, occurred due to depletion of lithium by volatilization. This initial lining out of the catalyst was performed in the single-pass configuration, with the recycle pump off. When stable activity was observed, the recycle loop was started and the labeled C_2 species introduced.

Ultra-high-purity CH₄ (99.9% minimum), high-purity N₂ (99.99%), and industrial O_2 (99.5% minimum) were used without further purification. Ethane- $1,2^{-13}C_2$ (99 atom % ¹³C) and

(16) Ekstrom, A.; Lapszewicz, J. A. J. Phys. Chem. 1989, 93, 5230.

ethylene- $1,2^{-13}C_2$ (99.3 atom % ¹³C) were supplied by MSD Isotopes.

To facilitate flow of the two C_2 compounds, the cylinders containing these gases were pressurized with methane to 1000-2000 kPa. Flows of all gases were controlled by separate electronic mass flow controllers (Brooks Div., Emerson Electric Co.). The valving of the gas supply to the reactor was such as to allow rapid partial or complete substitution of CH₄ flow with mixtures of the ¹³C labeled C₂ compounds in CH₄.

Feed and product gas were analyzed by gas chromatography (GC) using a Chromosorb 102 column coupled to thermal conductivity (TCD) and flame ionization detectors (FID) in series. The system was calibrated against standard gas mixtures (CIG Ltd., Australia) of similar composition to the product mixture. Identical responses were assumed for ¹²C and ¹³C species. The effluent from the reactor was connected to the inlet system of a quadrupole mass spectrometer (VG SX-200) operated in the multiple ion monitoring mode. The reaction was run with the isotope added until the mass spectrometer indicated constant composition. This is necessary since some CO₂ exchanges with the catalyst (see Figure 5).

Samples of feed and product gas were also collected in an infrared gas cell (10 cm path length). The collection was made during periods of constant composition. Gas-phase FTIR spectra were obtained with Digilab FTS 20/80 and 15/80 spectrometers. The spectra were recorded at 0.25 cm⁻¹ resolution by the coaddition of 256 scans.

Results

The experiments performed in this study were designed to vary selectivity, by changes in temperature and CH_4/O_2 ratios, from optimum levels and to determine if the selectivity decreases observed were due to product oxidation. Experimental conditions and results for the two sets of experiments prior to the addition of the labeled C₂ species are given in Tables I and II. The experiments were comparative: each day of running an experiment at 740 °C was first performed under conditions which gave optimum selectivity; conditions were then varied to give decreased selectivity.

Recycling the gas has the effect of lowering O_2 conversion and C_2 selectivity. This is probably due to inhibition by CO_2 , which has previously been observed to decrease conversion rates.¹⁷

The ¹³C contents of the reactants and products were monitored by MS and FTIR spectroscopy. The signals for m/e = 44 and 45 were used to determine ¹²CO₂ and ¹³CO₂, and the signal for m/e = 31 was used to determine ¹³C₂H₆; total C₂H₆ was determined by GC analysis. It was not possible to use MS to determine

^{(17) (}a) Tyler, R. J.; Lukey, C. A. In *Proceedings of the Bicentenary Catalysis Conference—1988*; Royal Australian Chemical Institute: Sydney, 1988; pp 167–170. (b) Campbell, K. D.; Lunsford, J. H. J. Phys. Chem. 1988, 92, 5792.

		¹³ C ₂ H ₆ added, % v/v	$^{13}C/(^{12}C + ^{13}C)$							% CO	
temp, °C [CH ₄ /O ₂]	$^{12}C_2H_6^a$ loop on, % v/v		C ₂ H ₆		C ₂ H	СО	CO ₂		from C_2 oxidn		
			FTIR	MS	FTIR	FTIR	FTIR	MS	CO	CO ₂ ^b	
740 [90/10]	1.12	0.59	0.26	0.26	0.27	0.085	0.070	0.07	33	27	
680 [90/10]	0.51	0.5	0.39	0.40	0.38	0.04	0.05	0.03	10	10 ± 3	
740 [90/10]	1.20	1.1	0.34	0.42	0.37	0.14	0.15	0.12	35	34 ± 5	
780 [21/11]	0.61	0.56	0.23	0.29	0.28	0.21	0.18	0.15	75	62 ± 12	

TABLE III: Results for ¹³C₂H₆ Experiments

^a Yield of C_2H_6 with recycle loop on but no ${}^{13}C_2H_6$ added. ^bErrors reflect differences in FTIR and MS determinations.

TABLE IV: Results for ¹³C₂H₄ Experiments

				$^{13}C/(^{12}C)$	% CO.				
temp. °C	$^{12}C_2H_4^a$ loop	¹³ C ₂ H ₄ added.	C ₁ H	СО	C	O ₂	from C ₂ oxidn		
$[CH_4/O_2]$	on, % v/v	% v/v	FTIR	FTIR	FTIR	MS	CO	CO ₂ ^b	
 740 [90/10]	0.76	1.12	0.50	0.31	0.24	0.25	62	49 ± 1	
780 [20/10]	0.61	0.56	0.33	0.28	0.26	0.20	85	70 ± 9	
740 [90/10]	0.49	0.28	0.31	0.10	0.10	0.085	32	30 ± 2	
672 [90/10]	0.09	0.25	0.65	0.082	0.055	0.06	13	9 ± 1	

^a Yield of C_2H_4 with recycle loop on but no ${}^{13}C_2H_4$ added. ^b Errors reflect differences in FTIR and MS determinations.





the ¹³C content of carbon monoxide or ethylene, however, as the fragmentation of the various ethanes and ethylenes interfere with the signals for m/e = 26-30. Instead FTIR spectroscopy was used to determine ¹²C₂H₄ and ¹³C₂H₄, and ¹²CO and ¹³CO. Figures 1 and 2 show spectra for the product gas from the addition of a CH₄/¹³C₂H₄/O₂ mixture to Li/MgO at 740 °C. The region from 2225 to 2000 cm⁻¹ shows absorbance due to ¹²CO and ¹³CO (Figure 1a), and that from 1000 to 800 cm⁻¹ absorbance due to ¹²CH₄ and ¹³C₂H₄ (Figure 2a). Each figure also shows a difference spectrum obtained by subtraction of ¹²CO and ¹²C₂H₄, respectively. This was achieved by measurement of the spectrum of the product gas from the addition. In each case a clean spectrum of ¹³CO (Figure 1b) and ¹³C₂H₄ (Figure 2b) was obtained. The FTIR technique was also used to determine ¹²C₂H₆ and ¹³C₂H₆, and ¹²CO₂ and ¹³CO₂; these may be compared with the MS deter-



Figure 2. FTIR spectra of ${}^{12}C_2H_4$ and ${}^{13}C_2H_4$: (a) product gas from $CH_4/O_2/{}^{13}C_2H_4$ mixture over Li/MgO at 740 °C; (b) difference spectrum, (a) minus ${}^{12}C_2H_4$.

minations. The following lines (in cm⁻¹) were used for quantitative measurements: 2169 (¹²CO); 2121 (¹³CO); 950 (¹²C₂H₄); 945 (¹³C₂H₄); 822 (¹²C₂H₆); 821 (¹³C₂H₆); 681 (¹²CO₂); 662 (¹³CO₂). Equivalent sensitivities were assumed for equivalent rotational lines of ¹²CO and ¹³CO and for ¹²CO₂ and ¹³CO₂ and for the Q branches of the hydrocarbons. This could lead to some systematic error but it is expected to be small. Because of the comparatively weak absorbance of the ethane feature, results obtained by FTIR for ¹²C₂H₆ and ¹³C₂H₆ are considerably less accurate than those for the other species.

Results for eight experiments are given in Tables III (${}^{13}C_2H_6$ addition) and IV (C_2H_4 addition). In all cases, except that of

 $^{13}C_{2}H_{4}$ addition at 672 °C, the amount of added C₂ compound was in the range of 0.5-1.5 times the amount of C₂ produced by reaction. For that of ¹³C₂H₄ at 672 °C, 2.8 times that produced was added. Thus the addition of the C₂ material did not represent a gross perturbation to the gas compositions.

Agreement between the FTIR and MS determinations is acceptable, given the modest amounts of labeled material added to these mixtures. If all the CO_x was derived from C_2 oxidation then the ¹³C content of CO_x would be equal to that of the C₂. Thus the proportion of CO_x derived from C_2 can be calculated from the ratio of the ¹³C content of CO_x to the ¹³C content of the C_2 . The results show that C_2 oxidation accounts for 10-85% of the carbon oxide production depending on the conditions of temperature and CH_4/O_2 ratio. For those experiments with added ${}^{13}C_2H_4$, no labeled ethane was detected; thus these species do not equilibrate to any extent.

Discussion

Source of C_2H_4 . The results for experiments in which ${}^{13}C_2H_6$ was added (Table III) show ¹³C contents of both ethane and ethylene. If secondary reactions of the ethane are the source of the ethylene then the ${}^{13}C$ content of both C₂ hydrocarbons must be the same. This is in fact the case within the experimental errors of the results presented in Table III. Clearly this is the expected result since further reactions of ethane have previously been identified as the most probable source of ethylene.^{6,12} Recently, evidence for this conclusion has been derived from the determination of primary selectivities by extrapolation to zero conversion,10 and from the similarity in composition of ethanes and ethylenes from an equimolar CH₄/CD₄ mixture.^{8,9}

 C_2 Oxidation as a Source for Carbon Oxides. Results for both labeled ethane and ethylene addition present a consistent picture. At 740 °C and at hydrocarbon selectivities of greater than 70%, C_2 oxidation contributes 30–60% of the CO_x . Addition of ${}^{13}C_2H_4$ at this temperature seems to result in more of the CO_x arising from C₂ oxidation than does addition of the equivalent amount of ${}^{13}C_2H_6$. This would be consistent with conversion of ethane to ethylene being a prerequisite to oxidation of the C_2 hydrocarbons. At the higher temperature of 780 °C C2 oxidation makes a greater contribution to CO_x for both ${}^{13}C_2H_6$ and ${}^{13}C_2H_4$ addition; thus in this case C₂ oxidation is an important reason for the decreased selectivity. However, at the lower temperature of 670-680 °C it is clear that very little of the carbon oxides are derived from C₂ oxidation, and thus this cannot be the reason for reduced hydrocarbon selectivities under these conditions.

A possible source of carbon oxides at the low temperature is the methylperoxy radical, CH₃O₂. Significant amounts of CH₃O₂ have been calculated to be present relative to CH₃ under these conditions.^{9,12} Purely homogeneous conversion of CH₃O₂ to CO and CO_2 is, however, unlikely, since selectivities observed⁹ when CH₄ was replaced with CD₄ and the flow rate was reduced to compensate for the lower rates of conversion with CD4 remained constant. Such behavior is not consistent with a gas-phase process. However, conversion of CH_3O_2 to CO_x could occur on the catalyst.

At higher temperatures the importance of CH₃O₂ is reduced because of the increased rate of the decomposition reaction:

$$CH_3O_2 \rightarrow CH_3 + O_2 \tag{-1}$$

Product (C_2) oxidation is clearly more important at higher temperatures. There are a number of possible mechanisms for C_2 conversion to carbon oxides. The first is that the C_2 species competes effectively for the oxygen and produces CO_x from a surface-promoted reaction. This, however, on simple concentration considerations implies that the rate of the ethane/O2 reaction over Li/MgO is at least 2 orders of magnitude faster than that for methane/ O_2 . Experiments with ethane/ O_2 mixtures alone over oxidative coupling catalysts have usually been performed at very different hydrocarbon:oxygen ratios than those used for methane/ $O_2^{4,12}$ so that a valid comparison of the relative rates is not possible. However, Asami and co-workers have studied the conversion of ethane over a PbO/MgO catalyst;¹⁸ equivalent

TABLE V: Propane and Propylene Concentrations in Exit Gas from Recycle Reactor, for Experiments with and without ¹³C₂H₄ Addition

temp, °C	additive	C ₃ H ₆ , % v/v	C ₃ H ₈ , % v/v
740	none	0.049	0.034
	1.12% ¹³ C ₂ H ₄	0.091	0.034
780	none	0.028	0.018
	0.56% ¹³ C ₂ H ₄	0.039	0.018
740	none	0.026	0.026
	0.28 % ¹³ C ₂ H₄	0.041	0.025
672	none	0.004	
	0.25% ¹³ C ₂ H ₄	0.016	

ethane conversions and oxygen consumptions were observed at contact times approximately 5% of those observed for CH_4/O_2 mixtures.¹⁹ Thus competition for O_2 is a possible explanation for the C_2 oxidation.

An alternative explanation is that the C_2 species compete for the CH₃ radicals produced from methane. The following reactions may be considered:

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{5}$$

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5 \tag{6}$$

$$CH_3 + C_2H_4 \rightarrow CH_4 + C_2H_3 \tag{7}$$

$$CH_3 + C_2H_4 \rightarrow C_3H_7 \tag{8}$$

The propyl radical produced in (8) undergoes a facile decomposition to produce propylene:

$$C_3H_7 \to C_3H_6 + H \tag{9}$$

Carbon monoxide is produced by further reactions of the C_2H_3 radical:

$$C_2H_3 + O_2 \rightarrow HCO + HCHO$$
 (10)

$$HCO \rightarrow CO + H$$
 (11)

Carbon monoxide is also formed from further reactions of HCHO. The relative rates of reactions 5-8 were calculated for the conditions of these experiments by using evaluated rate constants reported in a review by Tsang and Hampson.²⁰ Rates for reaction 5 were corrected for small falloff effects by using data provided by Tsang and Hampson.²⁰ Methyl concentrations were taken from the measurements by Campbell et al.⁷ on Li/MgO by MIESR; as these measurements were done for low CH₄ concentrations (31 Torr) and 675 °C, the rates were also evaluated for CH₃ concentrations 100 times those reported by Campbell et al. The results are presented in Figure 3 and show that the abstraction and combination reactions 6-8 are important competitive processes to the methyl coupling reaction, particularly at the lower CH₃ concentration. The calculations cover the C2 concentration range 0-10% v/v to include conditions likely to be encountered in practical reactors. To some extent these reactions must regulate the total methane conversion and may represent an intrinsic limitation to the conversion and selectivity. Further evidence for the importance of reaction 8 may be obtained by comparing the concentration of C_3H_6 in the exit gas with and without ${}^{13}C_2H_4$ addition. Results for C_3H_6 and C_3H_8 measured by GC are given in Table V; they show a substantial increase in every case in C_3H_6 but not in C_3H_8 when ${}^{13}C_2H_4$ is added. Previous work^{8b} with deuterium labeling of methane also showed that C3 hydrocarbons are formed by methyl attachment to ethylene. Thus it is likely that purely gas phase competitive processes involving reactions

⁽¹⁸⁾ Asami, K.; Shikada, T.; Fujimoto, K.; Tominaga, H. Ind. Eng. Chem. (19) Asami, K.; Hashimoto, S.; Shikada, T.; Fujimoto, K.; Tominaga, H. (19) Asami, K.; Hashimoto, S.; Shikada, T.; Fujimoto, K.; Tominaga, H.

Ind. Eng. Chem. Res. 1987, 26, 1485. (20) Tsang, W.; Hampson, R. F. J. Phys. Chem. Ref. Data 1986, 15, 1087.



Figure 3. Ratios of rates for abstraction and combination reactions 6–8 to rate for methyl coupling (reaction 5). (a) $[CH_3] = 2.0 \times 10^{13}$ radicals cm⁻³; (b) $[CH_3] = 2.0 \times 10^{15}$ radicals cm⁻³.



Figure 4. Relationship between ¹³C content in CO and CO₂ for experiments with added ¹³C₂H₆ or ¹³C₂H₄ to CH₄/O₂ mixtures over Li/MgO catalyst. T = 672-780 °C. Line has unit slope.

with CH_3 are at least as important as surface-promoted C_2/O_2 reactions in producing carbon oxides and hence reducing selectivity.

Isotopic Composition of CO and CO₂. Figure 4 presents a plot of the relationship between the ¹³C content in CO and CO₂. The data, though scattered, are reasonably well described by a line of unit slope. The departure of the data from the line of unit slope could be due to systematic errors in the assumption of equivalent FTIR sensitivities for ¹²CO and ¹³CO, or to a direct route to CO₂ which does not require CO to CO₂ conversion. If the first reason is correct then the ¹³C/¹²C ratio in CO and CO₂ is approximately the same. It implies that CO is the primary product and further oxidation is the source of CO₂. Clearly additional measurements are required to reliably establish whether this is also true for other



Figure 5. Exit gas concentration of ${}^{13}C_2H_6$ and $\% {}^{13}C$ in CO₂ as a function of time during switches between CH₄/O₂ and CH₄/O₂/ ${}^{13}C_2H_6$ mixtures. Li/MgO catalyst at (a) 740 °C, and (b) 780 °C.

catalysts and conditions. However, the predicted and observed²¹ product from the purely gas phase oxidation of hydrocarbon/oxygen mixtures under these extremely fuel rich conditions is CO. The oxidation of CO to CO_2 may proceed on the surface and thus lead to identical isotopic composition for CO and CO_2 .

¹³C Exchange with Catalyst. Changes in the ¹³C₂H₆ content of the exit gas and of the % ¹³C in CO₂ were followed by MS as a function of time after addition and subsequent removal of added ¹³C₂H₆. Results for experiments at 740 and 780 °C are given in Figure 5. The proportion of ¹³C in CO₂ lags that of ¹³C₂H₆ both on addition and removal of ¹³C₂H₆, indicating an exchangeable pool of carbon dioxide on the catalyst. Integration of the difference between the ¹³C₂H₆ and the ¹³C in CO₂ indicates that the exchangeable pool was between 3.6 and 4.9 mg. This must represent the carbonate content of the catalyst. The Li content of this catalyst was determined to be 0.095–0.77% w/w. If all the Li is present as Li₂ CO₃ this is equivalent to 0.6–4.8 mg of CO₂ for 200 mg of catalyst. The results are therefore compatible with the presence of Li₂CO₃ on the catalyst.

Conclusions

Additions of small quantities of ${}^{13}C_2H_6$ and ${}^{13}C_2H_4$ to CH_4/O_2 mixtures over a Li/MgO catalyst in a recycle reactor show the following:

(i) Ethylene is produced by further reactions of ethane, which is the primary hydrocarbon product.

(ii) C_2 oxidation is an important source of carbon oxides for temperatures above 740 °C; however, below 700 °C C_2 oxidation is, at most, a minor source. Reactions of CH_3O_2 with the surface are a possible source of the low-temperature carbon oxide formation. Two mechanisms for C_2 oxidation are possible: competition with CH_4 for O_2 in a surface-promoted reaction, and competition for CH_3 by abstraction and combination reactions

⁽²¹⁾ Mackie, J. C.; Smith, J. G.; Nelson, P. F.; Tyler, R. J. Poster paper presented at 22nd Symposium (International) on Combustion, Seattle, August 1988.

leading to homogeneous formation of CO_x. Support for the importance of the homogeneous process consists of calculations which show that the rates of the competing reactions are comparable to the coupling reaction of CH_3 to form C_2H_6 , and the detection of increased concentrations of C_3H_6 when ${}^{13}C_2H_4$ is added to the

 CH_4/O_2 mixture. (iii) Results for the ${}^{13}C$ content of CO and CO₂, though scattered, are consistent with CO oxidation being the source of the CO₂.

(iv) There is an exchangeable pool of CO_2 on the catalyst which

Acknowledgment. We thank R. J. Tyler for his enthusiastic encouragement of this work, and C. A. Lukey for some calculations of conversion and selectivities. This project was supported by the Macquarie University/CSIRO Collaborative Fund and a NERDDP grant to the Broken Hill Proprietary Company, Melbourne Research Laboratories.

Registry No. CH₄, 74-82-8; CO, 630-08-0; CO₂, 124-38-9; Li, 7439-93-2; MgO, 1309-48-4; C₂H₆, 74-84-0; C₂H₄, 74-85-1.

Scanning Tunneling Microscopy and Tunneling Spectroscopy of the n-TiO₂(001) Surface

Fu-Ren F. Fan and Allen J. Bard*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712 (Received: September 18, 1989; In Final Form: February 6, 1990)

The (001) surface of a highly doped ($\sim 10^{19}$ cm⁻³) n-type TiO₂ crystal, following polishing, wet etching, and cleaning, was imaged in air with a Pt-Ir tip with a scanning tunneling microscope (STM). Good images of the surface could be obtained with the sample held at negative voltage (positive tip bias), with the high-resolution image showing only Ti atoms. Tunneling spectroscopy, involving the recording of i-V curves and dynamic conductance (di/dV)-V curves with the tip held over a given spot on the TiO₂ surface, was also carried out. The resulting curves show electron tunneling into the conduction band and from the valence band, as well as a prominent peak identified as a surface state about 0.3 eV below the conduction band edge.

Introduction

This paper deals with a new approach to the study of the TiO_2 surface to obtain structural and energetic information. Transition-metal oxides and chalcogenides are known to be catalytically active for a large number of thermal and photoinduced chemical processes. Following the initial report on the application of TiO_2 in the photolysis of water,¹ numerous reports on the application of TiO₂ electrodes and particles as useful materials for the photooxidation of organic and inorganic species have appeared.² From the earliest studies of chemical photoprocesses at TiO₂^{2d} it became clear that the surface energetics and surface states play an important role in the efficiency and range of applicability of this, and other, semiconductor materials. Theoretical calculations of surface electronic structure and experiments using surfacesensitive electron spectroscopic techniques (e.g., low-energy electron diffraction (LEED) and ultraviolet photoemission spectroscopy (UPS)) have been performed on various surfaces of this material. While progress has been made in understanding certain specific surface structures and defects, and chemisorption systems,³ observations on the atomic or near-atomic scale of the surface and its geometric defects and chemical adsorbates have hitherto not been possible. While information about surface energetics and surface states can be obtained by UHV techniques like UPS and inverse photoemission spectroscopy (IPS), there remains a need for complementary methods, especially ones that can be used with the sample under conditions of its use as a catalyst or electrode, e.g., exposed to gases or liquids.

Following the introduction of the scanning tunneling microscope (STM) by Binning and Rohrer,⁴ a number of studies have ap-

peared on the use of the STM to produce high-resolution topographic images and to provide electronic structural information about surfaces of semiconductors and metals, as well as adsorbate-covered surfaces.⁵ Studies of samples immersed in liquids and used as electrodes have also appeared. For example, there have recently been two communications concerning studies of TiO₂ with the STM.^{6,7} Gilbert and Kennedy⁶ imaged TiO_2 in air and investigated the effect of surface treatment (polishing, etching) on topography. Itaya and Tomita⁷ studied the $TiO_2/aqueous$ solution interface and the effect of substrate potential on the STM behavior. They found that good images could be obtained only when the n-type TiO_2 was held at potentials negative of the flat-band potential (i.e., with a TiO_2 accumulation layer at the interface). We report in this work the application of the STM and related spectroscopic techniques to the study of an n-type $TiO_2(001)$ surface in air and to the determination of surface electronic structures under these conditions.

Experimental Section

The (001) oriented n-TiO₂ single-crystal samples (Fuji Titan., ca. $5 \times 5 \times 1 \text{ mm}^3$) were mechanically polished to an optical finish by use of various grades of diamond and alumina polishing pastes ending with 0.05- μ m alumina. The samples were then etched in molten KHSO₄ at 620 °C for 30 min⁸ and then boiled in a mixture of HNO₃ (45% vol), HCl (45% vol) and HF (10% vol) for 1 h⁹ to remove the residue from the chemical etch. The samples were next thoroughly rinsed with Millipore reagent water. After drying, the samples were reduced to a bluish-gray color (indicating a ca. 10^{19} cm⁻³ doping density) by heating in H₂ at 800 °C for ca. 30

⁽¹⁾ Fujishima, A.; Honda, K. Bull. Chem. Soc. Jpn. 1971, 44, 1148. (2) (a) Semiconductor Electrodes; Finklea, H. O.; Ed.; Elsevier: Am- sterdam, 1988. (b) Bard, A. J. Science 1980, 2078 139. (c) Frank, S. N.;
 Bard, A. J. J. Am. Chem. Soc. 1977, 99, 303. (d) Ibid. 1975, 97, 7427.
 (3) See, e.g.; Henrich, V. E. Appl. Surf. Sci. 1979, 9, 143, and references therein.

⁽⁴⁾ Binnig, G.; Rohrer, H. Helv. Phys. Acta 1982, 55, 726.

⁽⁵⁾ See, e.g.; (a) Quate, C. F. Phys. Today 1986, Aug. 26. (b) Hansma, P. K.; Tersoff, J. J. Appl. Phys. 1987, 61, R1. (c) Kuk, Y.; Silverman, P. J. Rev. Sci. Instrum. 1989, 60, 165.

⁽⁶⁾ Gilbert, S. E.; Kennedy, J. H. J. Electrochem. Soc. 1988, 135, 2385. Itaya, K.; Tomita, E. Chem. Lett. 1989, 285.
 Fleishauer, P. D.; Chase, A. B. J. Phys. Chem. Solids 1974, 35, 1211.
 Johnson, O. W.; Park, S. H.; Deford, J. W. J. Appl. Phys. 1975, 46,

¹⁰²⁶