in our ability to predict the properties of polar molecules in solution.[9]

Supplementary Material Available: Appendices describing the calculation of effective Born radii (α) and approximate surface areas (SA) (4 pages). Ordering information is given on any current masthead page.

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(9) W.C.S. acknowledges the support of NSF Grant CHE89 11008. R.C.H. acknowledges the support of NIH National Research Service Award GM 13106. We also thank Professor Barry Honig for helpful discussions of electrostatic solvation.

Surface Concentrations and Residence Times of Intermediates on Sm_2O_3 during the Oxidative Coupling of Methane

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Received September 12, 1989
Revised Manuscript Received April 24, 1990

The use of Sm_2O_3 as a catalyst for the oxidative coupling of methane has been well studied and documented.[1-3] However, detailed information on the surface of a working Sm_2O_3 catalyst and the overall carbon reaction pathway is unknown. This communication presents results that delineate completely for the first time the nature of the surface-reaction steps of Sm_2O_3 and quantifies the working surface under steady-state reaction conditions.

The feasibility of using isotope switching experiments to study oxidative methane coupling has recently been shown.[4-6] Some of the conclusions drawn from these experiments include the participation of the lattice oxygen in the reaction along with significant surface holdup of the methane and CO_x products. However, it is difficult to obtain quantitative results from the majority of this work[5,6] due to the pulsing technique employed.[7]

The technique used in this study involved switching the isotopic composition of methane from $^{12}CH_4$ to $^{13}CH_4$ once the reaction had reached a steady state and subsequently following (by mass spectrometry) the evolution and decay of the different labeled reactants and products to their new steady-state values. Use of such a technique allowed the determination of surface coverages and intrinsic site activities as well as reaction pathways.[4]

The Sm_2O_3 (BET surface area = 1 m^2/g) was purchased from Alfa Products. Prior to reaction, it was pretreated by heating to reaction temperature in flowing oxygen and then holding at reaction temperature for 30 min prior to introduction of the reactants. The reaction conditions used in this work were as follows: catalyst weight = 100 mg; temperature = 600 °C; total pressure = 1 atm; CH_4 flow = 5 cm^3/min; $He/CH_4/O_2 = 94/10/1$. These conditions resulted in a CH_4 conversion of 9.1%, a CO_2/CO ratio of 1.4, and a C_2 selectivity of 25.7%. A straight-tube quartz reactor was used with an inlet i.d. of 4 mm which tapered to 1 mm after the catalyst bed. The catalyst bed was held in place by quartz wool, and in the absence of any catalyst the quartz reactor and quartz wool had negligible activity.

Figure 1 presents the transients obtained when the isotopic composition of methane is switched as described above. A trace amount of argon was present in one of the methane isotopes, which permitted correction for gas-phase holdup. The rapid relaxation of the methane signal indicates the lack of a long-lived adsorbed methane. This result is consistent with a similar observation made with the Li/MgO system[4] and in direct contrast with the results of Ekstrom and Lapszewicz.[5,6] This difference appears to be due to diffusion effects in the higher surface area and higher porosity Sm_2O_3 which was used by Ekstrom and Lapszewicz.[8] When using high-porosity catalysts, we observed isotopic transients with significant tailing, similar to those reported by Ekstrom and Lapszewicz.

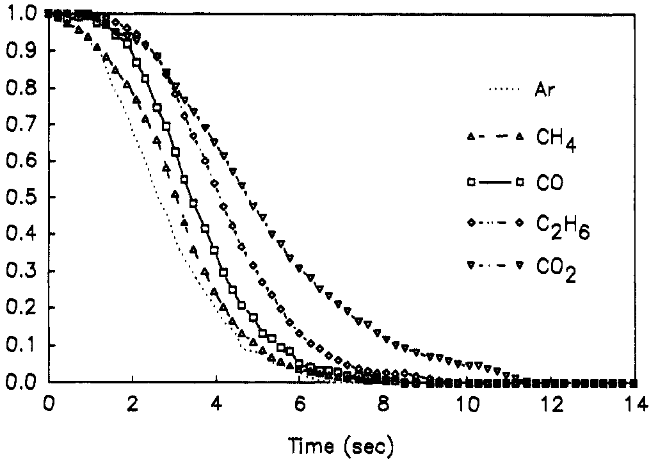

Figure 1. Carbon transients for the oxidative coupling of methane over Sm_2O_3. Each transient is the average of three separate experiments. The dotted line indicates an inert-gas tracer.

Table I. Surface Residence Times along the Carbon Reaction Pathway as a Function of Catalyst Loading

	surf. residence time of C,[a] s		
species	25 mg	45 mg	100 mg
C_2H_6	4.0 ± 0.7	4.1 ± 0.7	2.8 ± 0.7
CO_2	2.7	3.4	2.7
CO	2.3	2.4	1.7

[a] Data collection for Table I permitted the collection of only five or six data points per transient response, yielding the relatively large potential error of ±0.7 s.

The fact that the CO_2 transient trails the CO transient may suggest a possible multistep surface oxidation pathway. However, the possibility that CO_2 is formed as a primary product and not from further oxidation of adsorbed CO cannot be completely ruled out from this data. The lack of strongly adsorbed CO_2 is evident from the rapid relaxation of the CO_2 transient. This observation has been confirmed by a series of experiments in which the catalyst bed length was varied, resulting in no change (within experimental error) in the CO_2 residence time, indicating that readsorption of CO_2 was not important (see Table I). Although the surface residence times presented in Table I are subject to a relatively large error of approximately 0.7 s, they clearly show the lack of any relationship between catalyst bed length and surface residence time. Hence, no significant readsorption of any of the product molecules is indicated. By contrast, a similar set of measurements for CO_2 over a Li/MgO catalyst, which is known to form carbonates easily, indicated a 2-fold increase in residence time for CO_2 with a 2-fold increase in the amount of catalyst.[9]

These results are consistent with reports indicating that $Sm_2(CO_3)_3$ is stable up to only 600 °C in an atmosphere void of CO_2 and to 850 °C in 500 Torr of CO_2.[10] Under the conditions employed in this study, only 2.8 Torr of CO_2 was present. Therefore, surface carbonates would not be expected to be very stable or present in any large amounts under the reaction conditions used for this study.

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(1) Otsuka, K.; Jinno, K.; Morikawa, A. *J. Catal.* **1986**, *100*, 353.

(2) Otsuka, K.; Jinno, K.; Morikawa, A. *Chem. Let.* **1985**, 499.

(3) Otsuka, K.; Jinno, K.; Morikawa, A. *Chem. Lett.* **1987**, 483.

(4) Peil, K. P.; Goodwin, J. G., Jr.; Marcelin, G. *J. Phys. Chem.* **1989**, *93*, 5977.

(5) Ekstrom, A.; Lapszewicz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 5226.

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

(7) Soong, Y.; Krishna, K.; Biloen, P. *J. Catal.* **1986**, *97*, 330.

(8) Ekstrom, A., private communication.

(9) Peil, K. P.; Goodwin, J. G., Jr.; Marcelin, G. Manuscript submitted for publication.

(10) *Rare Earth Research II*; Vorres, K. S., Ed.; Science Publishers: New York, 1964.

Table II. Surface Coverages of Intermediates and Products

species	surf. residence time of C, s	$N_i^a \times 10^{-18}$	θ_i^b	intrinsic site TOF, s^{-1}
C_2H_6	3.1 ± 0.2[c]	2.9 ± 0.2	0.29 ± 0.02	0.32 ± 0.09
CO_2	4.0	3.2	0.32	0.25
CO	2.4	1.4	0.14	0.42
CH_4	0.3	5.6	0.56	

[a] Number of carbon atoms leading to products/gram of catalyst. [b] Based on an assumption of 1×10^{19} sites/g for the surface area of 1 m^2/g. [c] The error of ±0.2 s was determined from the average of three separate experiments. This relatively small error was made possible by a refinement in the data-acquisition technique, which increased the number of data points for each transient by an order of magnitude compared to those producing the results of Table I.

These results strongly suggest that surface carbonates are not involved significantly in this reaction on this catalyst. This contrasts with results for other catalyst systems such as Li/MgO and PbO/MgO[11,12] where the formation of surface carbonates was found to be important during the coupling of methane.

From the transients in Figure 1, the similarity in shape of the C_2H_6 and CO transients suggests that these product gases are formed via similar (parallel) surface reaction pathways. As seen in Table I, varying the catalyst bed length had no effect on these transients, indicating the lack of significant interaction of the product molecules with the catalyst surface.

The surface lifetimes cannot be attributed to adsorption/desorption of the product gases since the data in Table I indicates the lack of significant interaction of CO, CO_2, and C_2H_6 with the catalyst surface. Increasing the catalyst bed length had no effect on the holdup of the product gases, so readsorption of the product gases was not important. Thus, the surface lifetimes measured indicate the lifetime of formation of $^\bullet CH_3/C_2H_6$, CO, and CO_2. Note that surface oxidation of C_2H_6 does not seem to be important under these conditions.

The commonly accepted mechanism for methane coupling assumes gas-phase coupling of surface-generated methyl radicals. In addition, there have been numerous suggestions made that CO and CO_2 may be produced primarily as a result of gas-phase oxidation of these methyl radicals. However, these isotopic transient results suggest that the role of the catalyst surface is more than just a methyl radical generator. Given that the product gases do not strongly interact with the surface under these conditions, if the catalyst surface served only to generate methyl radicals with subsequent reaction of these radicals in the gas phase, the surface lifetimes of all the intermediates leading to the formation of CO, CO_2, and C_2H_6 (as measured by the areas under the respective transients and taking into account experimental error) would be identical. As seen from the data presented, this is not the case under these reaction conditions.

However, nothing in these results led to a disagreement with the hypothesized role of methyl radicals in C_2H_6 production, nor can one rule out a significant role for homogeneous gas-phase oxidation at much higher reaction temperatures.

The surface concentration of reaction intermediates (N_i) can be calculated by integrating the transient curves after correcting each for the gas-phase holdup and applying the formula[13]

$$N_i = (\text{area})(\text{rate of } CH_4 \text{ conversion})(\text{product selectivity})$$

Table II presents the results of the above calculation of surface concentrations and fractional surface coverages of intermediates leading to each product for the transients presented in Figure 1. The surface lifetimes presented in Table II are subject to a relatively small error of 0.2 s due to a refinement of the transient data acquisition technique, which increased the number of data points for each transient by an order of magnitude. In addition, each transient is based on the average of three separate experiments.

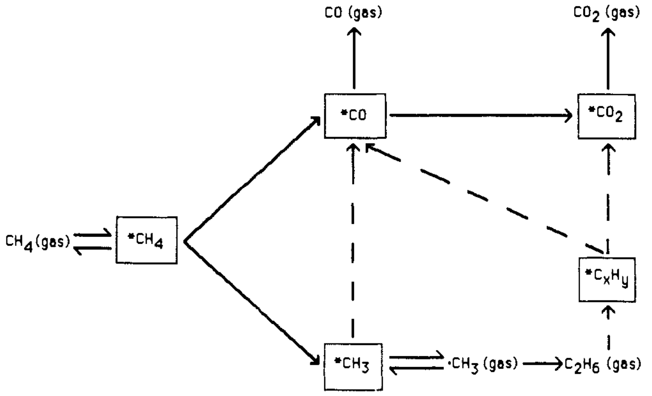

Figure 2. Proposed carbon reaction pathways for the oxidative coupling of methane over Sm_2O_3.

On the order of 50% of the Sm_2O_3 working surface was involved in the formation of products. Of this 50%, approximately 3/5 was involved in CO_x formation, with the remaining 2/5 being active for C_2 formation. Since surface lifetime is inversely proportional to the intrinsic site TOF (turnover frequency), as can be seen in Table II, the sites active for C_2 formation had a lower activity than sites active for the formation of CO_x. The reason the calculated coverages total more than a monolayer is probably due to the number of assumptions made in arriving at these numbers.

Figure 2 summarizes the proposed carbon reaction pathways that are consistent with these findings. Dashed lines are used to indicate pathways that cannot be completely ruled out from this data.

In conclusion, it appears that the surface of a working Sm_2O_3 catalyst is much more than a methyl radical generator. It is active in the formation of CO, CO_2, and possibly even C_2H_6. Also, surface carbonates do not appear to be present in any large amount, and readsorption of the product gases is not important.

Acknowledgment. Support for this work by the Gas Research Institute is gratefully acknowledged.

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[11] Aika, K.; Nishiyama, T. *J. Chem. Soc., Chem. Commun.* **1988**, 70.

[12] Korf, S. J.; Roos, J. A.; Bruijn, N. A.; Ommen, J. G.; Ross, J. R. H. *J. Chem. Soc., Chem. Commun.* **1987**, 1433.

[13] Yang, C.-H.; Soong, Y.; Biloen, P. *Proc. Int. Congr. Catal., 8th* **1984**, *2*, 3.

Are Chelates Truly Intermediates in Cram's Chelate Rule?

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Received April 2, 1990

In 1959, Cram and Kopecky[1] proposed that the steric outcome of additions of organometallic reagents to chiral α-alkoxy ketones rests on the ability of the reagent to chelate with the alkoxy substituent as well as the carbonyl oxygen. Reactions of this type are often highly stereoselective.[2-7] Recently, stable chelates

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[1] Cram, D. J.; Kopecky, K. R. *J. Am. Chem. Soc.* **1959**, *81*, 2748.

[2] Still, W. C.; McDonald, J. H. *Tetrahedron Lett.* **1980**, *21*, 1031. Still, W. C.; Schneider, J. A. *Ibid.* **1980**, *21*, 1035.

[3] Reetz, M. T. *Angew. chem., Int. Ed. Engl.* **1984**, *23*, 556.

[4] (a) Keck, G. E.; Boden, E. P. *Tetrahedron Lett.* **1984**, *25*, 1879. (b) Keck, G. E.; Abbott, D. E. *Tetrahedron Lett.* **1984**, *25*, 1883.

[5] Mead, K.; Macdonald, T. L. *J. Org. Chem.* **1985**, *50*, 422.

0002-7863/90/1512-6130$02.50/0