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NOTES

Steady-State vs Non-Steady-State Transient Kinetic Analysis of Surface Coverages during the Oxidative Coupling of Methane

The quantitative nature of the surface intermediates provide important clues to a reaction process. In general, the evaluation of such surface reaction intermediates is best conducted at steady-state working conditions (*1, 2*). The examination of the reaction intermediates in the catalyzed oxidative coupling of methane, however, has proven to be a formidable challenge due to the high temperatures employed.

Because of its greater simplicity and lower cost, non-steady-state transient kinetic analysis has been used by a number of workers in the study of methane oxidation (*3–5*). With the non-steady-state technique, the concentration level of one of the reactants is put through a step change and the resulting transients in product and reactant concentrations are obtained. The quantity of surface intermediates detected during this "real" transient may or may not relate to those existing under steady-state reaction since the surface is experiencing major changes.

Examination of the reactive surface intermediates under steady-state reaction conditions can best be accomplished by means of steady-state isotopic transient kinetic analysis. This technique entails an abrupt switch in the isotopic composition of one of the reactants, which does not disturb the steady-state condition, accompanied by the continuous monitoring (e.g., by mass spectrometry) of the relaxation and evolution of labeled reactants and products. A more complete description and discussion of the technique can be found elsewhere (*6, 7*). The feasibility of using steady-state isotopic transient techniques for studying the oxidative coupling of methane has been recently demonstrated (*8–11*).

The main difference between these two techniques is the unavoidable perturbation of the reaction environment with non-steady-state isotopic transient techniques. Results are presented that detail for the first time some of the problems with trying to relate amounts of "surface" species measured under non-steady-state conditions to concentrations of surface reaction intermediates existing during the steady-state oxidative coupling of methane.

All of the results presented were obtained with a Sm_2O_3 catalyst at 600°C. Reaction parameters were: 25 mg catalyst, $CH_4/O_2 = 10$, $(P_{CH_4} + P_{O_2})/P_{total} = 0.10$, pressure = 1 atm, total flow = 50 cc/min, CH_4 conversion = 4.5%, $CO_2/CO = 1.3$, C_2H_6 selectivity = 29%. The surface area of the catalyst was ca. 1 m^2/g. Under these conditions no C_2H_4 was detected. No reaction was observed in the absence of the catalyst. However, this does not imply that gas-phase reaction of surface-generated intermediates was absent. Three separate transient experiments were performed:

$$\text{steady state: } {}^{12}CH_4 + O_2 + He \Rightarrow {}^{13}CH_4 + O_2 + He$$

$$\text{non-steady-state(C): } CH_4 + O_2 + He \Rightarrow O_2 + He$$

$$\text{non-steady-state(O): } CH_4 + O_2 + He \Rightarrow CH_4 + He$$

where He was used as the inert carrier gas.

The transients obtained are presented in Figs. 1–3. Argon was present in low concentration in the $^{12}CH_4$ used in the first two

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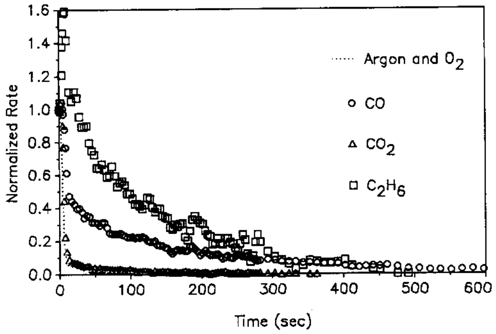

FIG. 1. Transients produced when the flow of O_2 was interrupted (non-steady-state). The argon curve represents holdup in the gas phase.

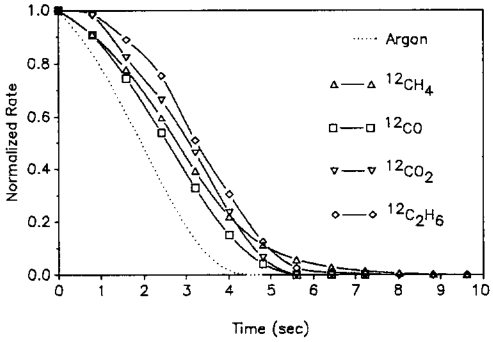

FIG. 3. Transients produced when the isotopic composition of CH_4 was switched from $^{12}CH_4$ to $^{13}CH_4$ (steady-state). The argon curve represents holdup in the gas phase.

transients and in the O_2 used in the third transient in order to mark the holdup due to the gas phase. Each transient is presented as a normalized rate curve, where a value of 1.0 at time = 0 is the steady-state rate. The integrated area under each transient curve (after the argon transient is subtracted to account for holdup in the gas phase) multiplied by the steady-state rate yields the surface concentration of all the reactive intermediates that led to the formation of that particular product gas (*12*). The presence or absence of multiple reaction steps does not affect this calculation.

The transients shown in Fig. 1 were acquired following the non-steady-state oxygen cutoff. The continued production of C_2H_6 and CO long after the removal of gas phase oxygen indicates the contribution to the reaction of the lattice oxygen of the catalyst. It is interesting to note the increase in the C_2H_6 rate when the flow of oxygen was shut off. Since there was an immediate decrease in the rate of CO_2 production, this increase in the C_2H_6 rate could be due either to the lattice oxygen of the catalyst preferentially assisting in forming C_2H_6 (via methyl radical formation) or to a decrease in the homogeneous gas phase oxidation of methyl radicals by the formation of gas phase methyl peroxide radicals leading to CO_2 since the level of gas-phase oxygen rapidly decreased after the cutoff in the non-steady-state experiment. However, a recent study (*11*) utilizing different catalyst bed depths and steady-state isotopic switching showed experimentally that homogeneous gas-phase oxidation is not important at a temperature this low. Thus, the increase in C_2H_6 formation would seem to be due to the more selective partial oxidation by lattice oxygen as opposed to oxygen coming to the catalyst from the gas phase. The active participation of the lattice oxygen during steady-state oxidative coupling of methane has been delineated and quantified by the authors in greater detail elsewhere (*8*, *13*, *14*)

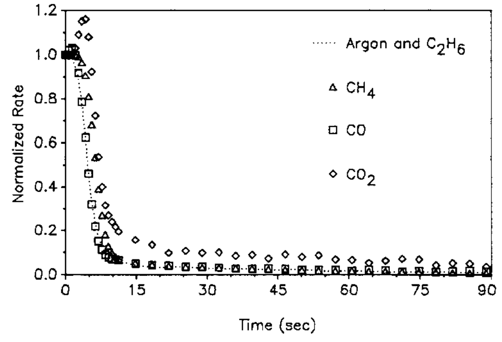

FIG. 2. Transients produced when the flow of CH_4 was interrupted (non-steady-state). The argon curve represents holdup in the gas phase.

The transients shown in Figure 2 were obtained following the non-steady-state

TABLE 1

Measured Carbon Surface Coverages for a Sm_2O_3 Catalyst

Switch type	Adsorbed C leading to product C atoms/g of catalyst $\times 10^{-18}$*			
	CH_4	CO	CO_2	C_2H_6
Non-steady State (O)	—	81.9	8.4	378
Non-steady State (C)	124	0.7	13.2	0
Steady-state	71.6**	1.9	3.1	5.1

* Experimentally determined error of $\pm 0.3 \times 10^{-18}$ C atoms/g except where noted.

** Larger potential error due to the large flow rate of CH_4 and short residence time.

methane cutoff. In the absence of CH_4, CO_2 became the main product. Continued production of C_2H_6 was not seen, and the C_2H_6 and argon transients relaxed together. The CH_4 transient indicates a surface reservoir of adsorbed CH_4 or CH_x which can desorb as methane, unreacted as far as the carbon is concerned. The term "adsorbed CH_4" will be used throughout this note to designate this surface species.

The transients obtained following a switch in the isotopic composition of CH_4 from $^{12}CH_4$ to $^{13}CH_4$ (under steady-state conditions) are presented in Fig. 3. All of the product gases exhibited significant surface holdup. Since only the carbon reaction pathway was being traced, the contribution of the bulk lattice oxygen did not interfere in the determination of surface coverages.

Table 1 gives carbon surface concentrations of all the surface intermediates leading to a particular product determined by integration of the non-normalized transients. As can be seen, measured surface coverages vary depending upon which transient curves were used. Only the steady-state isotopic transient data can be said to a priori accurately represent the working surface of the catalyst under steady-state reaction conditions. All of the non-steady-state techniques gave by-and-large incorrect estimations of the amounts of various carbon intermediates present on the catalyst surface. While it might be argued that the amount of adsorbed but unreactive CH_4 measured by the non-steady-state technique is reasonably close to that measured by the steady-state isotopic transient technique, given the high flow rate of CH_4 and the potential error in the estimation of adsorbed amount which can result (*11*) the concentrations of intermediates leading to products (CO, CO_2, C_2H_6) were grossly miscounted. In the case of the non-steady-state methane cutoff experiment the amount of intermediates leading to CO was reduced since in excess oxygen mainly CO_2 was formed. The contribution of the bulk lattice oxygen to reaction for Sm_2O_3 was measured and found to be similar to that measured for a Li/MgO catalyst (*8*). The non-steady-state transient (oxygen) data greatly overestimated the coverage in reaction product intermediates due mainly to the reaction of the bulk lattice oxygen with the flowing CH_4. Similar discrepancies in surface concentrations measured by non-steady-state techniques have been seen for CO hydrogenation (*6*) and NH_3 synthesis (*15*).

The results from the non-steady-state (oxygen) experiment cannot be related to the total amount of lattice oxygen that can participate during steady-state reaction since only a small amount of oxygen can be removed in the absence of a source of replenishing oxygen (i.e., the gas phase) due to the low reducibility of the catalyst under these conditions. However, the sum of the second row in Table 1 based on non-steady-state techniques does provide a measure of the total carbon on the catalyst surface. The sum of the third row, based on steady-state isotopic techniques, provides a measure of the total, very reactive carbon on the catalyst surface. The difference between these two numbers is due either to the presence of some less reactive carbon on the surface or, perhaps more likely, to the inherent error in the measurement of adsorbed CH_4.

In summary, although useful mechanistic

information can sometimes be obtained from transient curves produced by a step change in the concentration of one of the reactants, such curves should not be used to quantify surface coverages of reactive intermediates of specific products existing under steady-state reaction conditions.

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