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LETTERS TO THE EDITORS

Comments on "Blank Reactor Corrections in Studies of the Oxidative Dehydrogenation of Methane" by D. J. C. Yates and N. E. Zlotin

Yates and Zlotin (*1*) recently studied the conversion of methane and oxygen in a reactor which contained a lithium-doped magnesium oxide catalyst (Li^+/MgO). They concluded that the Li^+/MgO was primarily a "combustion catalyst" and that homogeneous reactions contributed significantly to the conversion of methane, as well as to formation of ethane and ethylene (C_2 products). These conclusions are contrary to those reached previously by Ito *et al.* (*2*), who concluded that the reaction was largely catalytic and that purely homogeneous reactions (*3*) accounted for less than 0.2% of the methane converted. The purpose of this letter is to point out the critical differences between the reactor systems employed by the two groups and to show how these differences resulted in the discrepancies that were reported.

The reactor used by Yates and Zlotin consisted of a fused-quartz tube, 2.4 cm in internal diameter with 12 cm of the tube being inside a three-zone furnace. The heated volume was 56 cc. At a typical flow rate of 50 cc min^{-1}, used in their experiments, the residence time corrected for a temperature of 700°C was ca. 20 s! Even with the 4.1 g of catalyst the free volume was ca. 49 cc.

By contrast the reactor used by Ito *et al.* (*2*) and described in Ref. (*4*) was a fused-quartz tube, 2.2 cm in internal diameter and 12 cm in length. This reactor was (i) filled with quartz chips to a depth of 5 cm above the catalyst bed and (ii) heated with a single zone furnace so that the temperature dropped sharply above and below the catalyst bed. With the quartz chips in place it is estimated that the residence time in a zone with $T > 600°C$ was <5 s. Thus, the residence time was less than one-fourth of that used by Yates and Zlotin. In both studies the total pressure was 760 Torr and the CH_4 partial pressures were ≤ 305 Torr.

An important factor which determines the extent of a homogeneous reaction is the presence (or absence) of *free volume*; that is, a volume which has no solid material. The role of the surface-to-volume ratio has long been recognized in homogeneous kinetic studies (*5*), and Chou and Albright (*6*) have demonstrated the effect during the oxidation of CH_4, albeit under somewhat different conditions than those of interest here. They observed that upon packing a tubular Pyrex reactor with 40–50 mesh Pyrex beads the conversion of methane at 540°C decreased from 85 to 0.2% at the *same residence time*.

In order to confirm this effect under conditions similar to those used in the catalytic oxidative coupling of CH_4 we have studied the homogeneous reaction in the two fused-quartz reactors described in Fig. 1. The inlet and outlet tubes were placed as indicated in reactor A so as to achieve a high degree of gas mixing in the reactor, which would provide a uniform temperature throughout the volume of the reactor. This configuration has an advantage over a tubular reactor of uniform diameter in which the gases must be heated to the reaction temperature in a volume that is not well defined. In such a case it is difficult to determine accurately a residence time. The free volume of reactor A was modified by adding fused-quartz rings, 3 mm i.d. × 5 mm o.d. × 2 mm length. Rings rather than quartz chips were used in this reactor so as

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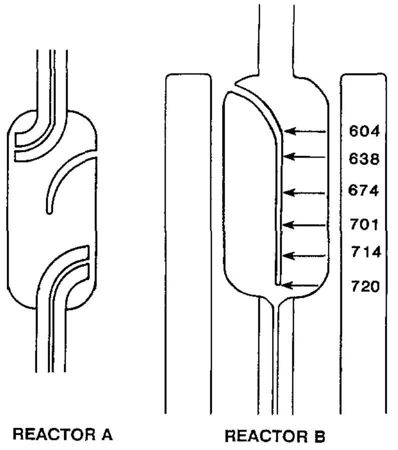

FIG. 1. Flow reactors used in the gas-phase kinetic studies. The temperature variation in degrees Celsius and the location of the furnace are indicated for reactor B.

to minimize the differences in the flow rates that were required to give the same residence time for the empty and the filled reactor. The volumes of the empty reactor and the reactor filled with quartz rings were 14.4 and 9.2 ml, respectively.

Reactor B was very similar to that used by Ito *et al.* (*2*) except that the total length was 7 cm instead of 12 cm. The heated length was approximately 7 cm in both cases. The empty reactor B had a volume of 23.3 ml, and with the single zone furnace the temperature profile indicated in Fig. 1 was observed. The gas flow was from the top, and in the previous catalytic study (*2*) the catalyst was placed at the bottom of the reactor so that the hydrocarbon product molecules would rapidly escape the heat zone via the capillary tube. In the present study the conversion of methane was determined in the empty reactor, in a reactor that contained a maximum loading of quartz chips, and in a reactor that contained quartz wool. The quartz chips, obtained from Thomas Scientific, were reduced to 20/40 mesh, and 28.4 g of this material occupied 12.9 ml of the reactor volume. Thus, the void volume, with the quartz chips in place, was 10.4 ml. In another configuration reactor B was loaded with 1.0 g of quartz wool, obtained from Heraeus, which occupied a volume of only 0.37 ml, based on the density of quartz.

The CH_4 conversion at 700°C, both with and without the rings in reactor A, is shown as a function of residence time in Fig. 2. For comparison the conversion obtained by Yates and Zlotin under similar conditions is also indicated in the figure. The conversion observed by Yates and Zlotin agrees very well with our data.

The most significant observation was the order-of-magnitude decrease in conversion which resulted when the quartz rings were added to the reactor. Similar results were previously obtained during the homogeneous oxidation of ethane, although at somewhat lower temperatures (*7*). In the reactor containing the quartz rings the CH_4 conversion was 0.25% at a residence time of 5.3 s and a temperature of 700°C. This may be compared with a blank reaction corresponding to only 0.2% conversion in our previous catalytic system at 720°C (*2*).

The methane conversions and product selectivities obtained with reactor B in three configurations are given in Table 1. Again, there was a marked decrease in methane conversion in going from the empty reactor to the reactor filled with

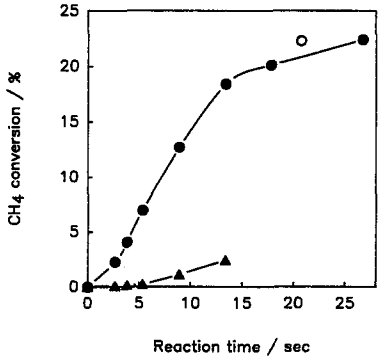

FIG. 2. Methane conversion at 700°C as a function of residence time in the reactor: ●, empty reactor; ▲, reactor filled with fused-quartz rings; ○, result from Ref. (*1*). Initial conditions: P_{CH_4} = 220 Torr, P_{O_2} = 115 Torr.

TABLE 1

Methane Conversion and Product Selectivity[a]

Reactor, loading	Residence time(s)	CH_4 conv. (%)	Selectivity (%)				C_2 yield (%)
			C_2H_4	C_2H_6	CO	CO_2	
B, none	3.7	11.9	17.0	16.2	60.9	4.5	3.9
B, quartz wool	3.7	5.5	14.6	23.9	58.1	2.2	2.1
B, quartz chips	3.7	0.96	1.2	10.1	56.9	0.2	0.2
A, none	26.7	30.3	10.3	4.8	58.9	25.9	4.6
Li^+/MgO and quartz chips[b]	ca. 4	38.2	29.1	13.9	2.8	54.2	16.4

[a] 305 Torr CH_4, 155 Torr O_2; 720°C.

[b] Data from Ref. (*2*).

quartz chips. The methane conversion in the reactor containing quartz wool was intermediate between the other two. In all cases the temperature at the bottom of the well was 720°C and the residence time, determined at this temperature, was 3.7 s. The discrepancy between the 0.2% conversion reported in Ref. (*2*) and the 0.96% conversion reported here for the reactor filled with quartz chips may reflect differences in the pressures of the reactants and errors associated with measuring small conversions. For comparison purposes the conversions and selectivities at 720°C, obtained in reactor A and in the normal catalytic system, are also included in the table. One should note that initial CH_4 and O_2 pressures of 305 and 155 Torr, respectively, were the same for each of these studies, and that the dilution ratio (D), as defined by Lane and Wolf (*8*), was ca. 0.60.

Clearly the homogeneous contribution during the catalytic conversion of CH_4 can be reduced to a negligible amount at 700–720°C by simply packing the free volume of the reactor with quartz chips or some other inert material. The homogeneous oxidation of methane involves a complex series of chain-branching reactions which could be affected by the presence of a surface. For example, the reaction

$$H_2O + M \rightarrow OH\cdot + OH\cdot + M \qquad (1)$$

is a source of OH· radicals, which are important intermediates in the branching process. If H_2O_2 were removed by a surface reaction

$$H_2O_2 \xrightarrow[\text{surf}]{} H_2O + \tfrac{1}{2}O_2, \qquad (2)$$

the hydroxyl radicals obtained from reaction 1 would no longer be available. We have developed a model, based on 142 elementary reactions, that accurately describes the data depicted in Fig. 2, including the effects of the quartz rings. According to this model the loss of H_2O_2 at surfaces adequately accounts for the observed decreased in conversion when the quartz rings are added. These results will be published separately.

It is surprising that Yates and Zlotin (*1*) and also Lane and Wolf (*8*) did not observe a significant increase in CH_4 conversion when quartz wool, or in the latter case also quartz chips, were added to their reactors. In neither study was the amount of quartz wool given; however, Lane and Wolf noted that the void fraction of their reactor filled with quartz chips was approximately 0.68. Their system was operated at $D = 0.75$, which is somewhat greater than the dilution ration of 0.59 used in reactor B of our study.

With respect to ther more general question concerning the role of Li^+/MgO in the oxidative dimerization of CH_4, Martin *et al.* (*9*) have recently studied the heterogeneous versus homogeneous processes. Although this group worked at a low *D* value of 0.12, which admittedly favors the catalytic reaction, they observed that the CH_4 conversion was negligible in an open reactor at temperatures up to 820°C. By contrast, 10% CH_4 conversion was observed over a Li^+/MgO catalyst at 770°C.

Yates and Zlotin reported that the CH_4 conversion at 720°C was 26.8% in the empty reactor and 39.2% in the reactor containing Li^+/MgO. One might conclude from these conversion data that the catalyst had only a marginal positive effect on the reaction. Upon closer inspection of the data, however, it is apparent that in the homogeneous reaction 65% of the O_2 was converted and in the heterogeneous reaction nearly 100% of the O_2 was converted. Under such oxygen-limiting conditions it is impossible to determine the true catalytic activity. Moreover, with the catalyst in place we estimated that more than 50% of the oxygen was consumed before the reagents reached the catalyst. Hence, it is not surprising that the CH_4 conversion obtained with the catalyst in place was only slightly greater than that observed without the catalyst.

One could question the need for a catalyst if the same results could be achieved in a homogeneous gas-phase system. Whereas comparable CH_4 conversions could be obtained by adjusting the residence time in the homogeneous reactor and the contact time over the catalyst, the C_2 selectivities and yields are superior over the Li^+/MgO catalyst, at least at pressures less than 1 atm. For example, the selectivities and yields are compared in Table 1 for the homogeneous reaction in reactor A and for a 3 wt% Li^+/MgO catalyst. At 30 and 38% conversions, obtained respectively in the homogeneous and heterogeneous systems, the corresponding C_2 selectivities were 15 and 43%. Yates and Zlotin presented similar data in their paper.

Finally, it should be pointed out that since our original publications on the effectiveness of the Li^+/MgO catalyst for the oxidative dimerization of methane (*2, 10*), several other groups have studied this system at reactant pressures ≤ 1 atm and have reported that the catalyst is indeed active and reasonably selective for the formation of ethane and ethylene (*11–18*). In all of these studies it was implied or concluded that the homogeneous reaction was negligible. Nevertheless, as pointed out by Lane and Wolf (*8*), and confirmed by us, larger *D* values result in a greater homogeneous component. Moreover, at reactant pressures well in excess of 1 atm the homogeneous reaction may become dominant, even when the free volume is limited. Hutchings *et al.* (*19*) observed that at 5.8 atm and at 560°C the methane conversion was only slightly less and the C_2 selectivity was somewhat greater in the absence of the catalyst, but at these temperatures the catalyst was far from its state of optimum performance. Onsager *et al.* (*20*) observed a decrease in conversion of CH_4 at $P(CH_4) \geq 3$ atm and essentially no change in selectivity when a reactor was filled with 7 wt% Li^+/MgO, compared to when it contained no catalyst. The temperature at which these comparisons were made was not given, and the CH_4/O_2 ratios used in these experiments were considerably greater than those normally used over this catalyst.

In summary, we have confirmed that the homogeneous oxidation of CH_4 was not a significant factor during the catalytic oxidative coupling reaction as reported in our earlier papers (*2, 10*). The homogeneous component, in general, is determined by the residence time of the gases in the heated zone of the reactor, the presence or absence of an "inert" solid in the reactor, and the partial pressures of the reactants. At reactant pressures substantially greater than 1 atm the homogeneous reactions may indeed become comparable to the heterogeneous reactions; however, more work is needed to establish the conditions under which this might occur. Based on the low pressure data, it seems unlikely that the C_2 yields achieved in the heterogeneous system will be obtained via purely homogeneous reactions.

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