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Comments on the Effect of Gas-Phase Reactions on Oxidative Coupling of Methane

The issue of gas-phase versus surface reaction during methane oxidative coupling is still not clearly settled as demonstrated by the controversy between Lunsford and co-workers (*1*) and Yates and Zlotin (*2*) concerning the interpretation of their previous results (*3, 4*). As our own work (*5*) is quoted by both authors, we felt it was appropriate to clarify once more this issue by presenting additional results that clear the controversy and make sure that our previous results and conclusions are properly interpreted.

Lane and Wolf (*5*) studied reactions in the gas phase during the co-feeding of methane and oxygen, and concluded that methane conversions as high as 32% with 29% C_2 selectivities may be obtained without a catalyst. The general trend in both catalytic and noncatalytic studies was that hydrocarbon selectivity decreased as conversion increased. It was also found that gas-phase reactions become important when reaction temperature is greater than 650°C, reactant partial pressures $P^* = (P_{CH_4} + P_{O_2})/P_{tot}$ (previously defined as dilution ratio) exceed 0.4, and residence times of reaction gases are longer than 0.1 min. In our previous work (*5*), however, the reactor design was not suitable to determine the heated volume precisely; that is why reciprocal flow rate was chosen instead of residence time. As reactor designs vary from group to group, the need to specify the residence time becomes necessary to determine the operating conditions to discern the relevance of gas-phase versus catalytic reactions. Another issue which was not clearly resolved was the effect of quartz chip packing on methane conversion in the absence of a catalyst. In this note we present additional information regarding both of these issues and compare their effect on the results presented by Hatano *et al.* (*1*) and Yates and Zlotin (*2*).

The experiments were conducted in fused silica reactors which were operated in the single-pass mode and were heated with a furnace over a 15-cm length. A detailed description of the feed and temperature control used, as well as furnace characterization, can be found elsewhere (*5*). A new reactor design (shown schematically in an insert in Fig. 1) which was used in this work has a well-defined empty heated volume that allows the precise determination and control of the residence time. The reactor consists of an inner quartz tube (9.5 mm o.d.) with a thermowell, placed concentrically inside another quartz tube (10 mm i.d.). An empty space of 4.3 cm^3 located in the middle provides the volume to carry the reactions in the absence or presence of other solids. Gases are fed into the reactor volume through the annular space between the two cylinders (prereactor) and exit the reactor through the 3-mm-i.d. capillary tube (postreactor). Due to the fast flows in prereactor and postreactor volumes, residence times in these two sections are very low and can be neglected. In order to determine the role of an inert material on methane conversion and product distribution, the reactor was operated with and without packing material. The quartz chips used in these experiments were broken fragments of fused silica placed in the reactor. The void fraction of the reactor filled with the packing material was 0.54. Extreme care was taken to prepare this material without any exposure to the ceramic or any metal environment since we have found that

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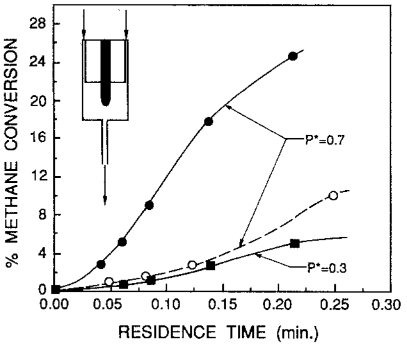

FIG. 1. The effect of residence time on methane conversion at $T = 750°C$. Solid lines correspond to experiments with an empty reactor at $P^* = 0.7$ and $P^* = 0.3$. The broken line corresponds to results obtained at $P^* = 0.7$ with the reactor volume filled with quartz chips.

quartz chips are susceptible to contamination when prepared in a clean ceramic mortar, resulting in a significant catalytic effect during the oxidation process. These findings are in a good agreement with the report by Martin *et al.* (*6*), who concluded that considerable error during methane studies may occur if the quartz reactors are contaminated with active materials. Experiments were repeated twice to verify reproducibility and were carried out at 750°C and at a methane-to-oxygen feed mole ratio of 2. Methane and oxygen were diluted in helium and experiments were carried out at reactant partial pressures of $P^* = 0.7$ and $P^* = 0.3$. Reaction products were analyzed via gas chromatography with a TCD detector (*5*). Methane conversions reported in this letter are based on the amount of carbon detected in the products. In all cases the carbon mass balances were closed to within 2%.

Figure 1 shows methane conversion vs residence time at reactant partial pressures of $P^* = 0.7$ and $P^* = 0.3$ for an empty reactor (solid lines). Data are also presented for an experiment conducted in the presence of quartz chips at $P^* = 0.7$ (broken line). The results clearly show that in an empty reactor operated with a concentrated feed with a small diluent flow (high P^*), methane conversion increases up to about 24% for a residence time of 0.225 min. Thus, for residence times longer than 0.1 min, methane conversion is significant and may contribute appreciably to the results obtained in the presence of a catalyst. On the other hand, when the feed is diluted with helium such that reactant partial pressure $P^* = 0.3$, methane conversion did not exceed 5% even at long residence times. Clearly, catalytic studies conducted under highly diluted feeds are not affected by the gas-phase-initiated reactions.

Yates and Zlotin, who investigated oxidative coupling of methane in the presence of Li/MgO catalyst (*4*), concluded that this particular catalyst is inefficient for the production of C_2 hydrocarbons. These authors compared their results with the data presented by Ito *et al.* (*3*), who investigated a Li/MgO catalyst under somewhat different operating conditions. The experiments of Yates and Zlotin (*4*) were conducted at residence times (calculated at room temperature) of approximately 1 min and at $P^* = 0.44$, i.e., in the region where gas-phase reactions become significant. These authors also conducted blank reactor experiments and found significant gas-phase conversions. Thus, their results should not be extrapolated to those of Ito *et al.* (*3*) since the latter authors worked at $P^* < 0.2$ (for the highest C_2 yields) and shorter residence times, i.e., in the region in which, according to our previous work and the results presented here, gas-phase reactions are not important. Undoubtedly, the results of Ito *et al.* (*3*) are representative of catalytic effects with a small contribution of gas-phase reactions whereas those of Yates and Zlotin (*4*) are affected by both catalytic and gas-phase-initiated reactions, as these authors have correctly recognized. Our previous results and those shown here clearly point out one of the main reasons for the discrepancy between the two authors and the need to consider carefully the range of operating conditions used in each experiment before extrapolating results from one work to another. Yates and Zlotin (*2*), on the basis of our earlier work in which we used the inverse flow rate, implied from this that we meant that residence time should not be employed in oxidative coupling studies. On the contrary, we recognized that residence time *is* an extremely important variable to be determined precisely, but this was not possible with our previous reactor design. Studies presented here clearly show that for the oxidative coupling of methane, residence time is an operating parameter that must be defined precisely.

If one considers a well-mixed reactor, the mass balance equation dictates that the reaction rate equals the difference between the inlet and outlet concentrations divided by the residence time. However, if the *conversion* is plotted at various values of P^*, the introduction of the inlet concentration to define conversion makes the reaction rate equal to the conversion divided by the residence time based on the methane flow rate instead of the total flow rate. While this has no effect in a first-order reaction, it has an effect for nonlinear kinetics. In this case, the conversion versus residence time curves shown in Fig. 1 will be shifted to the wider range of values corresponding to the residence time based on the methane flow rate. To appreciate this effect, the residence time shown in Fig. 1 must be multiplied by a factor of $30/14 = 2.14$ for $P^* = 0.7$, and by a factor of 5 for $P^* = 0.3$, which corrects for the methane flow rate instead of for the total flow rate. Thus, in terms of the residence time based on the methane flow rate, the difference in conversions for the same residence time based on the methane flow rate is even *greater* than those shown in Fig. 1. With regard to the difference between residence time and contact or retention time, due to the fact that in methane oxidative coupling the surface species are short lived, there is no real difference between the two definitions.

Hatano *et al.* in their Comments on "Blank Reactor Corrections . . . by Yates and Zlotin" (*1*) pointed out similar reasons for the discrepancies in the catalytic data obtained by these two groups. They also present data showing that an inert material (e.g., quartz chips) inhibits conversion of methane in the gas phase, while Yates and Zlotin found that quartz chips have little effect on methane conversion, in accord with our previous results which were obtained using a relatively small volume of quartz chips. To further clarify this point experiments were repeated in the new reactor where its empty volume was filled with quartz chips. The results of this experiment conducted at reactant partial pressure of $P^* = 0.7$ and various residence times (Fig. 1, broken line), defined in terms of the void volume, clearly show that at identical residence times, methane conversion in the reactor filled with quartz chips is much lower than that in the case of an empty reactor; this is in agreement with the results of Hatano *et al.* (*1*). In our previous report the volume of quartz chips was not specified, but it did not affect the methane conversion because it was small compared with the heated gas-phase volume of an empty reactor. While the velocity profiles in the empty reactor and in the reactor filled with quartz chips are not identical, the differences in flow distribution do not explain or justify the decrease in conversion. The decrease in methane activity in the presence of quartz chips is not yet explained, but it is suspected (*1*) that additional surface-assisted reactions are quenching the intermediates generated in the gas phase.

In this note, it is clearly shown that in addition to the conditions established in our previous work (*5*), the residence time of the reactants and the reactant partial pressure P^* should be clearly defined in order to compare results from different studies. This requires special reactor designs which minimize the effect of the pre- and postreactor heated volumes. It was found that the presence of quartz chips can inhibit gas-phase reactions when their volume is comparable with the gas-phase volume. Therefore, quartz chips can be utilized to minimize conversions that might occur in the prereactor volume. However, when a packing material is used it must be remembered that even a very small amount of active phase may contaminate it. In fact, a new reactor must often be used in a catalytic experiment in order to avoid contamination effects from the reactor walls, especially when working with alkali-doped catalysts, which are effective promoters in oxidative coupling reactions. Contamination of catalytic materials by minute traces of promoters can also be important in catalytic studies, which can explain why apparently similar materials often give different results (*2*).

In summary, extreme care should be exercised in the selection and definition of operating conditions during oxidative coupling experiments so that catalyst results are devoid of gas-phase reactions. While this is possible in laboratory reactors it may pose significant limitations in commercial reactors. In large-scale operations where the feed must be concentrated, not only the gas-phase reactions of methane are important, but the less documented issue of the oxidation of the hydrocarbon products can pose limitations on the attainable yields. Such effects are also very sensitive to the operating conditions used (*7*) and special reactor designs might be required (i.e., cycling feeds) to minimize the effect of the total oxidation of reaction products.

REFERENCES

1. Hatano, M., Hinson, P. G., Vines, K. S., and Lunsford, J. H., *J. Catal.* **124,** 557 (1990).
2. Yates, D. J. C., and Zlotin, N. E., *J. Catal.* **124,** 562 (1990).
3. Ito, T., Wang, J.-X., Lin, C.-H., and Lunsford, J. H., *J. Amer. Chem. Soc.* **107,** 5062 (1985).
4. Yates, D. J., and Zlotin, N. E., *J. Catal.* **111,** 317 (1988).
5. Lane, G. S., and Wolf, E. E., *J. Catal.* **113,** 144 (1988).
6. Martin, G. A., Bates, A., Ducarme, V., and Mirodatos, C., *Appl. Catal.* **47,** 287 (1989).
7. Kalenik, Z., Miro, E. E., Santamaria, J., and E. E. Wolf, in "Preprints of 3B Symposium on Methane Activation, 1989 Pacifichem Meeting, Honolulu, HI," p. 109, 1989.

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