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Reply to Hatano, Hinson, Vines, and Lunsford's Comments on "Blank Reactor Corrections in Studies of Oxidative Dehydrogenation of Methane"

In the contiguous letter to the editors, Hatano, Hinson, Vines, and Lunsford (*1*) have taken issue with the conclusions of our recent work (*2*). In particular, they question our conclusion that lithium carbonate on magnesium oxide "seems to be mainly a combustion catalyst, which happens to produce a little more than twice the amount of C_2's formed by homogeneous reactions under identical conditions. . . ." When we wrote this statement, we had at that time found another lithium-doped MgO catalyst which, while not as active as Li_2CO_3/MgO, has essentially no combustion activity. This work has since been published (*3*) but Hatano *et al.* do not mention it. In Table 1, we have summarized some of the data obtained using a lithium tetraborate (LTB) catalyst. It will be seen that at 720°C the 14% LTB catalyst produced little more CO_2 than did an empty reactor, but that the 3% Li_2CO_3 catalyst essentially produced only CO_2 and no CO. However, as a producer of C_2's, the Li_2CO_3 catalyst was superior in both yield and selectivity to the LTB catalyst. Nonetheless, we feel constrained to point out that the data in Table 1 show clearly that even the best of all of the lithium-doped catalysts had no more than double the yield and selectivity of the homogeneous reactions occurring in an empty reactor. The predominance of CO_2 in the product gases is shown in the original work (*4*); one of the runs is converted to the more convenient percentage of product composition in Table 1. It will be seen that the conversion, product distribution, selectivity, and yield for the Li_2CO_3/MgO catalysts studied by the two groups (*2*, *4*) are substantially the same. Furthermore, it should be stressed that the catalyst activity seems to be independent of the entirely different uncatalyzed reactions reported by the two groups.

In their discussion of our work, Hatano *et al.* also consider the oxygen consumption. They state,

> 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 oxygen was converted and in the heterogeneous reaction nearly 100% of the oxygen was converted. Under such oxygen-limiting conditions it is impossible to determine the true catalytic activity.

However, their argument applies with equal force to their own data. In their reactor, which presumably has no homogeneous consumption of O_2, they obtained with a catalyst essentially the same conversion. Apparently, they forgot that under identical conditions (see Table 2, this letter) their own results with a 7% Li_2CO_3 catalyst showed a 37.5% CH_4 conversion. If a 39.2% conversion corresponds to a 100% oxygen consumption, then clearly a 37.5% conversion corresponds to 95.7% oxygen consumption. As stressed earlier, the product gas compositions are the same for the two Li_2CO_3 catalysts, so it is evident that they, too, are running under "oxygen-limiting conditions" and they also did not "determine the true catalytic activity."

The homogeneous reactions between CH_4 and oxygen are then discussed by Hatano *et al.* (*1*). A long explanation is given of the differences in residence times be-

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TABLE 1

Reactions between Methane and Oxygen

Temp. (°C)	Reactor loading	Ref.	CH_4 conv. (%)	Product composition (mol%)				Selectivity to C_2's (%)	Yield of C_2's (%)	Ratio of CO_2/CO in exit gases
				CO	CO_2	C_2H_4	C_2H_6			
720	None	3	30.9	70.8	17.5	7.8	3.9	21.1	6.5	0.25
	14% LTB	3	33.7	61.5	21.6	12.3	4.6	28.8	9.7	0.35
	3% Li carb.	3	37.9	2.4	76.3	14.9	6.3	35.0	13.2	31.8
720	None	2	26.8	73.0	16.0	7.1	3.8	19.6	5.3	0.22
	3% Li carb.	2	39.2	2.1	75.7	15.6	6.6	36.5	14.3	36.0
	7% Li carb.	4	37.5	2.0	67.7	20.4	9.9	46.5	17.4	33.8

Note. Other details can be found in Table 3A in Ref. (*2*), Table 3 in Ref. (*3*), and Table II in Ref. (*4*). Feed rates and catalyst weights were the same as those in Refs. (*2–4*).

tween our reactor and theirs used earlier (*4*), ours being 20 s and theirs 5 s. No explanation was given (*1*), however, of how this residence time was determined from their original reactor data (*4*). We note that they have still not reported data using a replica of the original reactor (*4*), as instead of using a 12-cm reactor, they now use one 7-cm long (Ref. (*1*), Fig. 1, reactor B). It will be seen from the figure that this reactor had a temperature gradient of 116°C over the lower 5.2 cm of the reactor. Under such circumstances, it seems to us that not even an approximate residence time can be calculated. Furthermore, the temperature profile is undefined—was it obtained under static conditions or with the feed flowing? Was the reactor empty, or did it contain silica wool or chips? We do not propose to discuss in any detail such vague data ob-

TABLE 2

	Ref. (*4*)			Ref. (*2*)			Ref. (*6*)		
	Table 2		Text	Table 3A		Text	Table 2		
	Run 4	Run 8							
Reactor material	FS[a]	FS	FS	FS	FS	FS	FS	FS	FS
Reactor diameter (cm)	2.3 o.d.	2.3 o.d.	2.3 o.d.	2.4 i.d.	2.4 i.d.	2.4 i.d.	0.95 i.d.	0.95 i.d.	0.95 i.d.
Reactor length (cm)	12	12	12	24	24	24	45	45	45
Reactor heated length (cm)	7	7	7	12	12	12	15	15	15
Reactor loading	FSC[b] 3% Li/MgO	FSC 7% Li/MgO	FSC	FSW[c] 3% Li/MgO	Empty	FSW	Empty	FSW	FSC[d]
Temperature (°C)	720	720	720	720	720	720	800	800	800
He flow (cm^3/min)	19.7	28.0	—[e]	28.2	28.2	28.2	12.5	12.5	8.25
CH_4 flow (cm^3/min)	19.9	14.3	—	14.0	14.0	14.0	25.0	25.0	16.5
O_2 flow (cm^3/min)	10.3	7.7	—	7.8	7.8	7.8	12.5	12.5	8.25
CH_4/O_2 ratio	1.93	1.86	—	1.8	1.8	1.8	2.0	2.0	2.0
Dilution ratio[f]	0.60	0.44	—	0.44	0.44	0.44	0.75	0.75	0.75
CH_4 conversion (%)	38.2	37.5	0.2	39.2	26.8	26.8	30.7	33.8	30.5
C_2's selectivity	43.0	46.5	—	36.5	19.6	19.6	19.8	20.9	22.3

[a] FS fused silica.
[b] FSC fused silica chips.
[c] FSW fused silica wool.
[d] Bed porosity 0.68, Ref. (*6*).
[e] Data not given in Ref. (*4*).
[f] Flow (CH_4 + O_2)/total flow.

tained with reactor B. In addition, no precise information was given on the feed composition or flow rates. Obviously, we have the same reservations about the data obtained in reactor A. The results shown using this reactor in Fig. 2 are undefined, as for example, no temperature profile or feed rates are disclosed.

In general, residence time is not an exact parameter to use in heterogeneous catalysis. The IUPAC manual on catalysis states clearly (*5*) that "Contact time and residence time are terms which may be misleading for flow systems in heterogeneous catalysis and should be avoided." It is of interest that other workers in the field of partial methane oxidation have followed this approach. They state, "The volume of the reactor in which the gas-phase reactions take place is not known; thus instead of using residence time, the results are reported in terms of inverse volumetric feed flow rate" (*6*). We agree entirely with the authors of Refs. (*5*) and (*6*), and consider that "residence time" is a parameter that should not be employed in scientific discussions of heterogeneous catalysis. Still less can it be meaningfully invoked when one is studying reaction systems which are simultaneously homogeneous and heterogeneous in nature.

Perhaps we should mention here that when we began the work reported in our first paper (*2*) it was our intent to reproduce the earlier work on the Li_2CO_3/MgO catalyst (*4*). To this end, we endeavored, as well as possible from the sparse experimental description given, to build a reactor as close as possible to that used in the original work (*4, 7*). As good practice demands, we spent time studying the system without the catalyst. This led to the divergence between the two groups. We found (Table 2, this letter), using one of their reported conditions (Ref. (*4*), Table 2, Run 8), essentially the same conversion as they did when using Li_2CO_3/MgO catalyst (39.2 vs 37.5%). We found, however, 28.6% conversion in our empty reactor, rather than the 0.2% they reported. After our paper appeared in print, Lane and Wolf (*6*) published a paper which essentially confirmed our work. Not only did they find 30% conversion in an empty reactor, but they also found that this reaction was essentially unaffected by the presence or absence of fused silica chips or fused silica wool. Hence, if we may stress the obvious, we have a situation where two independent groups of workers (*2, 6*) using similar overall reactor geometry, find evidence of very significant homogeneous reactions between CH_4 and oxygen, using He as diluent. On the other hand, another group of workers (*1*), using very similar feeds, diluents, and temperatures, find no homogeneous reactions in a reactor filled with silica chips.

We would like to draw attention here to Table 1 in Ref. (*6*), where a summary of literature conditions is given for experiments in the cofeeding of CH_4 and O_2. Perusal of this table shows that of 21 entries, no less than 11 contained missing data on such critical topics as reactor material and size. In one case, even the amount of catalyst was not given. Obviously a large amount of ill-defined work has been published in this area of catalysis. In their introduction, Lane and Wolf (*6*) state, "Due to the similarity of results obtained in our preliminary work with and without catalysts, it was deemed important to systematically study the degree of oxidative coupling of methane that can occur in the absence of catalysts." This they proceeded to do. Despite this systematic study, we note that in their letter Hatano *et al.* barely mention Lane and Wolf's work. Clearly, the results of Ref. (*6*), as far as empty reactors are concerned, are entirely opposite to those reported in Ref. (*1*).

At the end of their note (*1*), Hatano *et al.* state that "several other groups have studied this system . . . and have reported that the catalyst is indeed active and reasonably selective for the formation of ethane and ethylene," and that "In all these studies it was *implied or concluded* that the homoge-

neous reaction was negligible" (emphasis added). We have read such of these references as are available to us and note that in all the cases where the work is published as letters (*8–10*), the authors did not conclude that the homogeneous reactions were negligible—they just do not mention them. In the one full paper referred to (*11*), it should be stressed that the catalyst used was different (LiOH and MgO) and that the feed consisted of the mixture of $CH_4/O_2/He$ and CO_2. In discussing their blank experiments, these authors state that "Blank reactor tests showed negligible conversions of CH_4, C_2H_6, or C_2H_4 occurred in the presence of oxygen at 720°C." The amount of CO_2 used in these blank experiments is not given (*11*). The only way we can understand the lack of reactivity of C_2H_4 at these high temperatures is by a strongly suppressive effect of CO_2 which is presumably added to the feed during the blank reactor studies.

We conclude that only in three studies (*1, 2, 6*) has the question of blank reactor corrections in methane oxidation been discussed or even measured in any detail. One group, using short reactors with steep temperature gradients, finds suppression of homogeneous reactions by the addition of fused silica chips to the reactors. Two other independent groups of workers (*2, 6*) find essentially that the homogeneous oxidation of methane is the same in the empty reactor as in one filled with silica chips or silica wool. Clearly, more experimental work under very carefully controlled conditions is needed to resolve these differences.

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