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Supported Lithium Tetraborate as a Catalyst for the Continuous Oxidative Dehydrogenation of Methane

Recent work from our laboratory (*1*) has shown that quite extensive noncatalyzed gas-phase reactions take place between dilute methane and oxygen mixtures in the region 600–720°C. The main products were found to be mostly CO and CO_2, together with some C_2H_4 and C_2H_6. Since then, other workers have published (*2*) detailed studies on the gas-phase oxidation of methane, in general agreement with our data. Furthermore, our work showed that one of the catalysts previously studied (*3–5*) for this reaction, namely Li_2CO_3 on MgO, while doubling the amount of C_2's formed homogeneously, also oxidized almost all of the homogeneously formed CO to CO_2. Hence, if a catalyst that would not oxidize CO to CO_2, while still forming C_2H_4 and C_2H_6, could be found, it would be of considerable importance.

We have found that lithium tetraborate (LTB) supported on MgO does not oxidize CO, while showing activity for the formation of C_2's. To investigate the effect of the support, catalysts have also been prepared using silica and alumina.

EXPERIMENTAL

The horizontal reactor was made entirely from fused silica, and full details have been published earlier (*1*), together with details of the furnace and GC analysis used. In this and previous work, a small amount of ethane was present in the methane. We have since obtained methane of stated purity 99.99%, and GC analyses showed no detectable amount of C_2's to be present. Reaction data obtained in an empty reactor using this high-purity methane were found to be identical with those reported earlier (*1*).

The MgO (99.9%, cat. 12287) was obtained from Aesar, Johnson Matthey, Inc., Seabrook, New Hampshire, as was the $Li_2B_4O_7$ (99.9%, cat. 12592). The silica used was Cab-O-Sil (300 m^2/gm) from the Cabot Corp., Boston, Massachusetts; it was air-calcined at 500°C before use. The alumina was high-purity extrudate (180 m^2/gm) from Engelhard Inc., Newark, New Jersey; it was calcined at 500°C and ground before use. All the catalysts contained 14% Li (as LTB) and were made with MgO (cat. A), SiO_2 (cat. B), and Al_2O_3 (cat. C). For example, catalyst A was made by suspending 6.0 g of MgO in 100 cc of methanol and adding to it, while stirring, a suspension of 10.2 g of LTB in 50 cc of methanol. After the mixture was stirred for a short time, the methanol was removed by bubbling air through it, while heating it on a warm water bath. After all the liquid had evaporated, the drying and calcining steps were identical with those used earlier (*1*). Catalysts were also prepared containing 7% Li as LTB using methanol and also using water as the suspending medium. The data for both the 7% Li catalysts were identical, so that the choice of the suspending medium is not critical.

RESULTS AND DISCUSSION

Previous work using a silica tubular reactor (*1*) showed that, for the particular geometry and gas residence time used, quite significant thermal reactions take place between methane and oxygen in the temperature range 600–720°C. This was found to occur both with $CH_4 : $ air mixtures (ratio 1 : 2.5) and with $CH_4 : O_2 : $ He mixtures, using the same $CH_4 : O_2$ ratio. When using 3%

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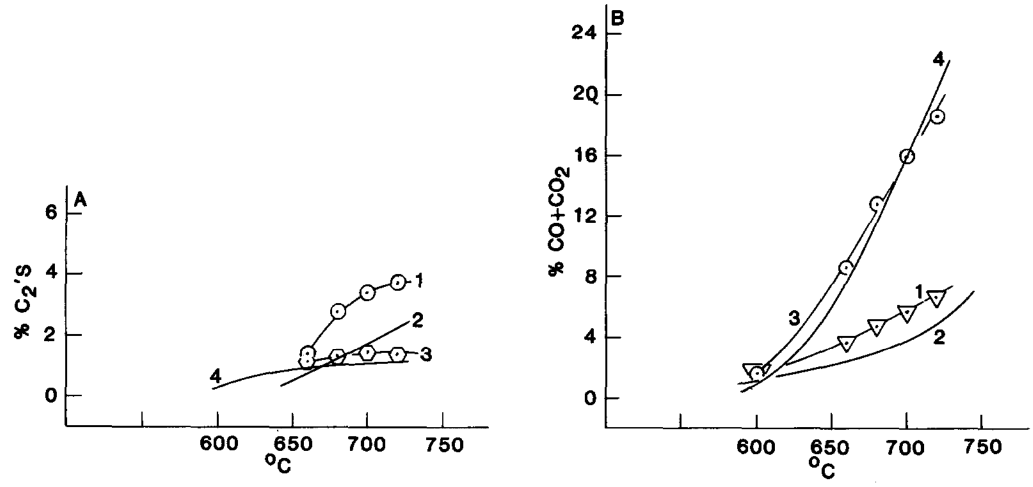

FIG. 1. (A) Composition of exit gas with CH_4 : air feed. (1) ⊙, C_2H_4 formed with catalyst A containing 14% Li on MgO. (2) C_2H_4 formed in an empty reactor (Ref. (*1*)). (3) ⊙ and (4) C_2H_6 formed under the same conditions as those of (1) and (2). (B) Same feed. (1)▽, CO_2 formed with the same catalyst. (2) CO_2 formed in an empty reactor (Ref. (*1*)). (3) ⊙ and (4) CO formed under the same conditions as those of (1) and (2).

Li (as Li_2CO_3) on MgO, the production of C_2H_4 at 700°C was found to be twice that made homogeneously. Apart from the increases in C_2 yield and selectivity, the carbonate catalyst essentially converted all of the homogeneously formed CO to CO_2 (*1*).

The data with our new catalyst are strikingly different. Figure 1 shows that when using 14% Li (as LTB) the amount of CO in the exit gas (at 700°C) is identical with that formed thermally, while only 1.5 times as much CO_2 was present compared to homogeneous reactions. The addition of LTB has essentially suppressed the CO oxidation activity of the MgO support, while still forming a significant amount of C_2's. None of the tetraborate-based catalysts have as stable an activity as those made with Li_2CO_3 on MgO, and further work is continuing on this topic.

Tests of unsupported LTB showed it to have no catalytic activity, the products being identical with those obtained in an empty reactor. In this respect, it resembles Li_2CO_3, which has been reported to be inactive in the absence of MgO support (*3–5*). Evidently, the catalytic sites made from either carbonate or borate of lithium on MgO must reside at the interface between those compounds and the support. Nevertheless, our data shown conclusively that there must be at least two types of sites operative when Li_2CO_3 is supported on MgO (Table 1). The first is even more active than

TABLE 1

Exit Gas Composition[a]

Temp. (°C)	Reactor loading	Carbon-containing compounds (mol%)				
		CH_4	CO	CO_2	C_2H_4	C_2H_6
600	None	97.8	0.8	1.2	0	0.2
600	14% LTB	96.7	1.6	1.5	0	0.2
600	3% Li carb.	87.3	1.6	9.1	0.7	1.2
650	None	91.4	5.4	1.8	0.5	0.9
660	14% LTB	85.1	8.6	3.7	1.4	1.2
650	3% Li carb.	69.0	1.4	22.4	4.5	2.7
700	None	76.7	16.7	3.8	1.8	1.0
700	14% LTB	73.5	15.9	5.7	3.4	1.5
700	3% Li carb.	66.4	0.80	25.0	5.3	2.4
720	None	71.4	20.2	5.0	2.2	1.1
720	14% LTB	69.7	18.6	6.6	3.7	1.4
720	3% Li carb.	66.5	0.8	25.6	5.0	2.1

[a] Excluding water and oxygen. The values are averages of at least three chromatographic analyses obtained at each temperature. Feed flow rates: CH_4, 14 cc/min; air, 36 cc/min. The data for 14% Li are for catalyst A, and those for 3% Li are from Ref. (*1*).

TABLE 2

Exit Gas Composition[a]

Temp. (°C)	Reactor loading	Carbon-containing compounds (mol%)				
		CH_4	CO	CO_2	C_2H_4	C_2H_6
600	None	97.8	0.8	1.2	0	0.2
600	14% LTB on SiO_2	97.1	1.5	1.0	0	0.3
600	14% LTB on Al_2O_3	92.3	0.3	6.9	0	0.5
650	None	91.4	5.4	1.8	0.5	0.9
650	14% LTB on SiO_2	91.2	6.1	1.4	0.4	0.8
650	14% LTB on Al_2O_3	86.8	1.1	11.4	0	0.6
700	None	76.7	16.7	3.8	1.8	1.0
700	14% LTB on SiO_2	78.4	15.5	3.4	1.5	1.1
700	14% LTB on Al_2O_3	78.3	6.9	14.2	0	0.6

[a] Excluding water and oxygen. The values are averages of at least three chromatographic analyses obtained at each temperature. Feed flow rates: CH_4, 14 cc/min; air, 36 cc/min.

pure MgO for the oxidation of CO to CO_2, while the second type is responsible for the formation of C_2's. When LTB is used, the first type is absent, as the amount of CO in the exit gas is identical with that formed thermally. However, there are evidently some sites in the borate catalyst that form CO_2 from CH_4, as we find a little more CO_2 in the exit gas than in an empty reactor.

To further study the effect of the support, we have made two borate catalysts using silica (cat. B) and alumina (cat. C). The data for the silica catalyst are almost identical with those obtained using an empty reactor; i.e., the catalyst is inactive in producing higher hydrocarbons from CH_4 (see Table 2). Our earlier study (*1*) showed that a reactor filled with silica wool gave data identical to those obtained with an empty reactor. The present results showed that silica, in the form of high-surface-area Cab-O-Sil, is also inactive, even in the presence of 14% Li as LTB. There are, in contrast, quite dramatic effects when LTB on alumina is used. Table 2 shows that while C_2H_4 is invariably produced by thermal reactions, no C_2H_4 is in the exit gas whenever catalyst C is used. Also, the amount of ethane formed by this catalyst is less than that produced thermally, although finite. Hence, all the C_2H_4 produced thermally and/or possibly formed initially by the catalyst is rapidly oxidized to CO_2. Although some CO remained (Table 2), it is much less than that found using an empty reactor. It seems that the acidic support forms no C_2H_4 when doped with 14% Li as LTB; the neutral support, SiO_2, behaves as if no catalyst at all were present in the reactor, while the alkaline support (MgO) is the only one that shows any significant C_2 synthesis activity.

Finally, in Figs. 2 and 3 we have further compared the supports and lithium salts for their formation of carbon oxides. Figure 2 shows that CO produced thermally is not

TABLE 3

Reactions between Methane and Air[a]

Temp. (°C)	Reactor loading	Total CH_4 conversion	Product composition (mol%)				Selectivity C_2's (%)	Yield C_2's (%)
			CO	CO_2	C_2H_4	C_2H_6		
700	None	25.4	71.2	16.9	7.7	4.2	21.7	5.5
	14% LTB	29.9	60.0	21.5	13.0	5.5	31.2	9.3
	3% Li carb.	38.4	2.4	74.5	15.8	7.2	37.4	14.3
720	None	30.9	70.8	17.5	7.8	3.9	21.1	6.5
	14% LTB	33.7	61.5	21.6	12.3	4.6	28.8	9.7
	3% Li carb.	37.9	2.4	76.3	14.9	6.3	35.0	13.2

[a] Flow rates: CH_4, 14 cc/min; air, 36 cc/min. The data for the empty reactor and for the 3% lithium carbonate on MgO are taken from our previous work (*1*); the data for 14% Li as LTB are for catalyst A.

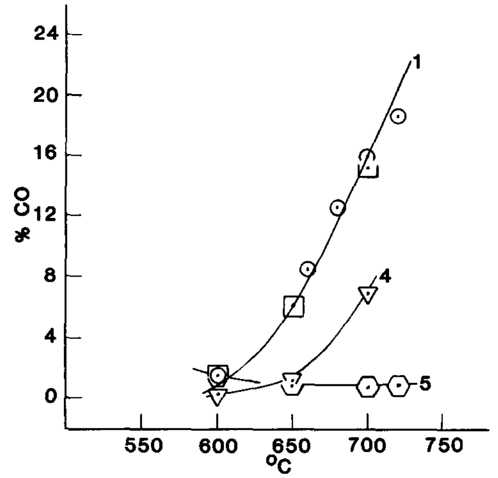

FIG. 2. Carbon monoxide content of exit gas with a CH_4 : air feed. (1) The line represents data obtained using an empty reactor (Ref. (*1*)). (2) ⊙, data obtained with catalyst A; no line is drawn as the points essentially superimpose on line (1). (3) ⊡, data obtained with catalyst B; again no line is drawn. (4) ▽, data obtained with catalyst D. (5) ⊙, data obtained with a 3% Li (as carbonate) on MgO catalyst (Ref. (*1*)).

TABLE 4

Ratios of Carbon Dioxide/Carbon Monoxide in Exit Gases[a]

Temp. (°C)	Empty reactor	14% Li (as LTB) on SiO_2	14% Li (as LTB) on MgO	3% Li[b] (as carbonate) on MgO	14% Li (as LTB) on Al_2O_3
600	1.2	0.7	0.9	5.7	23.0
650	0.3	0.2	0.4	16.0	10.4
700	0.2	0.2	0.4	31.3	2.0

[a] Excluding water and oxygen. Feed flow rates: CH_4, 14 cc/min; air, 36 cc/min.

[b] Data from Ref. (*1*).

oxidized by the LTB supported on either MgO or SiO_2, and hence neither catalyst has any CO oxidation activity. The highest oxidation activity is found (*1*) with 3% Li (as carbonate) on MgO, while the LTB on alumina catalyst has an intermediate activity. This could be due to the fact that not all of the alumina surface is covered by the LTB. It seems that all of the MgO surface is covered by the LTB, but the detailed comparison can be made only when using MgO and Al_2O_3 of the same surface area. In our case the Al_2O_3 area is much larger than that of the MgO. Clearly, more work is needed to characterize the system; e.g., detailed measurements need to be made on the surface area of the LTB and of the catalysts as prepared (i.e., after calcination) and after running. At this point, we should mention that, in contrast to data reported for LiOH supported on MgO (*6*), no Li_2CO_3 must be formed in our tetraborate systems when the catalyst is exposed to methane and oxygen at 700°C. If it were, we would not find the high CO content in the exit gas which is characteristic of the homogeneous reactions occurring in an empty reactor.

Figures 2 and 3 show that the catalysts most active in the complete combustion of CH_4 to CO_2 are the least active in formation of CO and vice versa. In Table 4, we give values for the ratio of CO_2 to CO from the

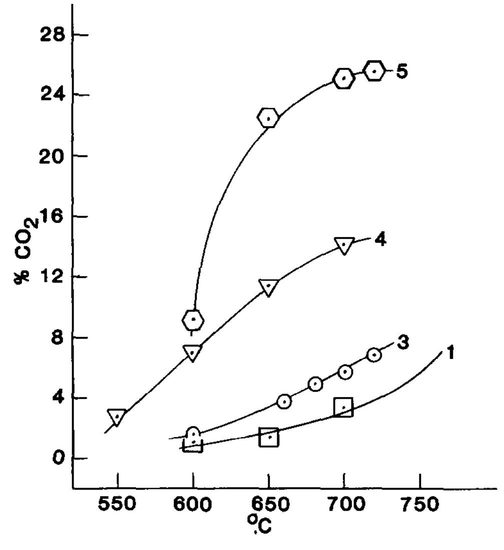

FIG. 3. Carbon dioxide content of exit gas with CH_4 : air feed. (1) The line represents data obtained using an empty reactor (Ref. (*1*)). (2) ⊡, data obtained with catalyst B; no line is drawn as the points essentially superimpose on line 1. (3) ⊙, data obtained with catalyst A. (4) ▽, data obtained with catalyst C. (5) ⊙, data obtained with a 3% Li (as carbonate) on MgO catalyst (Ref. (*1*)).

present work, together with earlier data (*1*) with a Li_2CO_3-on-MgO catalyst. The first column contains the data obtained from an empty reactor, and they are very close to the data obtained with 14% Li (as LTB) on silica. The values for borate supported on MgO are essentially the same as those in the first two columns for 600°C, but are a little higher at 650 and 700°C. The data in column 4 show that dramatically more CO_2 is made when Li_2CO_3 is used, rather than LTB. The CO_2/CO ratio is below unity at all temperatures for the LTB catalyst, in contrast to the carbonate catalyst which makes at 600°C nearly six times as much CO_2 as CO, with the ratio increasing to 31 at 700°C.

When Li_2CO_3 is supported on MgO we find somewhat higher selectivity and yield toward the formation of C_2's than those for the LTB-based catalyst. Nevertheless, the carbonate-based catalyst converts essentially all of the homogeneously formed CO into CO_2, while the LTB-based catalyst has but little, if any, activity for CO oxidation. Furthermore, the carbonate catalyst forms still more carbon dioxide by some additional combustion of methane.

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