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Blank Reactor Corrections in Studies of the Oxidative Dehydrogenation of Methane

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Measurements have been made on the activity and selectivity of both magnesium oxide and lithium-doped magnesium oxide catalysts for the oxidative dehydrogenation of methane and have been compared with thermal (homogeneous) reactions in the same reactor. In addition to the use of methane, oxygen, and helium as the feed, methane and air mixtures have been used. Detailed experiments with our particular empty reactor, and residence time, showed that significant quantities of ethane and ethylene were formed at operating temperatures in the absence of a catalyst. Furthermore, under the same conditions large quantities of carbon monoxide were formed in our empty reactor; the carbon monoxide was found to be converted readily to carbon dioxide in the presence of either pure magnesium oxide or lithium-doped magnesium oxide.

INTRODUCTION

Methane conversion to useful hydrocarbon products is well known to be a difficult process, either through dehydrogenation to higher hydrocarbons or by the oxidative dehydrogenation route (*1–7*). In the latter case, interesting data have been reported by Lunsford and co-workers (*6, 7, 9*) using magnesium oxide-based catalysts in silica reactors. Other workers have used metal reactors (*1, 3*) which are unsuitable for this reaction as the reactor walls are themselves quite active in the formation of oxidation products from methane under high-temperature conditions.

The main products of the reaction over lithium-doped magnesium oxide catalysts using methane–oxygen–helium mixtures were found to be ethane and ethylene, together with considerable quantities of carbon dioxide from combustion (*6, 7*).

We have attempted to reproduce the data given in one of the above papers, but have found, at least with our particular reactor configuration and residence times, that the extent of noncatalyzed thermal reaction taking place in any empty reactor is very significant at temperatures where the catalyst shows the highest activity (approximately 700°C). It is possible, therefore, that corrections for this may have to be made for some conditions under which the catalyst shows significant activity.

Such corrections have not been discussed in any detail in previous papers (*6, 7, 9*).

EXPERIMENTAL

The horizontal reactor was made from fused silica of internal diameter 2.4 cm. The first 11 cm of the reactor was outside the furnace followed by 12 cm inside the furnace (see Fig. 1). At this position in the reactor, there was an internal seal to a fused silica capillary tube (i.d. 0.20 cm), which continued for the rest of the reactor length. Hence a relatively long residence time was used over the catalyst bed (the volume of the heated large-diameter portion was 56 cc), and then a short exit residence time was obtained through the use of a capillary tube to rapidly remove the unreacted feed and products. The three-zone furnace was identical with that used in earlier work on the catalytic growth of fila-

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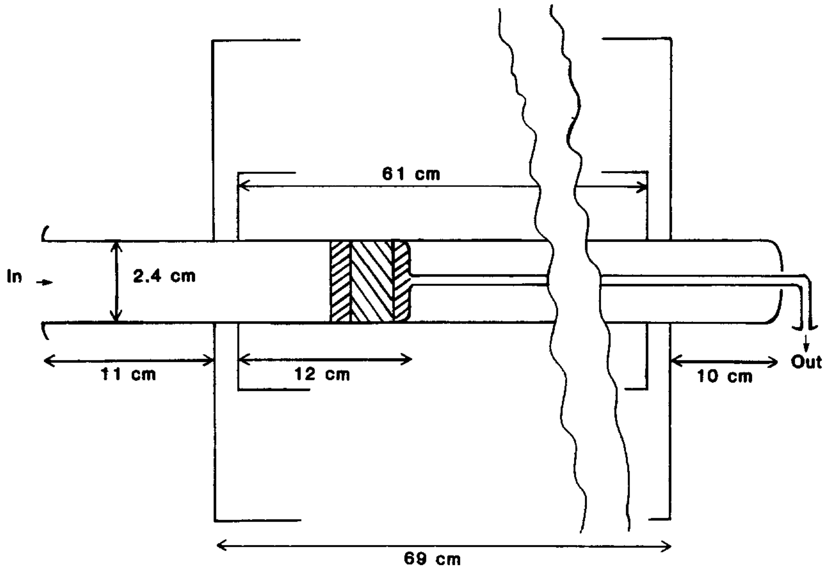

FIG. 1. Design of reactor and its location in the furnace.

mentous carbon from ethane (*8*) and was obtained from Thermcraft Inc., Winston-Salem, North Carolina. As the furnace had two end windings, the center winding of the furnace (46 cm) could be adjusted to be constant in temperature to ±1°C.

Some blank experiments were done with a much shorter (33-cm single-zone) furnace, manufactured by Thermoline Co., Dubuque, Iowa, Model 21100. This furnace was positioned so that the beginning of the heated zone, at the inlet, was at the same point on the reactor as that used with the longer furnace. Hence, about half of the exit capillary was at room temperature when using the short furnace.

For feed and product analysis, a Hewlett–Packard Model 5890A gas chromatograph was used, with a thermal conductivity detector and a gas sample loop of 1.0 cc. The metal column used was 10 in. long and $\frac{1}{8}$ in. diameter packed with 100/120 mesh Carbosieve S-II supplied by Supelco Inc., Bellefonte, Pennsylvania. Calibration was done with a standard mixture containing CO, CO_2, CH_4, C_2H_2, C_2H_4, and C_2H_6 in nitrogen, obtained from Scott Specialty Gases, Plumsteadville, Pennsylvania. All other gases were obtained from Air Products and Chemicals, Tamaqua, Pennsylvania. The helium was high purity grade, 99.995%; the methane was instrument grade, 99.7%; the oxygen was extra dry grade, 99.6%; and the air was zero grade (THC < 1.0 ppm). The only gas with detectable impurities was methane, which contained 0.136% C_2H_6 and no C_2H_4 as determined by our GC analysis. The helium, air, and oxygen were dried before use with molecular sieve indicating dryers obtained from Chrompack, Raritan, New Jersey. Gas flows were controlled by mass flow controllers, obtained from Tylan Corp., Carson, California.

The gaseous products were passed through a small glass U-tube with indicating "Drierite" calcium sulfate obtained from W. H. Hammond Co., Xenia, Ohio, to remove water before entering the GC loop. The desiccant was replaced before each experiment.

CATALYST PREPARATION

The magnesium oxide had a purity of 99.9%, Cat. No. 12287, and was obtained from Aesar, a division of Johnson Matthey

TABLE 1A

Methane Conversion as a Function of Temperature

Temp. (°C)	Total conversion (%)		
	Empty reactor	Pure MgO	3% Li on MgO
550	0	4.5	26.0
600	1.8	13.5	33.8
650	8.0	28.3	39.0
700	22.3	34.6	39.4
720	26.8	35.0	39.2

Note. Feed: methane, oxygen and helium. Flow rates: CH_4, 14 cc/min; O_2, 7.8 cc/min; He, 28.2 cc/min.

Inc., Seabrook, New Hampshire. The lithium carbonate was obtained from the same source, purity 99.999%, Cat. No. 10734, Puratronic grade.

The MgO was suspended in water (typically 20 g in 150 cc of water), and while being stirred in a beaker on a magnetic stirrer, a suspension of lithium carbonate was added (typically, 3.2 g in 100 cc of water to give 3 wt% Li in the finished catalyst). After the mixture was stirred for a short time (15–20 min) the water was removed, while stirring continued, by heating. After only a thick paste was left, the beaker was transferred to a preheated air oven (at 120°C) and dried overnight. The catalyst was then transferred to shallow glass petri dishes and put into a muffle furnace (in air) at 120°C. The latter was then heated at its natural heating rate, taking about 45 min to reach 510°C, and held overnight at this temperature. After being cooled to room temperature and ground to a powder, the catalysts were pressed in a die at 10,000 psi, and then ground again until the particles passed through a 10-mesh sieve, being retained on a 20-mesh sieve. No data were obtained on unsieved catalysts in a powder form. The catalysts were held in place in the reactor by plugs of quartz wool.

RESULTS

We have made extensive experiments with reactors containing no catalyst, some with quartz wool and some without. Little difference was detected due to the presence of quartz wool.

Table 1A contains data on methane conversion as a function of temperature for three cases: the empty reactor, the reactor with pure MgO, and the reactor with 3% Li on MgO, with a feed consisting of CH_4, O_2, and He. Analogous data are given in Table 1B with a feed of CH_4 and air, using the same $CH_4 : O_2$ ratio.

Table 2 contains data on the same three reactor loadings as those in Table 1A, but lists the product composition as a function of temperature.

Table 3A contains values of methane conversion, product compositions, C_2 selectivity, and C_2 yield obtained using methane : helium : oxygen mixtures at 700 and 720°C for the empty reactor, for the same reactor containing pure magnesium oxide, and for the same reactor containing 3% Li on MgO catalyst, all prepared as described above. Selectivity was calculated as the number of moles of methane converted to C_2 products divided by the total number of moles of methane reacted. Yield was de-

TABLE 1B

Methane Conversion as a Function of Temperature

Temp. (°C)	Total conversion (%)		
	Empty reactor	Pure MgO	3% Li on MgO
550	0	9.5	5.3
600	2.4	20.3	14.0
650	10.4	31.9	35.7
700	25.4	34.3	38.4
720	30.9	35.1	37.9

Note. Feed: methane and air. Flow rates: CH_4, 14 cc/min; air, 36 cc/min.

TABLE 2

Exit Gas Composition[a,b]

Temp. (°C)	Catalyst	Carbon-containing compounds (mol%)				
		CH_4	CO	CO_2	C_2H_4	C_2H_6
600	None	98.2	1.1	0.7	0	0
	Pure MgO	86.5	5.9	7.6	0	0
	3% Li/MgO	69.0	2.7	24.2	2.1	2.0
650	None	92.7	5.6	1.0	0	0.7
	Pure MgO	72.8	7.0	18.6	0.6	1.0
	3% Li/MgO	65.8	1.3	25.0	5.0	2.9
700	None	79.9	14.9	2.9	1.4	1.0
	Pure MgO	67.5	4.9	24.6	2.0	1.1
	3% Li/MgO	65.4	0.7	25.9	5.5	2.5
720	None	75.2	18.1	4.0	1.8	0.9
	Pure MgO	67.1	4.5	25.1	2.3	1.0
	3% Li/MgO	65.5	0.7	26.1	5.4	2.3

[a] Excluding water and oxygen.

[b] The values are averages of at least three chromatographic analyses obtained at each temperature. Feed flow rates are: CH_4, 14 cc/min; O_2, 7.8 cc/min; and He, 28.2 cc/min. In all cases 4.1 g of catalyst was used.

fined as a product of selectivity and conversion. Comparative data from earlier work obtained under similar composition and flow rate conditions, but with 7% Li on MgO catalyst, are also given. Table 3B contains data obtained in this work with the same reactor and catalyst as those in Table 3A but using methane : air mixtures. The catalyst charge in all experiments was 4.1 g.

Figure 1 shows the design of the reactor, and its position in the furnace. Figures 2A and 2B show the ethane, ethylene, and carbon oxide content in the product gases as a function of temperature using methane : oxygen : helium feed, for both the thermal and the catalytic reactions. Figures 3A and 3B show the data obtained with air : methane mixtures under the same conditions. In both series of experiments, the methane : oxygen ratio was kept at 2 : 1, with a total flow rate close to 50 cc/min, measured at room temperature.

It can be seen from the above results that there is a high conversion of methane in the empty reactor to carbon oxides at 650°C and above. Therefore we investigated the possibility that our relatively long (49-cm) heated exit capillary may have been a problem. This was done in experiments using the same empty reactor, but with a 33-cm single-zone furnace. Despite the fact that only about half of the length of the exit cap-

TABLE 3A

Reactions between Methane and Oxygen[a]

Temp. (°C)	Reactor loading	Total CH_4 conversion	Product composition (mol%)				Selectivity C_2's (%)	Yield of C_2's (%)
			CO	CO_2	C_2H_4	C_2H_6		
700	None	22.3	73.9	14.4	6.9	4.8	20.9	4.7
	Pure MgO	34.6	15.2	75.5	6.0	3.2	17.4	6.0
	3% Li/MgO	39.4	2.1	74.8	15.8	7.3	37.6	14.8
720	None	26.8	73.0	16.0	7.1	3.8	19.6	5.3
	Pure MgO	35.0	13.7	76.3	7.1	2.9	18.2	6.4
	3% Li/MgO	39.2	2.1	75.7	15.6	6.6	36.5	14.3
	7% Li/MgO[b]	37.5	2.0[c]	67.7[c]	20.4[c]	9.9[c]	46.5[d]	17.4[d]

[a] Flow rates: CH_4, 14 cc/min; O_2, 7.8 cc/min; and He, 28.2 cc/min.

[b] Data taken from Ref. (*7*, Table II, Run 8).

[c] These values of product composition were calculated from values of the partial pressure of the products, together with the given value of methane conversion (37.5%) in Ref. (*7*). It should be noted that the above calculated product compositions are not consistent with the selectivity and yield values given in their Table II (46.5 and 17.4%).

[d] From Ref. (*7*, Table II).

TABLE 3B

Reactions between Methane and Air[a]

Temp. (°C)	Reactor loading	Total CH_4 conversion	Product composition (mol%)				Selectivity C_2's (%)	Yield of 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
	Pure MgO	34.3	11.9	78.9	6.2	3.0	16.9	5.8
	3% Li/MgO	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
	Pure MgO	35.1	11.9	77.7	7.3	3.0	18.6	6.5
	3% Li/MgO	37.9	2.4	76.3	14.9	6.3	35.0	13.2

[a] Flow rates: CH_4, 14.0 cc/min; air, 36 cc/min.

illary was now heated, we obtained the same results as those in Figs. 2 and 3. This is consistent with the fact that when using the long furnace, the volume of the heated wide part of the reactor is about 54 cc, while the volume of the heated capillary is about 1.5 cc, thus giving corresponding residence times for the gases.

DISCUSSION

With our reactor and furnace arrangement we have found that the oxidation of

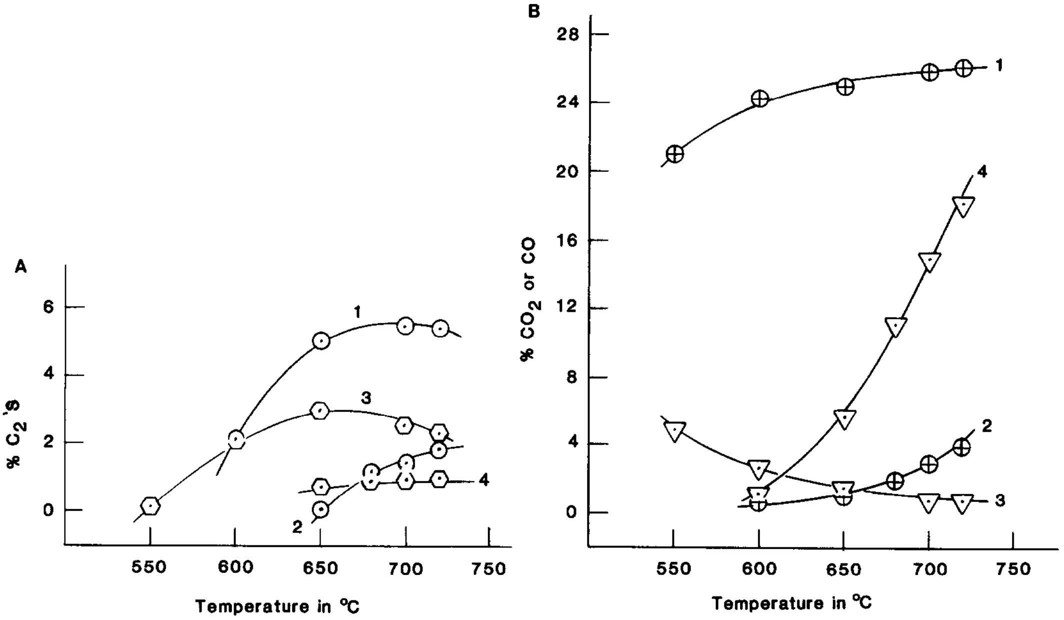

FIG. 2. (A) Composition of exit gas with $CH_4 : O_2 :$ He feed. (1) C_2H_4 formed from a 3% Li on MgO catalyst. (2) C_2H_4 formed in an empty reactor. (3) and (4) C_2H_6 formed under the same conditions as those of (1) and (2). (B) Composition of exit gas with $CH_4 : O_2 :$ He feed. (1) CO_2 formed from 3% Li on MgO catalyst. (2) CO_2 formed in an empty reactor. (3) and (4) CO formed under the same conditions as those of (1) and (2).

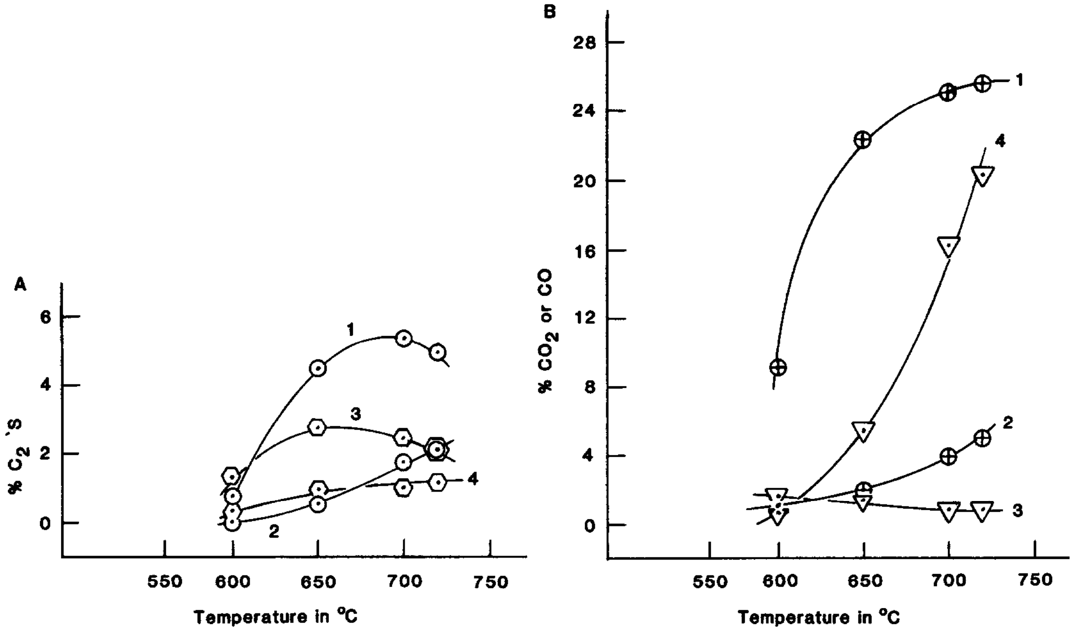

FIG. 3. (A) Composition of exit gas with CH_4 : air feed. (1) C_2H_4 formed from a 3% Li on MgO catalyst. (2) C_2H_4 formed in an empty reactor. (3) and (4) C_2H_6 formed under the same conditions as those of (1) and (2). (B) Composition of exit gas with CH_4 : air feed. (1) CO_2 formed from a 3% Li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

methane proceeds to a considerable extent in a reactor containing no catalyst. This is true both with the methane : oxygen : helium mixtures (Table 1A, Fig. 2) and with methane : air mixtures (Table 1B, Fig. 3). In particular, Table 1A shows that at 720°C the total methane conversion due to thermal reaction was 26.8%. In the presence of pure MgO the conversion was 35.0%, while 3% Li on MgO gave a conversion of 39.2%. These results are in marked contrast with those reported in Ref. (*7*). The authors state that "In the absence of the catalyst, conversion of CH_4 was only 0.2% under the same experimental conditions" (referring to their Table II, where data obtained at 720°C are listed). We are unable to account for this discrepancy. One possible explanation for such a disagreement could well be a difference in reactor configuration which could affect the course of the thermal reactions since some of them, apparently, are radical chain reactions. Unfortunately, no drawing of the reactor or of the reactor position in the furnace was given in the earlier work (*7*, *9*), so a direct comparison is not possible between the two groups of investigators. Nevertheless, as can be seen from Tables 1A and 3A our results with lithium-doped MgO (3% Li) are not very different from those obtained earlier with 7% Li on MgO. This similarity extends to the product distribution and selectivity, as well as to the total methane conversion. Thus, the reasonably good agreement between the present data for a 3% Li on MgO catalyst and earlier data (*7*) reported for a 7% Li on MgO leads one to the conclusion that this similarity should also be found in the absence of a catalyst, as both bodies of work were performed with reactors made from silica, of 1-in. in diameter.

Table 2 presents a compilation of the average data obtained directly from the chromatographic analysis of the exit gas composition over a range of temperatures from

600 to 720°C. In the empty reactor, at 600°C only small amounts of CO and CO_2 were detected. As the temperature increased, the amount of CO in the exit gas increased 18-fold while the amount of CO_2 increased by a factor of less than 6. At 700 and 720°C small amounts of ethylene and ethane were formed, but CO remained the main product of the thermal reaction (see Figs. 2A and 2B). The same trend was found for the methane : air mixtures (see Figs. 3A and 3B).

In the presence of pure MgO, a large increase in the total methane conversion was observed at 550 and 600°C. In addition, a change in the character of the product distribution was recorded. The much higher methane conversion resulted almost entirely in the formation of oxides of carbon, predominantly carbon dioxide. This trend continued at 700 and 720°C, when even less CO was formed relative to CO_2. As far as the formation of C_2's was concerned, small amounts of ethylene and ethane were produced at 650°C, but at 700 and 720°C, the presence of MgO gave only a few more C_2's than the thermal reaction did (Table 2). With Li-doped MgO, a much larger amount of CO_2 was formed at 600 and 650°C, and at all temperatures much less CO was found in the product gas. However, the main effect of the addition of lithium carbonate was the large increase in the amount of C_2's, which will be discussed later.

The data presented in Tables 3A and 3B show that at 700 and 720°C the total methane conversion in the presence of both catalysts is slightly higher than that in the thermal reaction. The product distribution and selectivity are, however, completely different. The major product of homogeneous reaction between methane and oxygen is carbon monoxide (71 to 74% of the total reaction products for both methane : air and methane : oxygen : helium mixtures), with the selectivity toward C_2 formation about 21% and a very low C_2 yield (~5%). In the presence of MgO the major product of the reaction appears to be carbon dioxide (75–79%). It is interesting to note that the selectivity in the reaction catalyzed by MgO is even less than the selectivity in the thermal reaction. It seems that pure MgO is quite an effective catalyst for the oxidation of CO and CH_4 to CO_2, but cannot be considered of any utility in C_2 formation.

Lithium-doped magnesium oxide catalysts show the same oxidation tendency as pure MgO; in fact, they are even more active in the conversion of CO to CO_2. However, the selectivity and yield toward C_2 production both increase significantly in comparison to the thermal reaction or the reaction over pure MgO catalysts, in agreement with earlier work (*7*). The main product of the reaction still remains carbon dioxide. Our results at 720°C are in reasonable agreement with the data reported earlier for a catalyst containing 7% Li on MgO (*7*). It will be seen that conversion, selectivity, and yield are almost the same in both studies, although the catalyst used in this work was somewhat less active and selective than that found earlier. However, our sources of magnesium oxide and lithium carbonate were different and, furthermore, relatively few details were given in the earlier work on catalyst preparation.

In conclusion, as we find, in our system, such an extensive conversion of methane in an empty reactor, it seems to us that the precise function of the catalyst is extremely complex, as both homogeneous and heterogeneous reactions are important. It is also evident from our work that it can be misleading to describe lithium on magnesium oxide as an efficient catalyst for the production of C_2 hydrocarbons. It 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, but at the drastic cost of converting essentially all of the carbon monoxide produced thermally to undesirable carbon dioxide.

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