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The Oxidative Dehydrogenation of Ethane over Chlorine-Promoted Lithium–Magnesium Oxide Catalysts

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The addition of chlorine to a Li^+–MgO catalyst improves considerably the ethylene yield that may be attained during the oxidative dehydrogenation (OXD) of ethane. While operating at 650°C, Li^+–MgO catalysts, produced via a sol-gel method or by adding HCl to an unsintered Li^+–MgO catalyst, promoted a C_2H_6 conversion of 75–79% at a C_2H_4 selectivity of 70% after 50 hr on stream. Even after 250 hr the ethylene yield was 45%. Chlorine was slowly lost from the catalysts as a result of reaction with H_2O, but the evidence indicates that the improved activity and selectivity is largely a result of heterogeneous rather than homogeneous chlorine-promoted reactions. Over the modified catalysts the rate of C_2H_6 conversion was increased relative to the rate of C_2H_4 conversion. The presence of chlorine in the solid significantly decreased the amount of CO_2, a poison for the OXD reaction, that was taken up by the catalyst. Thus, CO_2 formed during the OXD of C_2H_6 may be less effective in poisoning the active centers on a chlorine-modified catalyst. The presence of chlorine also may alter the reactive forms of oxygen on the surface (e.g., O^- ions) so that they are capable of activating the weaker C–H bond in ethane, but are less effective in activating the stronger C–H bond in ethylene. With respect to the oxidative coupling of CH_4, these results demonstrate that at 650°C the primary step, which includes the activation of CH_4 and reactions involving $CH_3\cdot$ radicals, is responsible mainly for the CO_x products, not the subsequent oxidation of C_2H_4 and C_2H_6. This would be the case even at relatively high partial pressures of C_2H_4 and C_2H_6.

INTRODUCTION

The oxidative coupling of methane yields mainly ethane as the primary product while the more desirable product, ethylene, is formed via secondary reactions, which may be oxidative or nonoxidative in nature (*1*). Ideally, one would like to have a catalytic process in which the oxidative dehydrogenation (OXD) of ethane occurs concurrently with the oxidative coupling reaction so that ethylene is the principal hydrocarbon product. Several groups have shown that larger ethylene-to-ethane ratios may be achieved by introducing chlorine into the catalyst or by passing a chlorine-containing compound over the catalyst during the reaction (*2–12*). Although many of the chlorine-containing catalysts initially show considerably improved activity, total C_2 (ethane plus ethylene) selectivity and high ethylene-to-ethane ratios, these advantages are soon lost unless chlorine is continuously added to the system. We have recently found, however, that a Li^+–MgO–Cl^- catalyst, prepared by a sol-gel method, is capable of maintaining a high level of methane conversion and a favorable ethylene-to-ethane ratio for periods in excess of 200 hr on stream (*13*).

The improved ethylene selectivities over the chlorine-containing catalysts suggest that it may be possible to modify a metal oxide so it is capable of activating methane and ethane, but not ethylene. Such a concept is consistent with the C–H bond strength of three types of hydrocarbon molecules. The C–H bond strengths of C_2H_6, CH_4, and C_2H_4 are 98, 104, and >108 kcal mol^{-1}, respectively. Differentiation in conversion of C_2H_6 and C_2H_4 based on C–H bond strength has been demonstrated previously over a Li^+–MgO catalyst (*14*). Although most oxidative coupling catalysts

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for which data is available exhibit hydrocarbon conversion activities that decrease in the order ethane > ethene > methane, Burch and Tsang (*15*) have recently reported that the activities over a LiCl/MnO_x catalyst decrease in the order $C_2H_6 > CH_4 > C_2H_4$, as expected from the C–H bond strengths. In making such a comparison one should realize that the relative reactivities of the three hydrocarbons may not be the same when comparing separate, pure component reactions as it would in competitive reactions. Nevertheless, in principle, based on this analysis it should be possible to achieve C_2 yields that are in excess of the empirical limit of ca. 25%. This assumes, of course, that the reaction is carried out at a sufficiently low temperature so the gas-phase oxidation of ethylene and ethane to CO_x is not a factor; i.e., the catalyst must operate at temperatures lower than about 720°C.

In the research described here we focused on the OXD of ethane over Li^+–MgO–Cl^- catalysts prepared by the sol-gel method and other techniques. Since HCl is evolved from the catalyst during the reaction, the role of chlorine-promoted gas-phase reactions in the production of ethylene was considered in detail. Otsuka *et al.* (*7, 8*) have suggested that these gas-phase reactions play a major role in the OXD reaction; whereas, Burch *et al.* (*2*) have concluded that surface reactions may be more important than gas-phase reactions in the synthesis of C_2H_4 from CH_4 over chlorine-modified oxidative coupling catalysts. The role of chlorine in the catalytic OXD of C_2H_6, as a reaction separate from the oxidative coupling of CH_4, has not been previously addressed.

EXPERIMENTAL

Catalysts. The sol-gel method used to prepare some of the catalysts will be described in detail elsewhere (*17*). Briefly, the method consists of the hydrolysis of a magnesium 3-methyl-1-butoxide which contained lithium nitrate in an ethanol/3-methyl-1-butanol solution. The chlorine was introduced as CCl_4, which is a catalyst for the preparation of the magnesium alkoxide. The white, gel-like material was placed in a vacuum oven and the liquid phase was evaporated, after which the solid was heated in a furnace at 500°C for 5 hr and at 750°C for 16 hr. The catalyst was then pressed, crushed, and sieved to 20–42 mesh and recalcined at 750°C. The catalysts prepared in this manner are designated by the symbol Li^+–MgO–Cl^-(SG).

Another set of catalysts was prepared by aqueous impregnation. Magnesium oxide (70.8 g, Fisher, ACS Certified) was added to stirred solutions that contained $LiNO_3$ and differing amounts of NH_4Cl. The water was evaporated to obtain a thick paste that was dried overnight at 130°C. The resulting solid was then calcined, sieved, and calcined a second time as described above. These catalysts are designated by the symbol Li^+–MgO–Cl^-(*X*) where *X* refers to the chlorine weight percent.

A third type of catalysts was prepared *in situ* in the catalytic reactor (see below) by treating an *uncalcined* Li^+–MgO material in flowing HCl. The uncalcined Li^+–MgO was heated to 350°C for 20 hr in a flow (60 ml min^{-1}) of 1% HCl in He. Subsequently, the solid was heated to 750°C in a gas stream composed of 60 ml min^{-1} 1% HCl/He, 23 ml min^{-1} O_2, and 13 ml min^{-1} He. The catalyst was then cooled to 650°C in the O_2/He flow prior to the addition of the reactant gases. This catalyst is designated as Li^+–MgO–Cl^-(is).

Reactor and analytical system. The catalytic reactions were carried out in high purity alumina tubes (Coors) filled with high purity alumina chips to reduce the homogeneous oxidation of hydrocarbons. The reactor which was 23 cm in length and 2.1 cm i.d. decreased in diameter from 2.8 cm o.d. to 0.7 cm o.d. at the exit. A stainless-steel reactor cap, constructed from a modified Swagelock union tee, accommodated a high purity alumina thermocouple well (Omega) that extended into the catalyst bed. The reactor was heated by a split furnace. The space between the reactor and the furnace was filled with molecular sieve to reduce thermal gradients. The reactor and the alumina chips were routinely washed with HNO_3 when the catalyst was changed.

The gases, ethane (99.0% min), ethylene (99.5% min), oxygen (extra dry), 10% N_2 in He, CO_2 (99.5% min), and 1% HCl in He were obtained from Matheson and were used without further purification. The flow of gases was regulated by mass flow controllers (MKS Model 1159A). The N_2 was used as an internal standard. Products were analyzed using a gas chromatograph (HP 5890A) equipped with a spherocarb column. The reactor was heated to 650°C in a N_2/He flow before admission of ethane and oxygen. All studies were carried out at atmospheric pressure, an ethane pressure of 290 Torr, and a C_2H_6/O_2 ratio of unity. This composition is probably approaching the explosion limit; therefore a similar reaction should not be carried out in a large free volume.

Two cold traps at the reactor outlet were used to remove HCl from the exit gas stream. The chloride concentration in the solution was measured periodically using a chloride test kit (La Motte Chemical). The chloride content of fresh and used catalysts was determined gravimetrically using $AgNO_3$. Inductively coupled plasma (ICP) analysis was used to determine the Li and Mg contents of the catalysts. The surface areas were measured using a Quantasorb Jr. surface area analyzer. The compositions and surface areas of the catalysts are summarized in Table 1.

RESULTS AND DISCUSSION

Catalytic performance. The remarkable ethane conversions and ethylene selectivities that can be achieved over a Li^+–MgO–Cl^-(SG) catalyst are shown in Fig. 1. During the first 25 hr of operation the C_2H_6 conversion remained steady at 79%, while the C_2H_4 selectivity decreased slightly before reaching a steady state at 70%. A C_2H_4 yield in excess of 55% was maintained for 50 hr, and even after 250 hr the yield was 45%. In order to achieve the high conversion levels obtained here it was necessary to use a CH_4/O_2 ratio of unity. To place these results in perspective it should be noted that Kolts (*18*) observed a C_2H_6 conversion of 56% and a C_2H_4 selectivity of 92% after 1 hr over a 0.5 wt% Li^+–MgO catalyst operating at 700°C, but after 16 hr the conversion had decreased to 31%, reducing the C_2H_4 yield from 51 to 30%. Morales and Lunsford (*14*) have reported a

TABLE 1

Physiochemical Characteristics of Catalysts before and after Reaction

Catalyst	Cl Content, (wt%)		Li/Mg[a]		Surface area (m^2g^{-1})	
	Before	After	Before	After	Before	After
Li^+–MgO–Cl^-(SG1)	12.3	1.2	0.19	—	—	1.8
Li^+–MgO–Cl^-(SG2)	17.6	8.0	0.27	0.20	—	1.7
Li^+–MgO–Cl^-(SG3)	—	—	—	0.13	—	1.2
Li^+–MgO–Cl^-(1.9)	1.9	1.6	0.22	0.25	0.9	0.7
Li^+–MgO–Cl^-(8.7)	8.7	5.6	0.21	0.17	0.7	1.6
Li^+–MgO–Cl^-(19.4)	19.4	13.8	0.29	0.25	0.9	0.7
Li^+–MgO–Cl^-(is)	—	7.2	—	0.21	—	1.5
Li^+–MgO	0	0	0.24	0.14	1.0	1.4

[a] Atomic ratio.

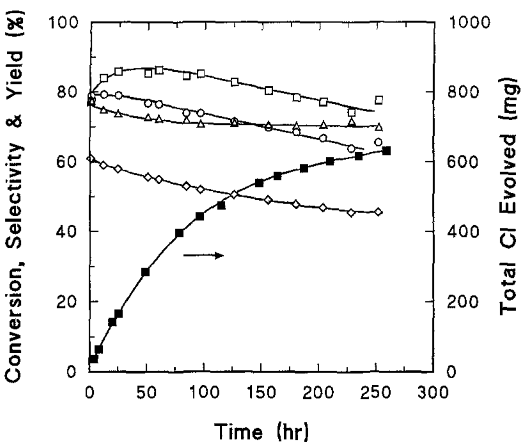

FIG. 1. OXD of ethane over Li$^+$-MgO-Cl$^-$(SG1): T = 650°C, FR = 60 ml min^{-1}, $P(C_2H_6)$ = 290 Torr, C_2H_6/O_2 = 1, M_{cat} = 5.2 g. □, O_2 conversion; ○, C_2H_6 conversion; △, C_2H_6 selectivity; ◇, C_2H_4 yield; ■, integrated amount of Cl released.

maximum yield of 34% over a 3 wt% Li$^+$-MgO catalyst at 650°C, but under oxygen-limiting conditions. Similarly good results were obtained with the other chlorinated Li$^+$-MgO catalysts, as indicated by the data of Table 2, although for the Li$^+$-MgO-Cl$^-$ catalyst the C_2H_4 productivities (space time yields) were not as great as those found over the catalysts prepared by the sol-gel method during times on streams less than 50 hr. The behavior of the Li$^+$-MgO-Cl$^-$(is) catalyst was very similar to the catalysts derived from the sol-gel for periods up to 150 hr on stream. It should be emphasized that it was necessary to add the chlorine via HCl to this catalyst *prior* to sintering.

From the data of Fig. 2 it is evident that the C_2H_4 productivity, over the Li$^+$-MgO catalyst, was less than that obtained over two Li$^+$-MgO-Cl$^-$(SG) catalysts. In order to compare the Li$^+$-MgO and the Li$^+$-MgO-Cl$^-$ catalysts with respect to conversion and selectivity, data were obtained for the Li$^+$-MgO catalyst at steady state at three different flow rates. The data for the Li$^+$-MgO-Cl$^-$ catalysts were obtained after long periods on stream (e.g., 200 hr). The results are summarized in Table 2 and

TABLE 2

Catalytic[a] and HCl-Promoted Homogeneous[b] OXD of Ethane

Catalyst[c]	C_2H_6 Conv. (%)	C_2H_6/Cl[d]	Selectivity (%)				C_2H_4 Yield (%)
			C_2H_4	CO	CH_4	CO_2	
Li$^+$-MgO-Cl$^-$(SG1)	65.4	3200	69.4	3.3	1.3	25.0	45.4
Li$^+$-MgO-Cl$^-$(SG2)	68.0	1400	67.2	1.3	1.6	29.2	45.7
Li$^+$-MgO-Cl$^-$(1.9)	32.9	4900	77.3	4.0	0.0	18.7	25.4
Li$^+$-MgO-Cl$^-$(8.7)	47.1	2500	75.7	1.3	0.7	22.3	35.6
Li$^+$-MgO-Cl$^-$(19.4)	54.6	750	72.0	1.5	1.8	24.7	39.3
Li$^+$-MgO-Cl$^-$(is)	64.4	1400	72.9	1.9	1.1	23.1	46.9
Li$^+$-MgO	30.7	∞	76.7	4.2	0.0	19.1	23.5
Li$^+$-MgO[e]	44.2	∞	73.8	4.1	1.1	21.0	32.6
Li$^+$-MgO[f]	69.2	∞	63.1	5.2	1.7	30.0	43.6
None	14.2	160	79.2	10.6	1.2	5.0	11.6
None	9.5	270	82.0	11.1	0.0	6.3	7.9
None	6.2	330	80.3	12.4	0.0	7.3	5.0
None	4.8	∞	58.9	16.1	0.0	24.8	2.8

[a] Data corresponds to final points in figures.
[b] Activity after 4–5 hr on stream.
[c] T = 650°C, FR = 60 ml min^{-1}, $P(C_2H_6)$ = 290 Torr, C_2H_6/O_2 = 1, M_{cat} = 5.2 g.
[d] Ratio of ethane-to-chlorine evolved from catalyst or added as HCl to gas stream.
[e] FR = 30 ml min^{-1}.
[f] FR = 15 ml min^{-1}.

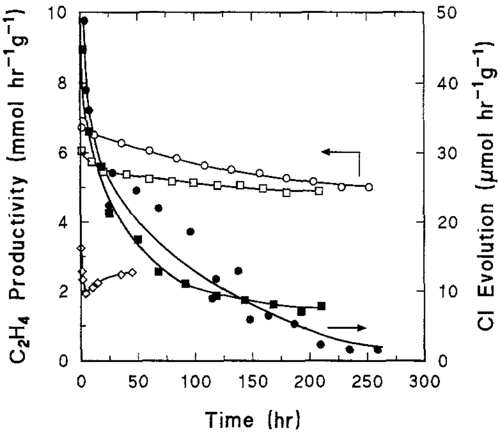

FIG. 2. Ethylene productivity and rate of Cl released during the OXD of ethane over Li^+–MgO–Cl^-(SG1), Li^+–MgO–Cl^-(SG2) and Li^+–MgO: $T = 650°C$, FR = 60 ml min^{-1}, $P(C_2H_6) = 290$ Torr, $C_2H_6/O_2 = 1$, $M_{cat} = 5.2$ g. ○, ●, Li^+–MgO–Cl^-(SG1); □, ■, Li^+–MgO–Cl^-(SG2); ◇, Li^+–MgO.

in Fig. 3, where it is evident that at a given level of conversion the C_2H_4 selectivity over a Li^+–MgO–Cl^- catalyst is greater than over a Li^+–MgO catalyst. These differences in selectivities became greater with increasing conversion, and, at ca. 70% conversion the difference in selectivity over the Li^+–MgO catalyst and a Li^+–MgO–Cl^-(is) catalyst was 10%. At these high levels of conversion and selectivity a difference in selectivity of 10% would be quite significant in a commercial process. For practical reasons it is also important that high partial pressures of ethylene can be achieved.

Catalyst deactivation via the loss of chlorine. All of the chlorine-containing catalysts slowly lost activity with time on stream. Since the materials had been extensively sintered at 750°C prior to carrying out the catalytic reactions at 650°C, it is doubtful that this loss in activity was a result of a decrease in surface area. Within an experimental error of ±0.2 m^2 g^{-1} the surface areas did not decrease, as indicated by the data of Table 1. Rather it seems likely that the loss in activity is a result of the loss of chlorine from the catalyst. For the Li^+–MgO–Cl^-(SG) catalysts this loss of chlorine as a function of time is shown in Figs. 1 and 2. It is apparent from these and other results that the loss in catalytic activity was not linearly related to the loss of chlorine from the catalyst. A close examination of the results of Fig. 1 indicates that the decrease in conversion was approximately linear with respect to time on stream; whereas, the rate of chlorine evolution was much greater at first than after 255 hr. Moreover, during a period of 255 hr the SG1 catalyst lost 90% of its chlorine, yet the ethane conversion decreased only 19%. This comparison indicates that a small percentage of the chlorine in the catalyst may be involved in promoting the activity. Furthermore, as the loss in activity is small after long periods on stream, the modified active sites are presumably stable under the comparatively mild operating conditions used in these experiments. Regeneration of the surface sites by the slow diffusion of chlorine from the bulk may occur during the shorter times on stream. Particularly with the catalysts prepared by the sol-gel method it is reasonable to assume that the chlorine is dispersed throughout the fresh catalyst.

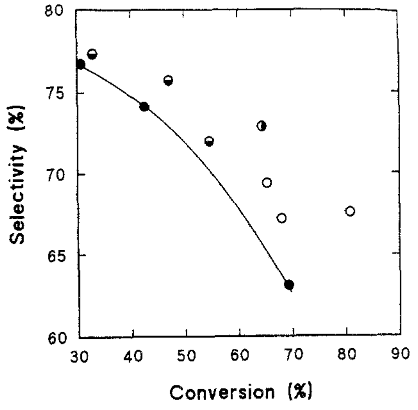

FIG. 3. Relationship between ethane conversion and selectivity to ethylene during the OXD of ethane over Li^+–MgO and chlorinated Li^+–MgO catalysts: ●, Li^+–MgO; ○, Li^+–MgO–Cl^-(SG) catalysts; ⊖, Li^+–MgO–Cl^-(ex. NH_4Cl); ◑, Li^+–MgO–Cl^-(is); data abstracted from Table 2.

Catalysts prepared with low chlorine contents (e.g., 1.9 wt%) exhibited little or no promotional effects, as shown in Table 1. Conversely, the addition of large amounts of chlorine by the reaction of HCl with a *sintered* Li^+–MgO–Cl^-(19.4) catalyst produced a catalyst that was relatively inactive at first, but increased in activity over a period of 50 hr on stream to a level that was consistent with the normal Li^+–MgO–Cl^-(19.4) catalyst (Table 2). For this catalyst the rate of chlorine evolution decreased as the activity increased, which is evidence against the significant involvement of gas-phase chlorine in the OXD reaction (see below). The addition of HCl to a sintered, fresh, or used Li^+–MgO had little promotional effect. These results further confirm the need for Cl^- ions to be uniformly dispersed throughout the catalyst.

The rate of chlorine loss from the Li^+–MgO–Cl^-(19.4) catalyst in the presence of various gases was studied. Helium, ethane, ethylene, oxygen, and carbon dioxide resulted in a chlorine loss of less than 2.8 μmol hr^{-1} g^{-1}. In the presence of moist helium in which the partial pressure of water was similar to that observed under reaction conditions, 15.9 μmol hr^{-1} g^{-1} of chlorine was lost, which may be compared with a loss of 15.2 μmol hr^{-1} g^{-1} during the OXD reaction. These results are in agreement with the findings of Burch and co-workers (*19*), who observed that water reacts with chlorine in a catalyst to produce HCl.

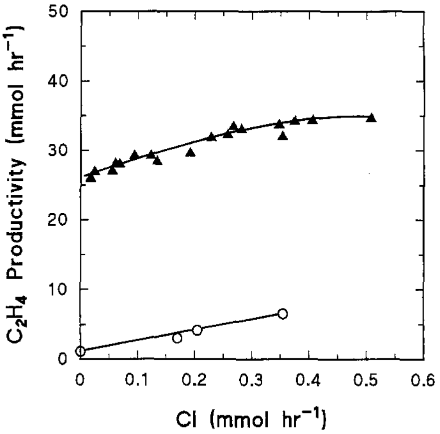

FIG. 4. Relation between ethylene productivity and rate of Cl evolution from Li^+–MgO–Cl^-(SG1), or addition of HCl over alumina chips: T = 650°C, FR = 60 ml min^{-1}, $P(C_2H_6)$ = 290 Torr, C_2H_6/O_2 = 1. ▲, Li^+–MgO–Cl^-(SG1); ○, alumina chips.

The origin of the chlorine effect. As noted in the introduction there is a considerable amount of disagreement in the literature concerning the role of gas-phase reactions involving Cl· atoms as a chain carrier in the OXD of ethane, particularly as the reaction relates to the oxidative coupling of methane. Such gas-phase reactions as

$$C_2H_6 + Cl\cdot \rightarrow C_2H_5\cdot + HCl \qquad (1)$$

and

$$HCl \rightarrow H\cdot + Cl\cdot \qquad (2)$$

are believed to be important, and whether one starts with Cl_2 or HCl the results would be the same because of the rather long chain lengths. The fact that the chlorine-modified catalysts deactivate with the accompanying loss of chlorine has led several researchers to suggest that atomic Cl· catalyzes the homogeneous gas phase OXD of ethane (*2*, *7–9*). Indeed, Burch and coworkers (*2*) have observed that HCl promotes the homogeneous OXD of ethane. In the gas phase over the Li^+–MgO–Cl^- catalysts such reactions also must occur, but the question is whether they occur at a rate which is significant relative to the heterogeneous, chlorine-promoted OXD reaction.

A comparison of the chlorine evolution with the ethylene productivity over two Li^+–MgO–Cl^-(SG) catalysts (Figs. 2 and 3) and the Li^+–MgO–Cl^-(19.4) catalyst treated with HCl, as described above, indicates that the contribution of the gas-phase chain mechanism is minimal. In a global sense there is no correlation between the rate of HCl evolution and C_2H_4 productivity. The relatively insignificant contributions of the gas-phase reactions are further illustrated by the data of Table 2 and Fig. 4. Here, the homogeneous component was determined by replacing the catalysts with alumina chips and by adding HCl in different amounts to the C_2H_6/O_2 mixture. In the absence of HCl the C_2H_4 productivity was quite small, although it should be noted that there was considerable scatter in the data for the homogeneous OXD of ethane. For example, in two runs, over a period of 15 hr the C_2H_6 conversions decreased steadily from 7 to 4% and from 12 to 5%. The C_2H_4 productivity in the gas phase increased linearly with the addition of increasing amounts of HCl. For comparison with the catalytic results, the data of Fig. 2 is replotted to show the C_2H_4 productivity as a function of the rate of chlorine evolution from the catalyst. At all concentrations of chlorine in the gas phase, it is evident that the C_2H_4 productivity was much greater when the Li^+–MgO–Cl^-(SG) catalyst was present. The ratio of the inlet ethane to the chlorine in the gas phase at the time the results were obtained is given for these and other systems in Table 2. It should be noted (i) that these ratios were much larger for the catalytic systems than for the purely homogeneous systems and (ii) that in general there was no correlation between the amount of chlorine present over the catalyst and the ethane conversion.

In order to determine possible synergistic effects between surface-generated gas-phase $C_2H_5\cdot$ radicals (*14*) and HCl in the gas-phase HCl was added to a C_2H_6/O_2 stream over a Li^+–MgO catalyst. This experiment was unsuccessful, however, because the HCl was extensively removed from the gas phase by the catalyst. When dry HCl was added over a prolonged period, and then C_2H_6 and O_2 were introduced, the catalyst was much less active than before the addition of HCl. In the presence of the C_2H_6 and O_2 (as well as water produced during the reaction) HCl was released, but the catalyst failed to regain its activity. Only when the HCl was turned off did the activity increase to the original value and even beyond. Clearly there exists an equilibrium between gas-phase HCl and the catalyst; therefore it is not possible to independently vary the partial pressure of HCl over an active catalyst. It appears unlikely that reactions such as

$$C_2H_5\cdot \rightarrow C_2H_4 + H\cdot \qquad (3)$$

and

$$HCl + H\cdot \rightarrow H_2 + Cl\cdot \qquad (4)$$

would be important because in the presence of O_2 the reaction

$$C_2H_5\cdot + O_2 \rightarrow C_2H_4 + HO_2\cdot \qquad (5)$$

would dominate.

Surface modification by chlorine. Although the positive effect of chlorine on the OXD reaction is not currently understood at the molecular level, it appears that the gross basicity of the catalyst is decreased. This loss in basicity apparently moderates the poisoning of the catalyst by CO_2. Korf *et al.* (*20*) have observed that CO_2 adsorbs strongly on a Li^+–MgO catalyst at 650–760°C and inhibits the oxidative coupling of CH_4. The initial loss in activity of the Li^+–MgO catalyst, prepared from $LiNO_3$, also results from a similar poisoning by CO_2. The loss in activity did not result from a decrease in surface area (Table 1), and it was observed that during the early stages of the reaction all of the product CO_2 was taken up by the catalyst. Pretreatment of a fresh Li^+–MgO catalyst with CO_2 eliminated the initial deactivation, confirming that chemical rather than physical changes were responsible for the deactivation of the unpromoted catalyst.

An experiment was carried out to compare the CO_2 uptake on a catalyst that was modified with chlorine and one that was not modified. The results of Fig. 5 show that the amounts of CO_2 adsorbed and reacted at 650°C on a Li^+–MgO and a Li^+–MgO–Cl^-(19.4) catalyst were very different. The results are expressed as the decrease in partial pressure of CO_2 that occurred as a gas stream flowed over the catalysts. For about 40 min all of the CO_2, which is equivalent to ca. 6.5 mmol, was removed from the gas phase over the Li^+–MgO catalyst. A much smaller amount of CO_2 was removed over the Li^+–MgO–Cl^-(19.4) catalyst. Both cat-

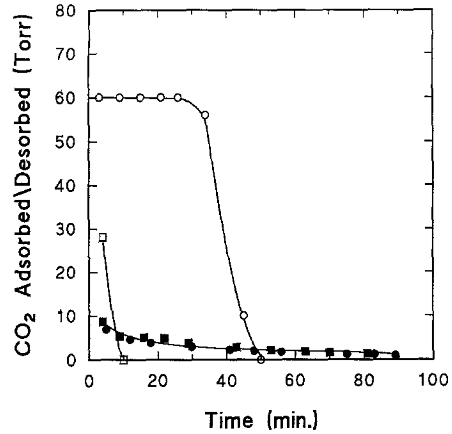

FIG. 5. Adsorption and desorption profiles of CO_2 on fresh Li^+–MgO and Li^+–MgO–Cl^-(19.4): T = 650°C, $P(CO_2)$ in He = 60 Torr, FR = 50 ml min^{-1}, M_{cat} = 5.0 g. ○, CO_2 adsorbed on Li^+–MgO; ●, CO_2 desorbed from Li^+–MgO after CO_2 adsorption; □, CO_2 adsorbed on Li^+–MgO–Cl^- (19.4); ■, CO_2 desorbed from Li^+–MgO–Cl^-(19.6) after CO_2 adsorption.

alysts evolved CO_2 at about the same rate when the gas stream was switched to pure He, and, in fact, the integrated amount of CO_2 that evolved from the Li^+–MgO–Cl^-(19.4) catalyst was comparable to the CO_2 uptake. That is, on this catalyst the CO_2 was reversibly adsorbed. By contrast the amount of CO_2 that desorbed from the Li^+–MgO catalyst in ca. 90 min. was only a small fraction of the amount of CO_2 adsorbed on the catalyst.

The improved activity of the chlorine-modified catalysts can be qualitatively accounted for by the observation that CO_2, a poison for the OXD reaction, is not as strongly adsorbed, but this effect does not address the better selectivities that may be achieved at a given level of conversion (Fig. 3). To attain these improved selectivities at a high conversion level would require (i) that the conversion of C_2H_6 to C_2H_4 be greater than the conversion of C_2H_4 to CO_x and (ii) that the ratio of C_2H_6 conversion-to-C_2H_4 conversion be greater in the chlorine-containing catalysts. The results of Table 3 indicate that such was indeed the case. In this experiment C_2H_6 and C_2H_4 were reacted separately with O_2. Although the conversions of C_2H_6 and C_2H_4 were both small in the absence of a catalyst, the C_2H_4 reacted more rapidly in agreement with other gas-phase studies (*15*). The reactivities of the two hydrocarbons are reversed over the catalysts, and for the chlorine-containing catalyst the ratio of C_2H_6 conversion-to-C_2H_4 conversion was considerably greater for the chlorine-containing catalysts. Had the experiment been carried out under differential conditions the differences in the rates of reaction for C_2H_6 and C_2H_4 would have been even greater. These results suggest that the strength of the C–H bond may indeed be used to differentiate the activation of C_2H_6 and C_2H_4 on these catalysts.

The exact manner in which the chloride ions in the catalyst act to improve the conversion and selectivity remains a matter of conjecture at this point. In the oxidative coupling of CH_4 over alkali chloride–$MnCl_2$ catalysts, Burch *et al.* have suggested that the improved C_2 selectivity results from the formation of a manganese oxychloride surface (*2*). For the Li^+–MgO catalyst it has been suggested that O^- ions on the surface of the catalyst are responsible for the activation of CH_4 and C_2H_6. Ethylene presumably may be activated on these same centers, although this would result in the formation of CO_x. The presence of Cl^- in the catalyst may decrease not only the

TABLE 3

Comparison of Ethane and Ethylene Conversion

Catalyst	C_2H_6 Conv. (%)	C_2H_4 Sel. (%)	C_2H_4 Conv. (%)	C_2H_6 Conv./ C_2H_4 conv.
None	6.0	55.9	7.0	0.86
Li^+–MgO	30.7	76.7	17.5	1.75
Li^+–MgO–Cl^-(is)	55.4	72.0	30.2	1.83
Li^+–MgO–Cl^-(SG3)	83.4	68.1	39.3	2.21

Note. T = 650°C, FR = 60 ml min^{-1}, $P(C_2H_6$ or $C_2H_4)$ = 290 Torr, C_2H_6/O_2 or C_2H_4/O_2 = 1, M_{cat} = 5.2 g.

overall basicity but also the reactivity of the O^- centers so that they do not attack C_2H_4 as easily. This concept is similar to that proposed by Grant and Lambert (*21*) to explain the role of chlorine in improving the selectivity of silver catalysts for the epoxidation of ethylene. According to their model chlorine acts to decrease the charge state of O(a), thus reducing the probability of a proton transfer from ethylene, which ultimately results in the formation of CO_2. On the more ionic MgO surface, we suggest that the O^- centers become $O^{\delta-}$ centers, which are less effective in abstracting hydrogen atoms from a hydrocarbon (i.e., C_2H_4). At the same time the $O^{\delta-}$ centers are less basic and therefore are not as extensively poisoned by CO_2. Thus, the catalytic activity for ethane OXD is greater.

CONCLUSIONS

The addition of chlorine to Li^+–MgO catalysts using several techniques improves both the activity and the selectivity in the OXD of ethane. Preparation of a catalyst via a sol-gel method yields a catalyst with the best performance, presumably because chloride ions are uniformly distributed throughout the material. Although water produced during the reaction promotes the loss of chlorine from the catalyst, the chlorine-catalyzed gas-phase dehydrogenation of C_2H_6 occurs at a rate that is small compared to the rate of C_2H_6 dehydrogenation on the catalytic surface. The presence of chlorine in the catalyst significantly decreases the uptake of CO_2, which is a poison for the OXD reaction. The chlorine may improve the activity of the catalyst by stabilizing the active sites with respect to poisoning by CO_2. In addition, the chlorine may reduce the charge on the O^- centers so that they are less reactive and do not attack C_2H_4 as readily.

These results suggest that it may be possible to fine tune an oxidative coupling catalyst so that it is able to activate methane and ethane, but not the desired product, ethylene. The results also confirm that if a catalyst can be operated at temperatures as low as 650°C, high partial pressures of ethylene can be achieved, even in the presence of excess O_2. Thus, in the oxidative coupling of methane the constraints on selectivity at this temperature are determined by the primary reaction, i.e., the reaction of methane, and not by the secondary reactions of ethane and ethylene, either on the surface or in the gas phase. Similar conclusions have recently been reached by Nelson and Cant (*22*), based on competitive reaction using labeled hydrocarbons.

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