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Effect of carbon dioxide on the selectivities obtained during the partial oxidation of methane and ethane over Li^+/MgO catalysts

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At $T \leqslant 650°C$ carbon dioxide either formed during reaction or added to the system increases the selectivity for the desired hydrocarbon products during the oxidative coupling of methane and the oxidative dehydrogenation of ethane reaction over Li^+/MgO catalysts. Similarly, CO_2 inhibits secondary reactions of $CH_3\cdot$ radicals with the surface of the Li^+/MgO. The improved selectivities are attributed to the poisoning effect that CO_2 has on the secondary reactions of alkyl radicals with the surface.

Keywords: Methane oxidation; ethane oxidation; methyl radicals; lithium/magnesium oxide; carbon dioxide effects

1. Introduction

The origin of CO_2 and its effect on Li^+/MgO as a catalyst for the oxidative coupling of methane has been the subject of several investigations [1–4]. Carbon dioxide is recognized as (i) a poison for the coupling reaction [3,4], (ii) it increases the activation energy for the conversion of CH_4 [4] and (iii) it stabilizes Li^+ in the catalyst by preventing the formation of volatile Li(OH) [3]. We now demonstrate that CO_2 has a fourth effect on the oxidative coupling reaction at intermediate temperatures; namely, it results in improved selectivity to C_2H_4 and C_2H_6 (C_2 compounds). The enhanced C_2 selectivity is achieved both by decreasing secondary reactions between $CH_3\cdot$ radicals and the surface, and by improving the selectivity for the oxidative dehydrogenation (OXD) of ethane. The latter effect may also be a result of inhibiting the reactions between radicals (in this case $C_2H_5\cdot$) and the surface.

2. Experimental

Most of the results reported here were obtained using a Li^+/MgO catalyst that contained 4 wt% Li; however, one catalyst contained 0.47 wt% Li. The catalysts were prepared by evaporating to dryness an aqueous slurry that contained the appropriate amount of Li_2CO_3 and MgO. The resulting material was calcined in air at 750°C for 16 h.

The conventional catalytic reactions were carried out in a 6.5 mm i.d. alumina reactor. The reactor was filled with fused-quartz chips above and below the catalyst bed in order to minimize homogeneous reactions. For the oxidative coupling reaction, CH_4, O_2 and He partial pressures of 200, 100 and 460 Torr, respectively, were used; for the OXD of ethane, the C_2H_6, O_2 and He partial pressures were 290, 290 and 180 Torr, respectively. All results were obtained under steady state conditions, usually after the catalysts had been on stream for >5 h. The maximum conversion of the limiting reagent was $<20\%$.

A matrix isolation electron spin resonance (MIESR) system was used to follow the secondary reactions between $CH_3\cdot$ radicals and the 4 wt% Li^+/MgO catalyst [2,5]. Samarium oxide was used as the radical generator because it is only moderately affected by CO_2 (see below). The $CH_3\cdot$ radicals produced by the reaction of CH_4 and O_2 over 0.15 g of Sm_2O_3 subsequently reacted with the 0.10 g of Li^+/MgO catalyst. Those radicals that did not react were trapped in an Ar matrix at 15 K and were analyzed by ESR spectroscopy. The total pressure in the region of the catalysts was 2.6 Torr, and the temperature was 650°C. The oxides were treated in flowing O_2 (70 ml min^{-1}) at 688°C for 30 min. After evacuating the system for 10 min, a mixture of reactants ($Ar/CH_4/O_2 = 3.8/1.1/0.05$ ml min^{-1}) was allowed to flow over the oxides at 650°C for 16 h before the first radical collection commenced. Subsequently CO_2 was added to the reactant mixture and the amount of Ar was reduced proportionally.

3. Results and discussion

The effect of CO_2 on selectivity, at a constant level of hydrocarbon conversion is most clearly evident from the results of table 1. It should be noted that with only quartz chips in the reactor the CH_4 and C_2H_6 conversions were 0.02 and 0.4%, respectively, under the conditions indicated in the table. The amount of catalyst was adjusted between experiments in order to attain nearly equivalent levels of CH_4 and C_2H_6 conversion. The addition of 23 Torr CO_2 resulted in an increase in C_2 selectivity during CH_4 oxidation from 44.6 to 64.0%. This observation provides an explanation for the improved C_2 selectivity that is often found when the results obtained with an integral reactor are compared with those obtained in a differential reactor. The addition of CO_2 produced a similar increase in selectivity to C_2H_4 during the OXD of ethane. The selectivity increased from 72.0 to 83.8%.

Table 1

Effect of CO_2 poisoning on selectivity during the partial oxidation of methane and ethane over Li^+/MgO catalyst

Hydrocarbon	Amount of catalyst (g)	CO_2 added (Torr)	Conv. (%)	Selectivity (%)			
				C_2H_6	C_2H_4	CO	CO_2
CH_4 [a]	0.1	0.0 (4.3)[b]	5.3	38.5	6.1	14.5	40.9
CH_4	0.5	0.0 (8.7)	11.2	45.0	11.2	4.9	39.0
CH_4	0.5	23.1 (2.5)	5.2	58.7	5.3	11.5	24.5
C_2H_6 [c]	0.05	0.0 (6.0)	5.6		72.0	9.0	19.0
C_2H_6	0.20	0.0 (13.5)	12.9		75.0	7.0	18.0
C_2H_6	0.20	17.8 (2.5)	5.3		83.8	7.9	8.3

[a] Li content = 4 wt%, $P(CH_4)P(O_2) = 200/100$ (Torr), total flow rate = 80 ml/min, $T = 650°C$.

[b] Numbers in parentheses are the amounts of CO_2 produced via the reaction, in Torr.

[c] Li content = 4 wt%, $P(C_2H_6)/P(O_2) = 290/290$ (Torr), total flow rate 60 ml/min, $T = 650°C$.

The effect of CO_2 on selectivity during the oxidation of CH_4 and C_2H_6 is further compared in fig. 1. Again the conditions were adjusted such that the conversions of the two hydrocarbons were approximately the same. The very similar effects of CO_2 in poisoning the CH_4 and C_2H_6 conversion and in improving the selectivities for

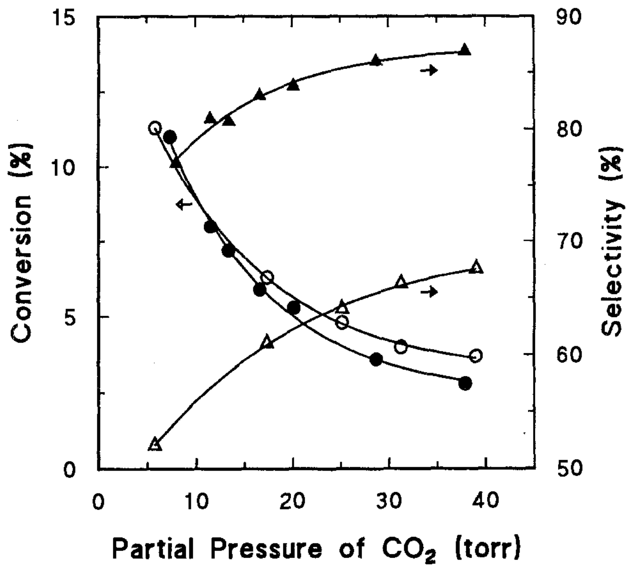

Fig. 1. Effect of CO_2 poisoning on the oxidative coupling of CH_4 and the oxidative dehydrogenation of C_2H_6 over a 4 wt% Li^+/MgO catalyst: (○) CH_4 conversion; (●) C_2H_6 conversion; (△) C_2 selectivity from CH_4; (▲) C_2H_4 selectivity from C_2H_6. Reaction conditions: $T = 650°C$, $P(CH_4)/P(O_2) = 200/100$ (Torr), $P(C_2H_6)/P(O_2) = 290/290$ (Torr); in the coupling reaction 0.50 g of catalyst was used and FR was 80 ml min^{-1}, in the OXD reaction 0.20 g of catalyst was used and FR was 60 ml min^{-1}.

the desired hydrocarbon products suggest that the activation of CH_4 and C_2H_6 occurs on a common site, and that the nonselective pathways involve a common type of intermediate. The intermediates are believed to be alkyl radicals (see below).

A collection of selectivity data for the OXD of ethane, obtained over a range of temperatures, is shown in fig. 2. No attempt was made to maintain a constant conversion during these experiments; the conversion levels varied from 0.5 to 20% (ratios of C_2H_6/O_2 varied from 10/1 to 1/15). Nevertheless, the selectivities fall reasonably well on a common curve, regardless of whether CO_2 was purposely added to the system or produced in the reaction. From the results of fig. 2 it is evident that CO_2 can have a more dramatic effect on C_2H_4 selectivity if the amount of CO_2 produced during the reaction is <5 Torr at $T<600$°C. A TPD study of the Li^+/MgO catalyst revealed a maximum in the desorption of CO_2 at about 620°C, that is associated with the conversion of active centers into CO_3^{2-} ions [4]. The selectivity in fig. 2 increased up to a CO_2 level of about 10 Torr, and then failed to increase further.

The results of the MIESR experiments, summarized in table 2, provide insight into the mechanism by which CO_2 improves selectivity. As demonstrated previously by Marcelin and coworkers [6], methane conversion over Li^+/MgO decreased dramatically with the addition of CO_2; however, CO_2 had less effect on methane conversion over Sm_2O_3. Similarly we have shown the CO_2 is a strong poison for $CH_3\cdot$ radical generation over Li^+/MgO [4], but by contrast, as shown in table 2, $CH_3\cdot$ radical formation over Sm_2O_3 is affected much less by CO_2.

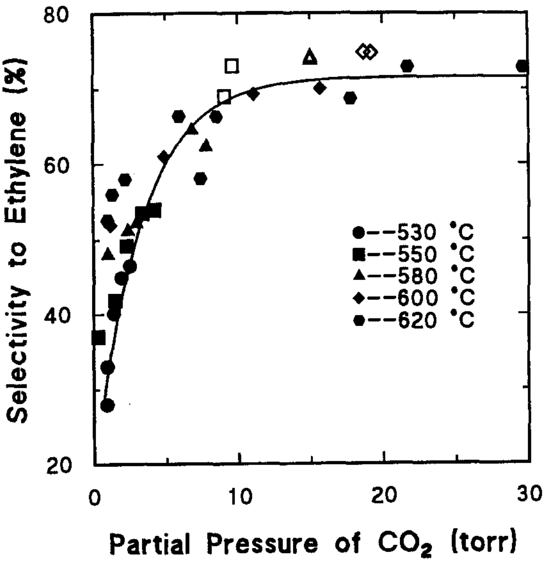

Fig. 2. Effect of CO_2 poisoning on the C_2H_4 selectivities obtained during the OXD of C_2H_6 over 0.47 wt% Li^+/MgO: solid symbols, CO_2 only produced during the reaction; open symbols, sum of CO_2 produced and that which was purposely added.

Table 2
Effect of CO_2 on methyl radical formation and surface reactions

$P(CO_2)$ (Torr)	Collection rate of radicals (a.u.)			$CH_3\cdot$ radical reacted over Li^+/MgO (%)
	Sm_2O_3|QC[a]	QC|Li^+/MgO	Sm_2O_3|Li^+/MgO	
0	15	21	26	67
0.26	11	1.9	13	~ 0
2.1	9	0.6	10	~ 0

[a] QC refers to fused-quartz chips.

In the MIESR experiment the conversion of CH_4 is small, and consequently the partial pressure of CO_2 produced during reaction is negligible. The amounts of $CH_3\cdot$ produced over the two catalysts should be additive, *provided* no $CH_3\cdot$ radicals react with the Li^+/MgO catalyst. Thus, one might expect a radical collection rate of 36 (in arbitrary units) when both Sm_2O_3 and Li^+/MgO were present; whereas the collection rate was only 26. The decrease is not caused by the reaction of a substantial amount of O_2 over Sm_2O_3, as we have shown in a separate experiment that only a small percentage of the O_2 was consumed at these low pressures. Rather, the difference is believed to be a measure of the rate of radical reaction with the Li^+/MgO. That is, 67% of the radicals produced over Sm_2O_3 must have reacted with the Li^+/MgO ($(15 + 21 - 26)/15 = 67\%$). But when CO_2 was added to the system, even at a level of only 0.26 Torr, all of the radicals produced by the Sm_2O_3 survived collisions with the Li^+/MgO and were collected. The Li^+/MgO catalyst in the MIESR system obviously appears to be much more sensitive to small amounts of CO_2 than in the conventional catalytic reactor, but one should recall that the mole fraction of CO_2 in the MIESR system is much greater than in the conventional reactor.

To observe the intrinsic activity and selectivity of a catalyst that is not significantly influenced by CO_2 poisoning, one would have to work at very high space velocities or at low partial pressures of reagents. Amorebieta and Colussi [7] studied CH_4 oxidation over Li^+/MgO in the 1–100 mTorr range, but they were primarily interested in the kinetics of the reaction and did not provide quantitative information on the selectivity. We have found that the reaction of 0.8 Torr each of CH_4 and O_2 over 4 wt% Li^+/MgO at 700°C yielded a C_2 selectivity of only 20% at a CH_4 conversion of 4.8%. Thus, in the absence of a significant level of CO_2 the C_2 selectivity was very poor.

The observation that CO_2 inhibits the reaction of $CH_3\cdot$ radicals with active centers on the surface of Li^+/MgO suggests that the improved C_2 selectivity during the oxidative coupling reaction may be due to this same effect. That is, the probability of coupling of $CH_3\cdot$ radicals would be enhanced relative to the probability of reaction with the surface to yield CO_2 via methoxide ions [8]. An analogous argument could be made with respect to $C_2H_5\cdot$ radicals, only in this case the reaction

$$C_2H_5\cdot + O_2 \rightarrow C_2H_4 + HO_2\cdot \qquad (1)$$

is the favorable reaction, rather than radical coupling.

Finally, a comment should be made concerning the effect of CO_2 on selectivity at higher temperatures. At reaction temperatures of 780–800°C Korf et al. [3] found that CO_2 had no effect on C_2 selectivity, but in their experiment the selectivity already was quite high (78%). Moreover, at these temperatures the homogeneous oxidation of C_2H_4 and C_2H_6 becomes a dominant source of CO_2 [9], therefore surface phenomena, including secondary reactions of alkyl radicals, become less important. But even at these elevated temperatures CO_2 has a negative effect on conversion, which indicates that the primary radical forming reactions still occur at the surface.

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