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LETTER TO THE EDITOR AND AUTHORS' REPLY

LETTER TO THE EDITOR

M. BAERNS

Ruhr-University Bochum, Chair of Chemical Technology and Chemical Reaction Engineering
POB 10 21 48, D-4630 Bochum, Fed. Rep. Germany

Reference is made to a recent article by R. Burch et al., Catal. Lett. 2 (1989) 249–256, on "The Importance of Heterogeneous and Homogeneous Reactions in Oxidative Coupling of Methane over Chloride Promoted Oxide Catalysts". The authors have concluded that ethylene formation is not affected by methyl chloride which may be present in the oxidative coupling reaction when chloride containing catalysts are used. They base their conclusion on experiments obtained in the absence and in the presence of a $LiCl/MnO_2$ catalyst. Unfortunately, the catalytic results are not fully conclusive for the following reasons:

(1) No evidence is presented that the selectivities shown in fig. 1 are real and not possibly disguised by carbonate formation, i.e. CO_2 consumption, with the solid surface (eq. (1)) which may contain Li_2O formed by reaction of LiCl with H_2O produced by the oxidative coupling reaction (eqs. (2) and (3)).

$$Li_2O + CO_2 \rightarrow Li_2CO_3 \tag{1}$$

$$LiCl + H_2O \rightarrow LiOH + HCl \tag{2}$$

$$2LiOH \rightarrow Li_2O + H_2O \tag{3}$$

Can the authors rule out this route of HCl formation which they have not mentioned in their scheme?

(2) The relationship between selectivity and time of operation (fig. 1) is rather meaningless unless the degree of methane conversion is specified. A much more informative plot would be the dependence of the concentrations of the various products on time of operation from which the steady-state or nonsteady-state behavior of the catalyst with respect to a rather likely carbonate formation could be derived. From the selectivity data presented it appears that the sum of the individual compounds has been set equal to 100% neglecting possible CO_2 consumption by carbonate formation (cp. (1)) and that the degree of methane conversion has not been measured but derived from the sum of the products.

From fig. 1 the authors conclude that the catalyst deactivated. This statement should be substantiated by the degree of conversion (cp. above) and not only by the loss of chlorine containing compounds; the change in selectivity with increasing time of operation might be due to a changing degree of methane conversion.

It would be greatly appreciated if the authors would reply to the above comments.

M. BAERNS
BOCHUM
16 August 1989

AUTHORS' REPLY

R. BURCH, E.M. CRABB, G.D. SQUIRE and S.C. TSANG

Catalysis Research Group, Chemistry Department, University of reading Whiteknights, P.O. Box 224, Reading RG6 2AD, U.K.

Professor Baerns [1] has raised some interesting questions concerning our previous letter [2]. We should like to make the following remarks in reply.

(1) Carbonate formation

Baerns questions whether our selectivity data are reliable because of the possible formation of Li carbonate. We can confirm that this is not the case because the carbon balances were good. The method of analysis which we used allowed all the carbon-containing products and the reactant methane to be determined quantitatively. Throughout the experiments described in our Letter [2] the carbon balances agreed within 2%, and usually within 1%. At the methane conversions observed ($< 10\%$) this would represent a *maximum* error in the C_2 selectivity of 10% and a more typical error of $< 5\%$. This is not sufficient to significantly alter our conclusions concerning the total C_2 selectivities, and, of course, could not in any case alter the C_2H_4/C_2H_6 ratio.

(2) Possible routes to HCl

Baerns asks whether we can rule out the formation of HCl by the hydrolysis of LiCl. We do not rule out this possibility. In fact, we expect the HCl to come from the hydrolysis of chloride compounds on the catalyst as we have suggested elsewhere [3]. The LiOH thus produced would be expected to slowly convert to $Li_2(CO)_3$ as Baerns suggests. However, the carbon balance mentioned above suggests that this is a slow process. We suspect that this is because the LiCl is only slowly hydrolysed under reaction conditions. The rate of loss of chlorine supports this contention. Thus, the *maximum* concentration of $HCl + CH_3Cl$ measured during our experiments was 100 ppm. Under our conditions this corresponds to a loss of only about 2% of the chlorine on the catalyst as HCl and

CH_3Cl during the course of the whole experiment. Assuming that hydrolysis of LiCl is a necessary first step in the formation of $Li_2(CO_3)$ we would not expect carbonate formation to be a serious problem.

(3) Correlation between conversion and time of operation

Baerns suggests that the relationship between selectivity and time of operation is rather meaningless unless the degree of conversion of methane is specified. This is a fair point so we now provide in table 1 information concerning the methane conversion as a function of time of operation. (The activity and selectivity were essentially independent of time of operation for the first 2 h.) As indicated above, we have determined the methane conversion by analysing the amount of methane present in the effluent stream and comparing this with the amount of methane in the reactant stream at the beginning of the experiment. Table 1 shows that the catalyst deactivated during the course of the experiment as stated in our original Letter.

Baerns raises the question whether the selectivity observed could be due to changes in the methane conversion. This is a valid question and there is no doubt that the overall selectivity in the methane coupling reaction can be affected by the methane conversion. However, we do not believe this is an important factor in the present work even though the catalyst is losing activity. Our reasons are as follows.

Table 1 shows that as the catalyst ages the selectivity for the formation of CO_2 increases at the expense of C_2H_4. This we attribute to the loss of LiCl from the catalyst with the result that some total oxidation sites on the MnO_x become exposed. However, even if all the additional CO_2 is assumed to come from oxidation of C_2H_4 the fact is that less C_2H_4 is produced with the aged catalyst than with the fresh catalyst. Since with the aged catalyst there is substantially

Table 1
Conversion and selectivity data for the methane coupling reaction over a $LiCl/MnO_x$ catalyst [a]

Time (min)	Conv (%)	Selectivity (%)				
		CO	CO_2	C_2H_4	C_2H_6	C_2H_4/C_2H_6
120	8.99	1.8	8.8	43.2	46.1	0.94
133	8.32	2.3	9.9	41.5	46.3	0.90
142	7.84	2.4	11.1	38.6	47.8	0.81
149	6.96	2.6	12.7	35.7	48.9	0.73
156	6.70	2.6	13.0	31.8	52.6	0.60
163	5.45	2.8	15.1	29.8	52.3	0.57
174	4.41	2.9	17.9	24.2	55.1	0.44
183	3.89	2.7	19.6	21.2	56.5	0.37
200	3.22	2.7	22.1	16.3	58.8	0.28

[a] temperature = 750 ° C; $CH_4:O_2:N_2 = 20:1:19$; pressure = 1 bar; 0.1 g catalyst; total gas flow = 60 $cm^3 min^{-1}$.

more O_2 in the gas phase, and since O_2 is effective in dehydrogenating C_2H_6 to C_2H_4 in the gas phase under reaction conditions, we would expect to see *more* C_2H_4 rather than less produced over the aged catalyst. The fact that the C_2H_4/C_2H_6 ratio decreases monotonically as the concentration of evolved chlorine-containing gases decreases, strongly suggests to us a correlation between ethene selectivity and the presence of chlorine-containing compounds in the gas phase.

As discussed in our original Letter we believe that chlorine radical reactions are important in determining the C_2H_4 selectivity. However, these chlorine radicals do not come from CH_3Cl, nor to any great extent from HCl, via purely gas phase dissociation reactions. The rate of decomposition of CH_3Cl or HCl is much to slow to be a significant source of Cl radicals.

It is apparent that gas phase radical reactions involving chlorine are only important under our experimental conditions within the confines of the catalyst bed which suggests that the catalyst is somehow involved in generating the chlorine radicals. This could occur if chlorine radicals simply desorb into the gas phase. However, this seems unlikely given the strength of a typical alkali metal-chlorine bond. An alternative possibility is that methyl radicals released from the catalyst surface interact with HCl in the gas phase just above the surface to give CH_4 and a chlorine radical.

In conclusion, we believe that our results are not invalidated because of carbonate formation. Furthermore, we reiterate that ethylene is not produced from ethane via purely gas phase reactions involving methyl chloride, but may be produced by chlorine radical reactions occurring within the catalyst bed. The source of the chlorine radicals may be HCl produced by hydrolysis of a metal chloride, but the generation of chlorine radicals from HCl seems to require the action of another radical in the gas phase close to the surface of the catalyst [3].

References

[1] M. Baerns, preceding Letter to the Editor.
[2] R. Burch, E.M. Crabb, G.D. Squire and S.C. Tsang, Cat. Lett. 2 (1989) 249.
[3] R. Burch, A.A. Dost, D.A. Rice, S.C. Tsang and G. Webb, Cat. Lett. 3 (1989) 331.

R. BURCH et al.
READING
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