Importance of the Specific Surface Area of the Catalyst in Oxidative Dimerization of Methane over Promoted Magnesium Oxide

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A low specific surface area was found to be the key factor for catalytic conversion of methane into ethane and ethylene over various metal-doped MgO catalysts, a result which could be important for other catalyst systems.

Various materials such as M(O)/Al_2O_3 [M(O) = metal oxide],[1] PbO/Al_2O_3,[2] Li^+–MgO,[3] Na^+–MgO,[4] Sm_2O_3,[5] $LaAlO_3$,[6] La_2O_3,[7] Li^+–Sm_2O_3,[8] LiCl/M(O) [M(O) = transition metal oxide],[9] $BaCO_3$, and $SrCO_3$[10] have been reported to be effective catalysts for the oxidative dimerization of methane. However, the role of the catalysts has not been studied extensively. Since methyl radicals have been observed,[3] active catalysts should be capable of bearing radical centres under the reaction conditions. Although this factor is essential, it is difficult to explain the effectiveness of such a variety of catalyst materials by a single factor alone. Although we have recently commented that the specific surface area is an important factor in this reaction over the Na^+–MgO system, the data are restricted.[4] We have thus measured the surface areas of a variety of doped MgO catalysts and found a good correlation between the surface area and the yield of C_2 compounds. This suggests that surface morphology is important for the title reaction.

Reactions were performed in a conventional flow reactor (8 mm o.d.) at 673—1073 K, and CH_4, air, and He flow rates of 1.5 ml min^{-1} (4.02 mmol h^{-1}), 3.75 ml min^{-1}, and 50 ml min^{-1} respectively. The CH_4/O_2 ratio was 2 ($2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$). Only a trace of products (0.06% yield of CO_2 and 0.03% yield of C_2 compounds) was observed in a blank run at 1023 K. Metal nitrates were added to MgO (Soekawa Chemical Co.) in water, then the samples were dried, pelletted, and weighed. Samples (2 g) were evacuated or heated in a He flow at 773 K for 1 h and at 1073 K for 2 h and used for the reactions. Some samples mounted in crucibles made of MgO were calcined at 1273 K for 2 h in a separate oven. The surface area was measured after the heat treatment by the Brunauer–Emmett–Teller (B.E.T.) method using N_2 adsorption at 77 K.

C_2 compounds (C_2H_6 and C_2H_4) were produced above 873 K and yields increased at 1023 or 1073 K over most catalysts. CO_2 was obtained with nearly constant yield (23 ± 5%) over all the catalysts at 1023 K. C_2 yields ranged from 0 to 20%, while the ethylene selectivity in the C_2 compounds was almost constant (50—70%) at 1023 K. Figure 1 shows the relationship between the surface area and yield of C_2 compounds at 1023 K. In general, the catalysts with smaller surface area are more effective for C_2 formation. This applies in particular for the alkali metal-doped MgO irrespective of the kind or amount of additive. The effect of doping on the specific surface area is interesting. As apparent from Figure 1, the area increased from 70 (no doping) to about 200 $m^2 g^{-1}$ (●) on doping with 0.2% of metal ions. However, on further increase in the extent of doping, the surface area decreases, as pointed out by others.[11] We can present the effects of doping in an alternative way by comparing samples having constant surface area (Figure 2). Although alkali metals are effective, their effectiveness is not unusual. Transition metals (Groups 5A, 6A, 7A, 8, and 1B) have a less significant effect on C_2 formation. Comparing catalysts doped with the same element, those with a higher content of additives had lower surface areas and led to higher C_2 yields. A similar trend is apparent for samples with the same composition but calcined at different temperatures. The surface area of pure MgO decreased from 70 to 17 $m^2 g^{-1}$ on calcination at 1273 K for 2 h, and the C_2 yield increased correspondingly from 4.4 to 9.0%. The C_2 selectivity also increased from 11.7 to 26.1%. The effects of such sintering are summarized in Table 1. Since MgO doped with alkali metals is more effective than pure MgO of the same surface area, alkali metal addition is important in increasing radical centres.[3,4] However, the specific surface area seems to be the most important factor in improving C_2 yields, as shown by Figure 1. Addition of alkali metal also has an important effect in decreasing the surface area.

The rate of methyl radical formation should be higher over catalysts with high surface area, but the rate of radical collision

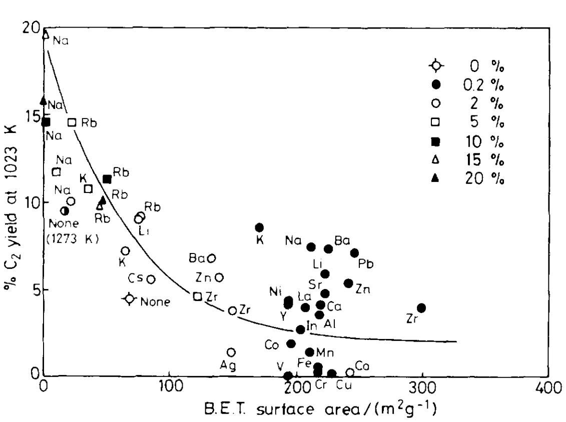

Figure 1. C_2 yield (C_2H_4 + C_2H_6) over various metal doped MgO catalysts at 1023 K as a function of the specific surface area, the different symbols indicating different extents of doping.

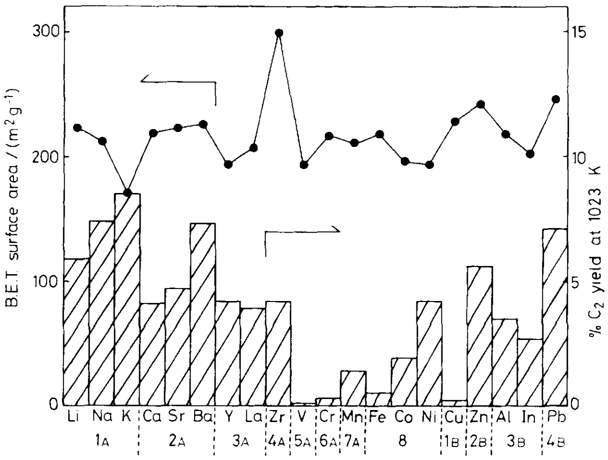

Figure 2. Effect of added metal element on C_2 yield at 1023 K (right ordinate) for 0.2% metal doped MgO. The specific surface area is shown on the left ordinate.

Table 1. Effect of sintering.

Sample (2 g)	Calcining temp./K	Surface area/ ($m^2 g^{-1}$)	C_2 select.[a] 1023 K (%)	C_2 yield[b] at 1023 K (%)
MgO	1073	70	11.7	4.4
	1273	17	26.1	9.0
0.2% Na^+–MgO	1073	212	22.2	7.4
	1273	7	30.0	9.8
2% K^+–MgO	1073	66	26.6[c]	8.3[c]
	1273	10	35.7[c]	13.2[c]
2% Cs^+–MgO	1073	85	14.9	5.6
	1273	7	30.1	8.2

[a] Select. = (2 × moles C_2 hydrocarbons produced)/(moles CH_4 reacted). [b] Yield = (2 × moles C_2 hydrocarbons produced)/(moles CH_4 in the feed). [c] Reaction data at 1073 K.

with the surface and the rate of CO_2 production (complete oxidation) should be also higher. Thus, there should be an optimum surface area of the catalyst for maximum probability of radical coupling. In the case of the MgO systems, the optimum area would be below 20 $m^2 g^{-1}$.

In the partial oxidation of ethylene over silver catalysts, supports with small surface area are reported to be effective for formation of ethylene oxide,[12] although the detailed mechanism of this reaction might be different from that for MgO systems. In the case of oxidation of methane, the methyl radical is formed on the *surface* and the radicals are considered to combine in the *gas phase*.[3] Thus, the morphological structure of the surface should be important. In this sense the title reaction may be termed a structure-sensitive reaction.

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