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Oxidative Dimerization of Methane over Promoted Magnesium Oxide Catalysts. Important Factors

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Various metal doped MgO samples were examined as catalysts for the conversion of methane to ethane and ethylene. Of these, 15 mol% Na^+-MgO was found to show the highest C_2 hydrocarbon yield (22.4%) with a C_2 selectivity of 57% at 1073 K at a CH_4/O_2 ratio of 2.0.

The title reaction has been studied over various oxides.[1-8] It has been reported previously that CH_4 and O_2 are converted to C_2 hydrocarbons (C_2H_4 and C_2H_6) with the high yield of 19.4% over 7 wt% Li^+-promoted MgO, and that the activity is related to the concentration of $[Li^+O^-]$ centers.[3, 4] We have now extended this work to various metal-doped MgO catalysts in order to study the role of the additives.

The reaction was performed by using a conventional flow reactor (8 mm o. d.) at temperatures between 673 to 1073 K. CH_4, air, and He were charged with 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 2.0 ($2CH_4 + O_2 = C_2H_4 + 2H_2O$). Metal nitrates were added to MgO (Soekawa Chemical Co.) in water; then the samples were dried, pelletted and weighed. Typically 2 g of sample was evacuated or treated in He at 773 K for 1 h and then at 1073 K for 2 h and used for the reaction.

Between 673 and 873 K, with most of the catalysts CO_2 was the major product, accompanied by small amounts of CO as a by-product. Above 873 K, the CO_2 yield did not increase appreciably. We express the activity of catalyst toward CO_2 production as the temperature where 50% of O_2 was converted. These values are shown as the abscissa in Fig. 1. On the other hand C_2H_6 and C_2H_4 are formed above 873 K, and their yields increase up to 1023 or 1073 K. It seems that CO_2

production and oxidative dimerization occur by different reaction paths, because the former occurs at lower temperature than the temperature at which the latter occurs. The percentage of C_2H_4 among the C_2 compounds is 50 to 70% for most of the catalysts. The activity of the title reaction was expressed as the % yield of C_2 hydrocarbons (2 x moles C_2 hydrocarbons produced /moles CH_4 in the feed) and is shown as the ordinate in Fig. 1. Generally a catalyst which is not active for the complete oxidation is active for the C_2 formation.

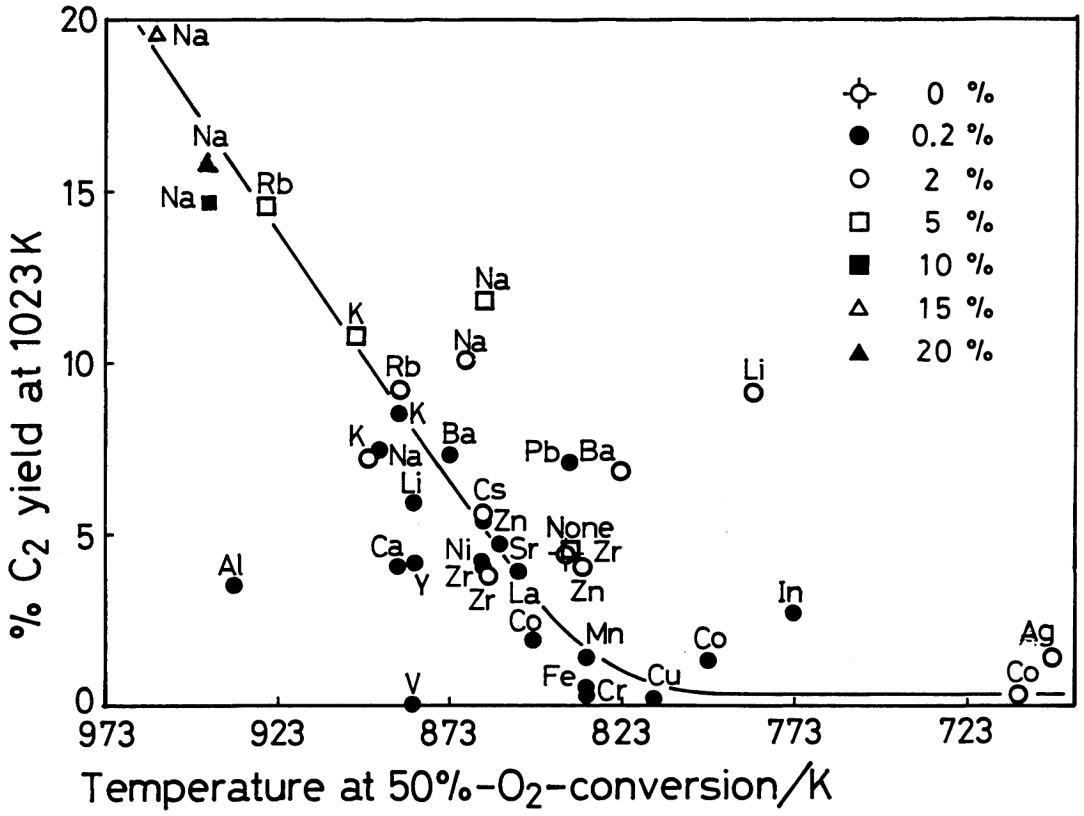

Fig. 1. Percentage C_2 yield (C_2H_4+C_2H_6) over various metal doped MgO at 1023 K as a function of the oxidation activity (abscissa). The oxidation activity is expressed as the temperature where the half of O_2 is converted. Doped metal content is shown by the symbols indicated in the figure.

The following tendencies of the catalysts were observed with respect to the chemical periodicity of the doped element: (1) MgO doped with the transition metals (5A to 8 elements and Cu) which are known as active elements for oxidation reactions are active for CO_2 production, but less active for C_2 formation. (2) The 3B, 4B, 3A, 4A, and alkali earth elements are not appreciably effective either for CO_2 or C_2 production. Among these, MgO doped with Al and In give results very

different from the trend shown in Fig. 1. (3) Alkali doped catalysts are less active in CO_2 formation and more active in the formation of C_2 compounds than the undoped MgO. It is to be noted that both reactions were promoted by the addition of 2% of Li. (4) Among alkali doped catalysts no chemical periodicity is observed, whereas Na and Rb give higher activities in C_2 formation. The C_2 yields over 2 mol% alkali doped MgO were 9.1%(Li), 10.1%(Na), 7.2%(K), 9.2%(Rb), and 5.6%(Cs) at 1023 K. On this level of doping, we did not observe the reported superiority of Li^+-MgO.[3]

Table 1. Activity of the oxidative coupling of methane,[a] the surface area, and the X-ray line broadening of various Na^+ doped MgO catalysts

Na^+ content /mol%	Reaction temp /K	C_2 compound yield/%	Selectivity for C_2 compounds /%	Surface area /$m^2 g^{-1}$	Line broadening of MgO(420) /rad x 10^3
0	1023	4.4	11.7	70[c] (-)[d]	3.8
2	1023	10.1	27.4	21 (37)	6.5
5	1023	11.8	30.8	11 (19)	4.7
10	1023	14.7	36.0	2 (-)	3.8
	1073	15.8	39.5		
15	1023	19.5 (6.4)[b]	54.3 (88.9)[b]	2 (-)	3.8
	1073	22.4 (6.7)[b]	56.8 (90.8)[b]		
20	1023	15.8	42.9	1 (10)	4.1
	1073	16.6	45.5		

a) CH_4/O_2 = 2.0; Selectivity = (2 x moles C_2 hydrocarbons produced)/(moles CH_4 reacted). b) CH_4/O_2 = 43.2; Selectivity = (moles carbon in C_2 hydrocarbons produced)/(moles carbon in all the products). c) BET method using N_2. d) Calculated from the line broadening. 15% Na^+-MgO sample was used as a standard.

The effect of alkali content was studied in the case of Na^+-MgO. The results at 1023 K or 1073 K are shown in Table 1, where the BET surface area after the pretreatment is also cited. The activity in C_2 formation increases with increase of Na content. On the other hand, as seen in Fig. 1 the activity in CO_2 formation decreases with a decrease of Na content. It is interesting to note that the surface area decreases drastically with the increase of Na content. The rate of

the methyl radical [3, 4] formation should be higher over the surface with high area, whereas, the rate of radical collision with the surface and the rate of CO_2 production should also be higher there. Thus, there might be a suitable surface area of the catalyst with maximum probability of radical coupling.

The catalysts were also studied by X-ray diffraction techniques. The Na doped catalysts give diffraction patterns assignable to the MgO lattice alone. The lattice parameters are barely changed by the doping. The lines, however, are broadened by Na addition, which is probably attributable to lattice distortion (see 2%, 5% Na^+-MgO in Table 1). On the other hand, it is considered that the line broadening due to lattice distortion is depressed by the particle growth of the sample with higher Na content (10 to 20% Na). Surface area was calculated by the line broadening data taking a 15% Na^+-MgO sample as a standard. The calculated area well corresponds with BET area for all the sample doped with Na^+, which suggests the lattice distortion exists in the similar extent for every doped samples. The lattice distortion in addition to the other factors might promote the radical formation.

In summary, the MgO catalysts to show the high yield of C_2 hydrocarbons were (1) ones with the poor ability in the complete oxidation, (2) ones with the small surface area and the lattice distortion by doping. Alkali doped catalysts have these natures. 15 mol% Na^+ promoted MgO showed the highest C_2 yields (22.4% at 1073 K), higher than any value previously reported.[1-8] When the CH_4/O_2 ratio was increased from 2.0 to 43.2 (flow rate of CH_4/air/He = 12.8 ml min^{-1}/1.48 ml min^{-1} /50 ml min^{-1}), the C_2 selectivities increased from 55 to 89% (1023 K) and 57 to 91% (1023 K).

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