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Oxidative coupling of methane on the superionic conductors

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Abstract

The reaction mechanism of the oxidative coupling of methane (OCM) has attracted world wide attention. In this paper a series of catalysts modified by Li^+, Na^+ containing superionic conductors or solid electrolytes have been tested for the OCM. It was observed that the addition of A_2BO_4 (A: Li^+, Na^+) compounds to La_2O_3 and Na^+ containing superionic conductors to CaO enhanced C_2 yield, and the C_2 yield of the modified catalysts was intimately related with their conductivities. The effects of Li^+ and Na^+ on the conductivity and catalytic performance were discussed. Only when Li^+ and Na^+ containing systems have high conductivity, the catalyst may have a good catalytic performance. A mechanism for interpreting the significant effects of alkali metals was proposed.

1. Introduction

Nowadays there is a special interest to convert methane to C_2 hydrocarbons. This process has been studied by more than 130 research groups during the last seven years. Lunsford et al [1] suggested that $[Li^+O^-]$ species are the active sites for the OCM reaction over the Li/MgO catalyst. For the Li/La_2O_3 system, however, there are no O^- species detected by ESR [2], instead, O^{2-} and O_2^{2-} species were detected which have relationship with the formation of CH_3. However, it is difficult to understand the effect of Li^+ in Li/La_2O_3 catalysts.

In fact, the presence of Li^+ or Na^+ is significant for improving the C_2 selectivity of the OCM reaction. From solid state chemistry it is known that Li^+ or Na^+ cations are able easy to form superionic conductors. The so-called superionic-conductors are solid electrolytes having ionic conductivity as high as liquid electrolytes.

A superionic-conductor has a special anion skeleton with suitable channels for cation migration in one, two or three dimensions, Li^+, Na^+ and other alkali ionic with small ionic size can easily migrate in the anion skeleton and on the catalyst surface.

In this paper, several types of superionic conductors having different conductivities, were supported on La_2O_3 and CaO. It was found that not all of the catalysts containing Li^+ (or Na^+) give high C_2 yields. Only those having high ionic conductivities have high activities and C_2 yields, and the C_2 yields are proportional to the conductivities.

2. Experimental

The catalytic reaction was performed in a fixed-bed reactor at ambient atmospheric pressure. The general reaction condition is as follows, $T=750°C$, $\tau=0.3$ s, $PCH_4/PO_2=4$, $FCH_4=80$

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ml/min, no diluent. The products were analyzed by gas chromatography (GC) using a F1 detector, a Poropak Q column and a methanation converter for CO and CO_2 analysis. The catalysts were prepared by impregnation method.

A digital conductivity meter was employed for the conductivity measurement. The conductivity cell was a home made quartz tube with Pt electrodes and an electrode tightener.

3. Results and discussion

3.1. Catalysts modified by A_2BO_4 (A: Li^+, Na^+; B: S, W, Mo)

Conductivities of A_2BO_4/La_2O_3 catalysts

Several A_2BO_2 compounds attributed to the superionic conductors, having different conductivities were supported on La_2O_3 to prepare the A_2BO_4/La_2O_3 catalyst. The mole ratio of A_2BO_4/La_2O_3 was 0.05:1. The conductivities of some catalysts are shown in Fig. 1. Pure La_2O_3 has quite low conductivity below 800°C. Above this temperature the conductivity increases slightly, mainly due to the generation of anion vacancy, which has a dominant contribution to this conductivity increase at higher temperature.

The La_2O_3-supported Li_2SO_4, Na_2MoO_4, and Li_2MoO_4 catalysts were shown to be in such conductivity sequence which is the same that for pure A_2BO_4 compounds [2]. The conductivity jumping temperature is a marked feature for the modified La_2O_3 catalysts. The jumping temperature of Li_2SO_4/La_2O_3 is as low as 400°C, which indicates that the catalyst has high ionic conductivity even at such a low temperature. The jumping temperature of Na_2MoO_4/La_2O_3 is about 600°C. There is a peak at about 650°C in the conductivity profile of Li_2MoO_4/La_2O_3, and its jumping temperature is as high as 750°C. These results show that the conductivities of the modified La_2O_3 catalysts are much higher than that of the anion conductivity of pure La_2O_3. The conductivities of the modified La_2O_3 catalysts are closely related to the A_2BO_4 compounds. The ionic conductivity is a bulk property of given compound. The bulk property is, nevertheless, related to the surface property. It is noted from Fig. 1 that the conductivity of Li_2SO_4/La_2O_3 catalyst is higher than that of pure Li_2SO_4 and La_2O_3. This implies that on the surface of Li_2SO_4/La_2O_3 a layer having high ionic conductivity would be formed, which makes contribution to the total conductivity. The layer of high ionic conductivity is supposed to be intimately related to the catalyst performance.

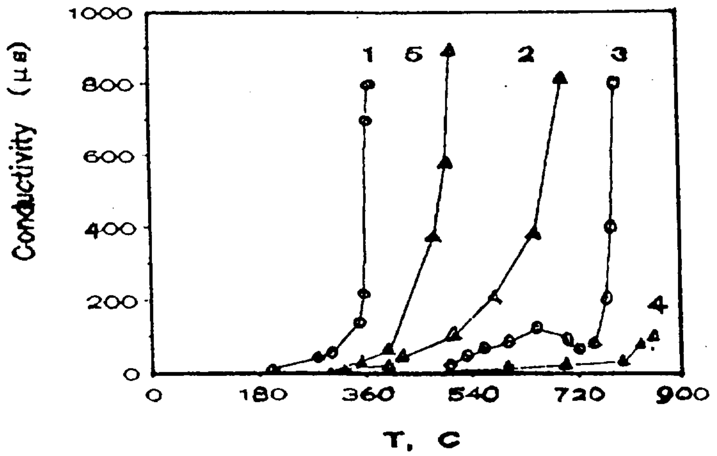

Fig. 1. Conductivity versus temperature for A_2BO_4/La_2O_3 catalysts and pure compounds. 1 – Li_2SO_4/La_2O_3; 2 – Na_2MoO_4/La_2O_3; 3 – Li_2MoO_4/La_2O_3; 4 – La_2O_3; 5 – Li_2SO_4.

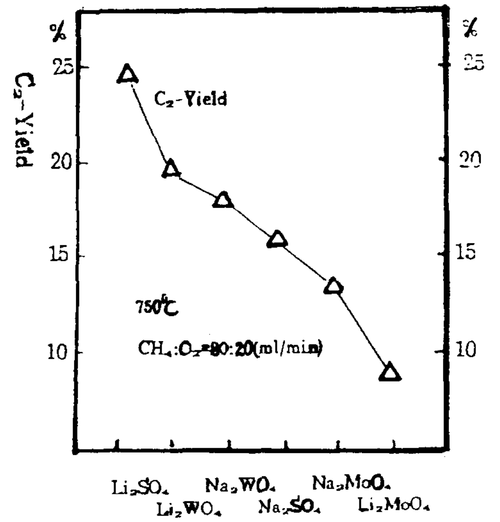

Fig. 2. C_2 yields for A_2BO_4/La_2O_3.

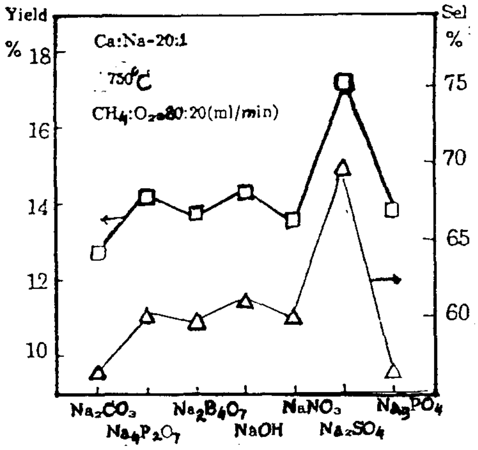

Fig. 3. C_2 yield and C_2 selectivity for Na^+ doped CaO.

Catalytic performance of the A_2BO_4/La_2O_3 catalysts

The activity of pure Li_2SO_4 is rather low. The activity of pure La_2O_3 is high, but its selectivity is relatively low, Li_2SO_4 doped La_2O_3 catalyst, however, has high activity and selectivity. This indicates that superionic conductors themselves may not be good catalysts. The modification of high active catalysts with superionic conductors would result in good performance.

The C_2 yields of the A_2BO_4/La_2O_3 catalysts are given in Fig. 2. The C_2 yield sequence of the catalysts with different A_2BO_4 compounds is as follows, $Li_2SO_4 \rangle Li_2WO_4 \rangle Na_2WO_4 \rangle Na_2SO_4 \rangle Na_2MoO_4 \rangle Li_2MoO_4$. This sequence is well coincident with the conductivity sequence of pure A_2BO_4 compounds, i.e., the higher the conductivity of the A_2BO_4 compound, the higher the C_2 yield of the doped catalyst. Li_2MoO_4 has relatively low ionic conductivity, and the C_2 yield of Li_2MoO_4/La_2O_3 catalyst is also low. This reveals that the presence of Li^+ or Na^+ ions having high conductivity may lead to producing the catalyst with a good catalytic performance and high C_2 yield.

3.2. Comparison of catalysts containing Na^+ compounds

A series of compounds containing Na^+ ions were supported on CaO. The mole ratio of Ca/Na is 20. CH_4/O_2 is 80/20 ml/min, reaction temperature is 750°C.

The result is given as Fig. 3. It was known that only Na_2SO_4 has high Na^+ migrating capacity. It was observed that only the Na_2SO_4/CaO catalyst has the nice C_2 selectivity and C_2 yield. From above result, it was proved that the ion migrating capacity of catalyst was tied up with catalytic performance again.

3.3. Effects of alkali metals

Alkali metal oxides and salts are most significant promoters for OCM. Baerns [3] has suggested that C_2 selectivity is intimately related with the basicity of alkali metal doped catalysts. Aika [4], however, found that the addition of alkali metal reduces the catalyst surface and then enhances the C_2 selectivity.

Amenomiya [5] has suggested a bifunction mechanism for oxidative coupling of methane over Bi_2O_3–K_2CO_3–Al_2O_3 catalysts. Lin [6] has discovered that the formation rate of methyl radicals on La_2O_3 is faster than that on Li/MgO catalyst, but no O^- species are detected by ESR on Li/La_2O_3 catalyst, instead, O_2^{2-} species are the dominant active oxygen species. Keller and Bhasin [7] proposed a redox mechanism for the transition metal oxide catalysts. From these models it is difficult to understand the significant effects of alkali metals on the oxidative coupling of methane.

From Fig. 1 it is noted that the conductivity of Li_2SO_4/La_2O_3 is higher than that of pure La_2O_3 or Li_2SO_4, The bulk reaction of Li_2SO_4 with La_2O_3 is not detected by XRD. It is thus suggested that the conductivity increase of Li_2SO_4/La_2O_3 catalyst is due to the fast migration of Li^+ ions over crystal surface of La_2O_3, when Li^+ ion with one positive charge migrates on the crystal surface of La_2O_3, the top O^{2-} ions on the crystal surface of La_2O_3 must be affected by the by-passing Li^+ ions. And $[Li^+O^{\alpha\ e}]$ center will be generated. In this paper the $[Li^+O^{\alpha\ e}]$ centers are proposed to be the active sites for methane activation. This is a general model suitable for different catalyst systems, such as, transitional metal oxides, alkaline earth oxides, and rare earth oxides. This argument is also supported by Lee and Oyama [8] that different catalysts have similar catalytic performance, and their activation mechanism would also be the same.

4. Conclusions

1. The addition of A_2BO_4 compounds to La_2O_3 and Na^+ containing superionic conductors to CaO enhances C_2 yields of OCM reaction. For the doped catalysts a direct correlation is observed between C_2 yields and conductivities of the superionic conductors.
2. The presence of Li^+ and Na^+ ions is not a sufficient condition for a good catalyst. Only when Li^+ ions have high conductivity the catalysts may have a good catalytic performance.
3. The fast migration of alkali metal ions over the crystal surface of La_2O_3 enhances the conductivity of the doped catalysts and improves the catalytic performance.

5. References

[1] C.-H. Lin, J.-X. Wang and J.H. Lunsford, J. Catal., 111 (1988) 302.
[2] Li Ying-li, Zhen Kai-ji et al., Chemical Journal of Chinese Universities, 13 (12) (1992) 1586-89.
[3] J.A.S.P. Carreivo and M.S Baerns, React. Kinet. Catal. Lett., 35 (1987) 349.
[4] E. Iwamatsu, T. Moriyama, N. Takasaki and K. Aika, J. Chem. Soc., Chem. Commun., (1987) 19.
[5] I.T.A. Emesh and Y. Amenomiya, J. Phys. Chem., 90 (1986) 4785.
[6] C. -H. Lin, J.H. Lunsford, J. Phys. Chem. 90 (1986) 534.
[7] G.E. Keller and M. M. Bhasin, J. Catal., 73 (1982) 9.
[8] J.S. Lee and S.T. Oyama, Catal. Rev.-Sci. Eng., 30 (1988) 249.