

Molybdate Compounds as Active and Long-living Methane Dimerisation Catalysts

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Oxidative coupling of methane with good C_{2+} selectivity and yield was achieved over a variety of molybdate compounds without losing their catalytic activity during 200 to 280 h of study.

Oxidative coupling of methane has become an important area of catalytic research. Detailed studies were published by Keller and Bhasin¹ and work has recently been reviewed by Hutchings² *et al.* Attention has been focused on the use of alkali and alkaline earth metal oxides (doped or undoped)^{3,4} pyrochlores^{5,6} and oxychlorides.⁷

The present study was motivated by previous work carried out in our laboratory, involving methane activation.⁸⁻¹⁰ Essentially, we sought catalysts with higher selectivity and conversion in C_{2+} products. Continuous cofeeding of CH_4 and O_2 under atmospheric pressure was used in the temperature range 640–800 °C.

Table 1 Oxidative coupling of methane over molybdate catalysts^a

Catalyst	<i>T</i> /°C	Conversion (%)	C ₂ H ₄ /C ₂ H ₆	<i>X</i> (C ₂₊)(%) ^b	<i>Y</i> (C ₂₊)(%) ^b
Na ₂ MoO ₄	729	60	3.3	12.0	7.2
Li ₂ MoO ₄	723	63	3.7	11.6	7.3
K ₂ MoO ₄	723	57	3.0	9.8	5.6
MgMoO ₄	728	57	3.3	13.5	7.7
BaMoO ₄	723	55	3.5	12.5	6.9
MnMoO ₄	729	57	3.2	9.8	5.6
CoMoO ₄	723	62	3.3	12.3	7.6
Fe ₂ (MoO ₄) ₃	730	53	3.4	13.0	7.0
CuMoO ₄	728	51	3.0	13.7	7.0
ZnMoO ₄	728	45	3.3	16.6	7.5
NiMoO ₄	728	—	—	—	—
Na ₂ WO ₄	720	51	3.1	11.5	5.9

^a All results refer to 24 h experiments. ^b $X(C_{2+}) = (\text{amount of } C_2H_6 + C_2H_4 + C_3H_6 / \text{Total amount of carbon products}) \times 100$; $Y(C_{2+}) = (\% \text{ conversion of } CH_4) \times X(C_{2+}) / 100$.

Table 1 presents the results obtained when a mixture of CH₄ (8.5 ml min⁻¹) and O₂ (7.5 ml min⁻¹) were continuously cofed through the catalyst in a U-tube of 8.0 mm diameter and 600 mm length. Molybdate (1 g) was used as catalyst in the form of a bed fixed in position with plugs of quartz wool. C₂₊ products began to form at 600 °C and increased by a factor of 15 when temperatures were raised by 150 °C. The products observed were C₂H₄, C₂H₆, C₃H₆, CO, CO₂, H₂ and H₂O_(g). In addition, small quantities of CH₃OH and HCHO (<2% of total products) were detected. Table 1 shows the values for the selectivities *X*(C₂₊) and yields *Y*(C₂₊) towards higher hydrocarbon products.

With the molybdates studied, *e.g.* alkali or alkaline earth (Na, Li, K, Mg and Ba) or transition metal containing (Mn, Co, Fe, Cu, Zn and Ni), the conversions were close to ≈60% and compare well with the highest values reported in the literature.^{2,11} The selectivity and yields of C₂₊ products are comparable with those obtained with some of the most active catalysts reported in the literature.¹²

Catalysts in Table 1 are shown to be reasonably active and selective. They possess intermediate metal–oxygen bond strengths¹³ which play a positive role in the catalysis. The similarity in the selectivities [*X*(C₂₊)] for a variety of molybdates reported in Table 1 suggests that the activation energies for the formation of C₂₊ compounds are also similar on these catalysts irrespective of the nature of the cation in the molybdate. One interesting feature in Table 1 is the favourable ratio (>3.3:1) of ethylene to ethane. The high selectivity to ethylene found in this study is much higher than those reported for alkaline earth metal oxide^{2–4} or rare earth metal oxide^{14,15} catalysts. On increasing the temperature from 620 to 760 °C, the amount of C₂H₆ in the product stream decreased while the amount of C₂H₄ steadily increased. This indicates that, at higher temperatures, C₂H₆ is dehydrogenated to C₂H₄ under the present experimental conditions. This effect becomes stronger as the temperature increases, and at 729 °C the ratio of C₂H₄ to C₂H₆ is already >3.3:1. Since the values of *Y*(C₂₊) and *X*(C₂₊) reported in Table 1 are similar for a variety of these compounds, it is clear that the cation of the molybdate does not play a significant role in catalysis. A pale grey colour appears on the molybdate catalyst during reaction under our experimental conditions. This colour disappears when the catalyst is cooled after the reaction. The formation of this M–O⁻ colour centre on the molybdate surface has been shown to be responsible for the activation of CH₄ *via* hydrogen

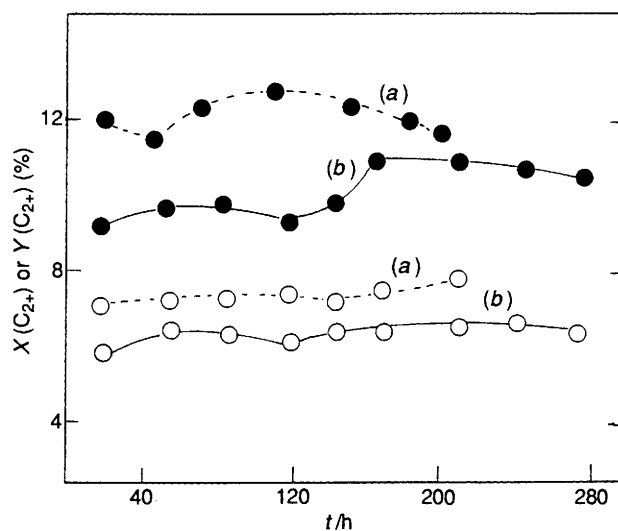


Fig. 1 ○, Yield *Y*(C₂₊) and ●, selectivity *X*(C₂₊) for CH₄ and O₂ continuously cofed over 1 g of (a) Na₂MoO₄ or (b) MnMoO₄ catalyst at 728 °C as a function of time

atom abstraction to form methyl radicals.^{11–13} Our experiments have confirmed the inability of molybdates to evolve C₂₊ products in the absence of gas phase oxygen. Also, the large and steady conversions reported in Fig. 1 and Table 1 indicate that with the mechanism taking place during the reaction, (*e.g.* Mars–Van Krevelen¹³ or other), the oxygen is not irreversibly depleted from the catalyst surface. This suggests, that an active surface oxygen species is generated only in the presence of O₂ and effects methane coupling. Therefore we suggest that above 600 °C (and preferably at 700–740 °C), the surface-adsorbed oxygen in the molybdate is responsible for the formation of C₂₊ hydrocarbons. Further studies using Na-polytungstates as catalysts are shown in the last row in Table 1.

Lead molybdate has been used by Baerns¹⁶ in catalytic conversion of CH₄ with relatively low conversions (1%) and *X*(C₂₊) of 19%. C₂H₆ was the major dimerisation product.

NiMoO₄ did not beneficially affect CH₄ oxidation in our studies (see Table 1), since it is stable (β phase) only up to 500 °C and thereafter decomposes to NiO.¹⁷ In our experiments, we have used molybdates with and without variable valency cation and our results (Table 1) suggest that the reductive and oxidative pathways originating from multivalent cations can be excluded in CH₄ activation.

Fig. 1 presents the conversion $Y(C_{2+})$ and selectivity $X(C_{2+})$ for Na₂MoO₄ and MnMoO₄ when CH₄ (8.5 ml) and O₂ (6.5 ml) are continuously cofed in a tubular reactor heated at 748 °C containing 1 g of these materials. As seen from Fig. 1 deactivation of these materials with time did not take place. One of the problems of the Li⁺/MgO catalyst as previously reported is the relative short life.^{3,18} The selectivity towards C₂₊ products is limited to a few hours.

The longest lived catalyst for CH₄ dimerisation until now has been reported to have a lifetime of 60 h, but with reduced conversion compared to the initial value.¹⁸ Both catalysts in Fig. 1 remained active throughout the run time (200 and 280 h). The C content was \approx 0.15% for both catalysts before reaction and 0.09% after reaction. Therefore no coking occurred during the process.

Further work will concentrate on the improvement of catalyst formulations for higher C₂₊ yields close to 20%. This limit has been suggested as the probable minimum for economic feasibility in this field.^{2,3,12} In our work, the catalyst was stable during the catalytic run (280 h) and high yields of ethylene have been obtained. The amount of ethylene greatly exceeds that of ethane.

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