NOTE

EFFECT OF REACTION TEMPERATURE ON THE SELECTIVITY OF OXIDATIVE METHANE COUPLING OVER LEAD OXIDE

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Abstract — In the oxidative coupling of methane over lead oxide, reaction temperature is a critical variable which determines the reaction pathway of methyl intermediates on the surface. Low temperature favors oxidation to carbon oxides, while high temperature favors desorption as methyl radicals.

Among potential routes of direct methane conversion, oxidative coupling to higher hydrocarbons over solid surfaces has been an active area of research in the past several years [1,2]. Various metal oxides have been employed, either as catalysts or as reagents. In the latter case, the materials were first reacted with methane in a stoichiometric manner and were then regenerated by dioxygen treatment in a separate step [3].

Evidence in the literature suggests that the critical process in both the catalytic and stoichiometric materials involves the generation of gas-phase methyl radical intermediates. Thus, from the fact that the distribution of C_2-C_7 hydrocarbon products are essentially identical for all catalyst systems they studied (mostly transition metal oxides), Jones et al. [4] have postulated that the gas phase methyl radical $CH_3\cdot$ is the first species to be formed upon methane activation. This is followed by gas phase hydrocarbon building steps. This mechanism contradicts the mechanism proposed earlier by Keller and Bhasin [3] for the same type of metal oxides. The earlier mechanism assumes the adsorbed methyl intermediates and surface hydrocarbon building steps. Jones et al. argued that it would be highly fortuitous for all these different metal oxide systems to have similar product distributions if the hydrocarbon building steps occurred via adsorbed species on the catalyst surface.

Among the materials found active for methane coupling is lead oxide. Hinsen et al. [5] and Bytyn and Baerns [6] reported that a 36% PbO/γ-Al_2O_3 catalyst produced at 1023 K a C_2^+ selectivity of 58% with a methane conversion of 8.9% [P_{O_2} = 7 kPa, P_{CH_4} = 70 kPa, P_{He} = 23 kPa, W/F = 1.55 g·s·cm^{-3}]. Otsuka et al. [7] reported that an unsupported PbO catalyst at 973 K

produced a C_2^+ selectivity of 47% [P_{O_2} = 0.4 kPa, P_{CH_4} = 18 kPa, P_{He} = 82 kPa, W/F = 0.002 g·s·cm^{-3}].

For irreducible oxides like Li/MgO, and more recently for rare earth oxides, the importance of gas phase reaction has been well established. By Electron Paramagnetic Resonance spectroscopy, Lunsford and coworkers [8,9] detected $CH_3\cdot$ in the gas phase over these materials during methane coupling. Kimble and Kolts [10] were able to simulate the distribution of hydrocarbon products over Li/MgO with known rate constants for gas phase reactions.

However there is a report which is apparently inconsistent with the above. At 748 K, Driscoll and Lunsford [11] detected gas phase methyl radicals over MgO and Li/MgO. Meanwhile Bi_2O_3, Bi_2MoO_6, and PbO were essentially inactive for radical production. The present authors noted that the temperature of the experiment was much lower than the temperatures previously employed in methane coupling over these oxides. Present work was performed to check the effect of temperature on the selectivity of methane coupling over supported lead oxide.

A 30 wt % PbO/Al_2O_3 was prepared by adding aqueous solution of $Pb(NO_3)_2$ (Alfa) to γ-alumina (Norton, BET area 250 m^{2}g^{-1}) followed by evaporation of water, drying at 390 K for 10 h, and calcining in air at 1000 K for 2 h. The reaction of methane took place in a flow reactor at atmospheric pressure with 1.0 g of the sample. The pressure of methane was kept at 50.5 kPa while that of dioxygen was varied, with the total flow rate maintained at 13.6 μmol s^{-1} with He diluent. Products were analyzed with a gas chromatography equipped with a thermal conductivity detector and a 2.5 m long, 3 mm diameter Porapak Q column.

The results of the reaction is shown in Table 1. There was no significant change in the rate of methane conversion and product distribution during 2-5 h of ex-

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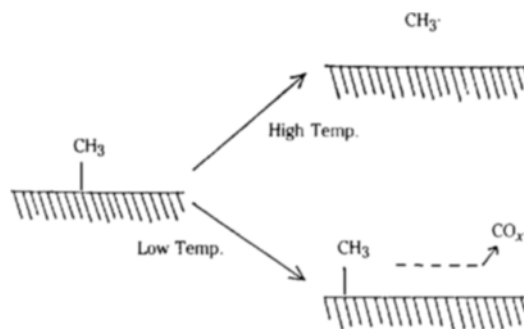**Table 1. Oxidative coupling of methane over 30 wt% PbO/Al₂O₃**

T (K)	O_2 (kPa)	CH_4 Conv., %	O_2 Conv., %	Selectivity, %			
				CO_2	CO	C_2H_4	C_2H_6
659	25	1.3	5.1	100.0	—	—	—
760	25	24.0	92.0	100.0	—	—	—
883	25	27.9	97.8	90.0	<0.1	4.3	5.7
883	5	4.8	88.4	81.2	—	2.1	16.7
1017	5	6.5	94.0	66.2	—	27.7	6.2

Catalyst weight: 1.0 g; Atmospheric pressure with [CH₄] = 50.5 kPa, [O₂] as indicated, and He diluent. Total flow rate: 13.6 μmol s⁻¹.

Fig. 1. A model to explain the effect of temperature on the formation of gas phase methyl radical during oxidative coupling of methane over PbO/Al₂O₃.

periment at each temperature. In general, selectivity to C_2-hydrocarbons, especially that of ethylene, increased with increasing temperatures. As in the case of samarium oxide [12], this is probably due to the activation energies of C_2 formation steps that are larger than those of CO_2 formation steps. This trend is opposite to that of usual selective oxidation of hydrocarbons on transition metal oxides, but has been widely observed for methane dimerization. At the same temperature, higher dioxygen pressure in the feed decreases the selectivity to C_2-products, but increases C_2H_4/C_2H_6 ratio of the products. These effects of dioxygen have been interpreted as dioxygen promotes the formation of carbon oxides by reacting with methyl intermediates and the formation of ethylene by oxidative dehydrogenation of ethane, the primary product of methane coupling [1].

The formation of C_2-hydrocarbons is observed at temperatures above 870 K. High conversions of methane was achieved even at lower temperatures, but product was mostly CO_2. On the other hand, considerable amount of C_2-hydrocarbons are reported to be formed below 870 K over Li/MgO [13] or La₂O₃ [5].

The failure to observe the gas phase methyl radicals over PbO in the experiment of Driscoll and Lunsford may have have been because at the low temperatures methyl intermediates formed on the surface rapidly convert to CO_2 before they are desorbed into the gas phase. The fact that a considerable methane conversion was achieved at 659 K and 760 K (Table 1) suggests that under the experimental conditions of Driscoll and Lunsford [11], surface intermediates might have been formed but escaped the detection by EPR because they could not desorb into the gas phase. At high temperatures, however, the methyl radicals can leave the surface before they react further and metha-

ne coupling proceed via the gas phase CH_3-intermediate. On the other types of metal oxides like Li/MgO and La₂O₃, the desorption of methyl radical may be much easier even at low temperatures. The process is illustrated in Figure 1.

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