Differences in Catalytic and Gas-phase Reactions in Methane Coupling

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Examination of the coupling reaction of methane in the gas-phase and over Pb–Mg–O catalysts reveals significant differences in certain kinetic parameters which are useful in determining the extent of homogeneous gas-phase contribution to the final product.

Recent reports have shown evidence for the oxidative coupling of methane in the gas-phase[1—5] and some have suggested that reported results labelled 'catalytic' actually may be due to homogeneous gas-phase reaction. This idea is of great importance since if a significant portion of the reaction occurs in the gas-phase little can be done in terms of catalyst development to improve the ultimate selectivity of the reaction. Recent reports have also suggested a limit to the attainable yield of hydrocarbon products from such a reaction.[6] Thus it is of importance to define whether the majority

Table 1. Summary of gas-phase and catalytic reactions.

Catalyst	Total surf. area (m^2/g)	CH_4 Conv.	C_2 Select. (%)	Activation energy (kcal/mol)[a]			
				CH_4	C_2	CO	CO_2
None	0.0003	0.2	51	53	48	73	33
None[b]	0.0006	0.1	50	56	50	71	31
Quartz wool	0.003	0.1	48	45	46	69	31
Quartz chips	0.005	0.1	45	43	47	73	30
MgO	1.4	2.1	37	37	76	10	37
Pb–Mg–O[c]	0.8	2.6	29	29	60	16	22

[a] 1 cal = 4.184 J. [b] Using straight-tube reactor. [c] 0.8 atom% PbO/MgO.
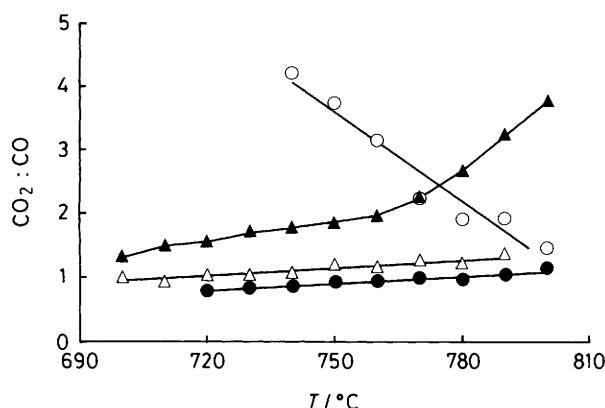

Figure 1. Effect of temperature on CO_2 : CO ratio for the oxidative coupling of methane in the gas-phase and in the presence of Pb–Mg–O catalysts. ○ Gas-phase, ● 0.2 atom% Pb–Mg, △ 0.4 atom% Pb–Mg, ▲ 0.8 atom% Pb–Mg.

of the reaction is taking place in the gas phase or on the surface. We have been investigating this question and believe that certain parameters exhibit sufficient difference between gas-phase and surface reaction so that the relative importance of the two pathways may be elucidated from reaction studies.

We have examined the oxidative coupling of methane over various Pb–Mg–O catalysts and in the gas-phase under a series of reaction conditions using a reactor design which minimizes the post-catalytic bed volume and hence homogeneous gas-phase reactions.[7] The reaction was studied between 973 and 1073 K using a CH_4 : O_2 ratio of 9 : 2. A 40% inert gas dilution and low conversions were used to minimize thermal excursions. The apparent activation energies were calculated from the Arrhenius plots which were linear within this entire temperature range and devoid of mass-transfer limitations.

According to currently accepted mechanisms, the surface abstraction of hydrogen from methane is the rate determining step, followed by desorption of methyl radicals which recombine in the gas-phase to form ethane.[8—11] Since the recombination of methyl radicals can be expected to have an activation energy of zero, for a purely gas-phase reaction, one should measure the same activation energy for methane consumption as for ethane production at high C_2 selectivites. Additionally, at comparable levels of conversion, the activation energy for CO_x formation should be independent of any external parameters such as available surface area.

Table 1 lists activation energies for the conversion of methane, for the formation of C_2 hydrocarbons (C_2H_6 and C_2H_4), CO, and CO_2, respectively, under a variety of

conditions. In an empty reactor tube, or one filled with either glass wool or quartz granules, the activation energies for C_2 production were virtually identical (48 ± 2 kcal/mol) (1 cal = 4.184 J) to the activation energy for total methane conversion. The latter depends somewhat on the presence of an 'inert material,' showing a decrease as the available surface area in the reactor is increased. This suggests that at these temperatures the gas-phase reaction is surface-initiated. These activation energies agree quite well with those reported by other investigators.[2,11]

Listed in Table 1 are measurements conducted in the presence of typical coupling catalysts, 0.8 atom% PbO/MgO. In these cases there was a noted increase in the conversion which, more importantly, was accompanied by a significant increase in the activation energy for C_2 production. It should be noted that in the absence of a catalyst C_2H_6 was the only hydrocarbon product observed. Thus, the increase in activation energy for C_2 production on catalytic systems can be ascribed to the catalytic dehydrogenation of ethane to form ethene which increases the apparent activation energy of total C_2 formation.

A second important difference in the kinetic parameters between gas-phase and surface catalysed reactions is a dramatic decrease in the measured activation energy for CO formation. The changes in activation energies are reflected in the CO_2 : CO ratio, shown in Figure 1, which shows a strong negative function of temperature in the case of gas-phase reaction, but exhibits a slight to strong positive dependence in the presence of a catalyst. The exact temperature dependence of this ratio is related to the nature of the surface and in particular to the 'oxidizing power,' as can be seen by noting the effect of PbO loading in PbO/MgO catalysts on the CO_2 : CO ratio. Although it can be argued that CO_2 is formed by many different routes, thereby casting doubt on the meaning of this information, all the experiments reported here were conducted at low conversions to minimize secondary reactions and thus the observed activation energies for CO and CO_2 production represent only those products formed from methane.

The lowering of the activation energy for CO formation observed when a catalyst was present suggests that a large portion of the CO_2-forming reaction occurs on the surface, possibly by oxidation of reaction intermediates. However, the choice of surface made little difference to the activation energy for the formation of CO_2. This suggests that the choice of surface, or catalyst, has an effect on the initial hydrogen abstraction step but not on subsequent steps leading to CO_x, since all surfaces have been shown to readily oxidize the intermediates to CO_x.

Thus we have shown that some kinetic parameters are highly sensitive to the main route by which the reaction

proceeds and a simple test, in this case measurement of the activation energies or $CO_2:CO$ ratio, can help to determine whether the reaction observed is taking place homogeneously in the gas-phase or is truely a surface-assisted reaction.

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