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THE ROLE OF HETEROGENEOUS REACTIONS DURING THE OXIDATIVE COUPLING OF METHANE OVER Li/MgO CATALYSTS

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SUMMARY
The role of heterogeneous and homogeneous reactions during the oxidative coupling of methane over Li/MgO was investigated by carrying out experiments at reduced pressure (60 Pa). The conclusion is that the radical reactions occurring in the gas phase play an essential role in the C2+ selectivity of the process. Our reaction model of consecutive reactions is confirmed. The selectivity of the active catalyst is mainly due to very high rates of methyl radical production which couple in the gas phase.

INTRODUCTION
The reaction mechanism of the oxidative coupling of methane over lithium doped magnesia is based on radical reactions which take place in the gas phase and on the catalyst surface (ref. 1,2,3,4). An effective way of discriminating between homogeneous and heterogeneous reactions is to carry out experiments at reduced pressures. At reaction pressures of 100 Pa and lower, radical reactions in the gas phase are strongly suppressed. In this way it is possible to determine the contribution of heterogeneous reactions to the overall kinetics.

For this purpose a low pressure reactor was designed and built, which can operate at pressures in the range of 10 to 500 Pa.

EXPERIMENTAL
The experiments were carried out in a low pressure reactor set-up shown in figure 1.

In the feed section a gas mixture can be prepared and stored in a feed gas container. From this feed gas container the gas mixture can enter into the reactor via valve K2 and a manually tuned leak valve R1. From there most of the gas is pumped off via three-way valve K4. Only a small amount of the product gas is used for analysis leaking via K5 and R2 into a quadrupole mass spectrometer (Leybold-Heraeus Q-200).
Figure 1. Flow scheme of low pressure reactor set-up.

Figure 2. Quartz micro fixed bed reactor used in the low pressure experiments.

Beside flow experiments also batch experiments were performed by closing valve K4 and leaving only a small gas leak to the mass spectrometer. At the low pressures applied (10-150 Pa) molecular diffusion is the main factor which determines the mixing of the reactor. The mixing time due to diffusion (D) is small compared to chemical reaction time ($K_i^*(d_i)^2$) meaning that the reactor in the batch mode can be considered as an ideally mixed batch reactor ($K_i^*(d_i)^2/D <= 0.005$) (ref. 5).

The reactor itself is a micro fixed bed reactor made of quartz. The post catalytic volume was kept as small as possible. Figure 2 shows the reactor.

The analysis is performed by the Q-200 which is controlled by a computer. The concentrations of the components in the gas mixture are determined via a multiple regression program. This program uses reference spectra of the pure components, first to determine which are present and next to quantify their concentrations.

The Li/MgO catalyst was prepared as described elsewhere (6). The process conditions used were: Temperature 600 - 800°C, pressure 30 - 150 Pa, CH$_4$/O$_2$ 5; the pseudo contact time (W/F) varied between 2500 - 20000 Kg cat.s./mole.

RESULTS AND DISCUSSION

Figure 3 and 4 show the oxidative coupling of methane at reduced total pressure in batch mode of operation for the non-catalytic and the catalytic oxidation. The rate of methane activation is very low
in the non-catalytic compared to the catalytic activation. It can be concluded that no gas phase reactions are occurring under these conditions. In the catalytic experiment almost no C$_2$ production is observed: the main products are the total oxidation products CO and CO$_2$.

![Figure 3. Methane batch oxidation no catalyst.](image1)

![Figure 4. Methane batch oxidation over Li/MgO.](image2)

At the low pressures applied the methyl radicals formed by hydrogen abstraction from methane can only react at the catalyst surface and cannot combine in the gas phase. For coupling they must transfer excess energy and at low pressures this is only possible at the catalyst surface. Because the coupling of methyl radicals has a higher reaction order than total oxidation, lowering of the pressure should favour total oxidation reactions. However, atmospheric experiments with varying diluent gas concentration show an increase in C$_2$+ selectivity with increasing helium diluent concentration (figure 5). In this experiment the partial pressures of methane and oxygen are lowered like in the low pressure experiments, but the total pressure remains at 100 kPa. Obviously, the coupling efficiency is increasing with increasing diluent gas concentration. An explanation for this can be found in the fact that the gas phase coupling of methyl radicals is favoured with increasing diluent concentration, because the excess coupling energy can be lost via collisions with third bodies. As it is known that gas phase reactions play an important role in the oxidative coupling of methane it can
be concluded that gas phase coupling of methyl radicals is the main source responsible for the high $C_2^+$ selectivity observed over Li/MgO catalysts at atmospheric pressures.

High concentrations of inert gas improve the coupling efficiency and thus reduce the oxidation of the radicals. This means that the homogeneous radical gas phase reactions do play a very important role in the $C_2^+$ selectivity which can be achieved. This also lays constrains on the comparison of different coupling catalysts. A different diluent concentration can mean a large difference in the $C_2^+$ selectivity.

From atmospheric experiments it was concluded that the reaction mechanism of the methane coupling to ethylene occurred via a model of consecutive reactions (7). Methane is first converted to a methyl radical by a hydrogen abstraction step occurring at the catalyst surface. These methyl radicals react further in gas phase to ethane which in turn is dehydrogenated to ethylene. The ethylene is burned to CO and the CO is catalytically converted to $CO_2$. In order to test whether the catalyst converts ethane to ethylene or oxidizes both directly we carried out ethane and ethylene activation experiments over Li/MgO catalyst at low total pressure.

Therefore $C_2H_6/O_2/Ne$ (5/5/1) and $C_2H_4/O_2/Ne$ (5/5/1) gas mixtures were fed to the low pressure reactor. Figure 6 and 7 show the ethane and ethylene oxidation experiments over Li/MgO catalyst as function of the temperature. Again gas phase oxidation does not occur (not shown) but with the Li/MgO catalyst oxidation sets in between 600°C - 800°C. Ethane is converted to ethylene which in turn is oxidized to CO and $CO_2$. Apparently, both hydrogen abstraction and oxidation reactions are taking place at the catalyst surface.

The best way to show that ethane is converted catalytically to ethylene and ethylene to CO is to carry out batch experiments. Figure 8 shows a batch experiment of an ethane oxygen mixture over Li/MgO
The fraction of ethylene is coming up first, followed by CO₂. The fraction of CO is nearly constant during the whole time.

This means that it is converted relatively rapid to CO₂. This last reaction is definitely catalyzed by the Li/MgO catalyst because the same experiments without catalyst show that CO and C₂H₄ are the main products (figure 9).
CONCLUSIONS

By means of low pressure experiments discrimination between homogeneous and heterogeneous reactions is possible. The role of the Li/MgO catalyst during oxidative coupling of methane is that of a methane activator which produces methyl radicals which couple preferably in the gas phase provided that a sufficient amount of third bodies is present. The experiments prove that the catalyst plays an important role in the conversion of ethane and the oxidation of ethylene to CO. Finally the catalyst is essential for the oxidation of CO to CO₂.

High diluent concentrations in the gas phase strongly influence the C₂⁺ selectivity by favouring the gas phase coupling of methyl radicals and preventing their oxidation.

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