Oxidative coupling of methane on silver catalysts

X. Bao, M. Muhler, R. Schlögl and G. Ertl

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6,
D-14195 Berlin, Germany

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Bulk silver catalysts were found to be active for the oxidative coupling of methane to ethane and ethylene if operated under oxygen-limited conditions at atmospheric pressure and at temperatures above 1020 K. The addition of small amounts of sodium phosphate as promoter increases markedly the C_2 selectivity (to values above 90%) and yield ($>10\%$) by efficient suppression of reaction steps leading to total oxidation. Further improvement of the yields might be achieved by more appropriate reactor design.

Keywords: methane; silver; oxidative coupling; C_2 selectivity

1. Introduction

The oxidative conversion of methane into ethane and ethylene (oxidative coupling) has been extensively studied in recent years [1–10]. Following the pioneering work by Keller and Bhasin [5], more than hundred materials were checked as catalysts for this process. Alkaline earth metal and lanthanide oxides, in particular promoted by alkali metals, were found to be efficient catalysts. Transition metal oxides, typically from Mn, V, Ni or Fe, were found to be less suited, albeit promising for partial oxidation of methane to C_1 oxygenates such as methanol or formaldehyde. Quite recently, even porous Ag films were found to be active, however, less than the quoted oxide materials [10]. According to Lunsford [4], the decisive step of the reaction consists in abstraction of a hydrogen atom from the methane molecule by a specific surface oxygen species, and the resulting methyl radicals may either dimerize to C_2H_6 in the gas phase or react further on the surface. Since the product molecules C_2H_4 and C_2H_6 react much more readily with oxygen than CH_4, it is not surprising that increasing conversion is generally accompanied by a loss of selectivity, so that rarely yields (given as the product of conversion and selectivity) exceeding 15% are achieved. However, considerable improvement of this situation was recently demonstrated to be possible by proper modification of the reactor design, in that the reactant mixture is recycled while the desired product molecules are continuously separated [9,10]. Very high yields appear to be accessible in this way such that this process becomes rather attractive for industrial applications.

In the present paper the results of an investigation of the oxidative coupling of methane on silver-based catalysts will be reported. This work was prompted by our preceding studies on the selective oxidation of methanol to formaldehyde which proceeds on Ag catalysts at high temperature (~ 920 K) with high selectivity (~ 90%) and almost complete conversion [11]. Treatment of silver with oxygen at atmospheric pressure and at these high temperatures was found to cause restructuring of the surface accompanied by the formation of a strongly held atomic oxygen species (denoted as O_γ) which initiates the catalytic transformation by hydrogen abstraction from CH_3OH [12,13]. It is to be expected that this species likewise reacts with CH_4 and hence silver was assumed to be also an active catalyst for oxidative coupling of methane. Apart from pure bulk silver, also samples promoted with varying concentrations of sodium phosphate were tested. This was initiated by reports on promoting effects of alkali metal additives on oxide catalysts [4], and by the hypothesis that well-dispersed polyphosphates formed at elevated temperatures might block active sites on the surface and thus suppress non-selective side reactions [14].

2. Experimental

Electrolytically refined silver (99.999%) and silver powder (Strem Chemicals Inc., 99.9995%) were employed as catalysts with particle sizes of about 100 and 20 μm, respectively. The specific surface areas as measured by nitrogen-BET were about 0.1 m^2/g.

Promoted catalysts were prepared from powder samples by impregnation in alkali phosphate containing solutions and subsequent heating. The promoter content (as expressed by the molar ratio with respect to the total amount of silver) was varied through the concentration in the solution. Prior to transfer into the reactor, the catalyst was usually calcined in air above 900 K for 30 min in order to improve its stability.

The experiments were performed with a downflow tubular quartz reactor of 400 mm length and 14 mm internal diameter. The reaction zone with about 80 mm length was located near the bottom of the reactor and was heated by a cylindrical electric furnace. The remainder of the reactor served as preheating zone and was usually kept at 570 K. A water bath surrounding the tube at 40 mm below the reaction zone enabled quenching of the gas mixture after contact with the catalyst. A silver net fixed in the center of the reaction zone acted as support for 2 g of the silver catalyst forming a bed of about 6 mm height. The temperature of the catalyst bed, typically in the range of 950–1100 K, was controlled by a proportional band temperature regulator using a shielded NiCr–NiAl thermocouple attached to the bottom of the catalyst bed.

CH_4 (Linde 99.5 vol%), O_2 (Linde 99.995 vol%) and Ar (Linde 99.999 vol%) were introduced into the reactor as premixed stream at 1 atm total pressure. A typical flow rate used was $CH_4 : O_2 : Ar = 120 : 30 : 40$ cm^3/min which corresponds to about 0.5 g s ml^{-1} contact time (W/F) for 2 g silver catalyst. The composition of the reaction products was analyzed by means of a computer-controlled quadrupole mass spectrometer (Balzers QMS 120) which was equipped with a two-step gas inlet system (Balzers GES 010). The inlet capillary tube was mounted directly at the bottom of the reactor, 80 mm below the catalyst bed. This arrangement prevented possible segregation effects by mass-dependent molecular diffusion and condensation problems, and permitted to perform on-line analysis without affecting the gas composition. The procedure for data analysis is described in detail in the appendix. Apart from analysis of the gas phase, condensation products were collected and identified by infrared spectroscopy.

3. Results and discussion

In order to attain steady-state conditions of the activity and C_2 selectivity, the samples were always operated in the reaction mixture at 1020 K for more than 1 h prior to collecting kinetic data. The long-term stability will be discussed in more detail later (cf. for example fig. 6).

Fig. 1 displays data on the C_2 selectivity and methane conversion as a function of temperature for both types of pure Ag catalysts and for two typical $CH_4 : O_2$ ratios (6 : 1 and 4 : 1, respectively). Above about 1040 K the reactivity (CH_4 conversion) becomes practically independent of temperature while the C_2 selectivity continuously rises. The conversion at high temperatures is limited by the supply of oxygen. If oxygen is present in large excess (e.g. $CH_4 : O_2 : Ar = 10 : 120 : 40$) complete conversion is reached at 1100 K. With the example shown here the selectivity reached values around 25–30% at 1100 K, while the C_2H_4/C_2H_6 ratio also increased with temperature and reached a maximum of about 1 : 1 at 1120 K.

The variation of activity and selectivity with the content of O_2 in the feed mixture (given as the $O_2 : CH_4$ volume percentage) at 1100 K is shown in fig. 2. In the absence of oxygen, obviously the selectivity would be highest, but the activity is negligibly small due to inefficiency of the metallic silver surface to attack the C–H bond of the methane molecule. The presence of surface oxygen (in the form of the O_γ species quoted in the introduction) presumably enables H-atom abstraction followed by recombination of the fragments. Hence, the higher the O_2 content in the gas phase the higher the methane conversion, which effect is, however, accompanied by a loss in selectivity, i.e. increasing participation of complete oxidation to CO_x. The yield of C_2 products, which is given by the product of C_2 selectivity times conversion, likewise increases with the O_2 content, but levels off as soon as the latter has reached a critical value. The sketched reaction mechanism has first been proposed by Lunsford [4] and involves both heterogeneous (i.e. surface catalyzed) and

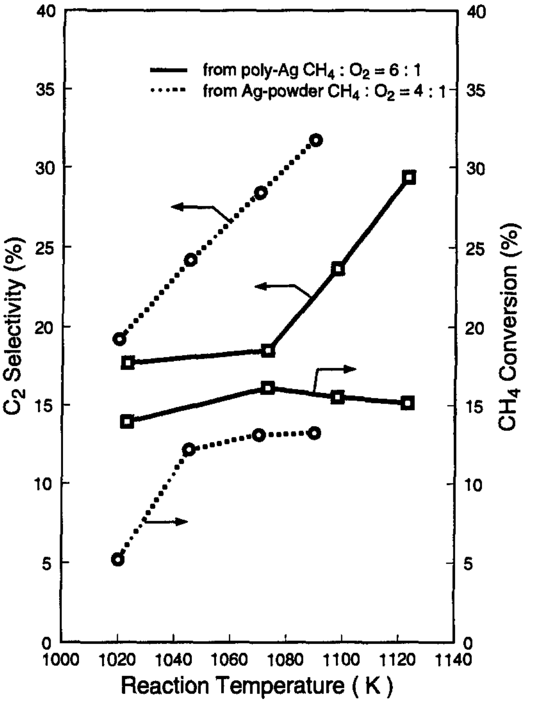

Fig. 1. Activity (= methane conversion) and C_2 selectivity of two Ag catalysts as a function of temperature.

homogeneous (e.g. recombination of gaseous methyl radicals) reaction steps. With this mechanism it is evident that the presence of excess oxygen will favour total oxidation, and an optimum O_2 concentration of about 10% in the feed gas was reported for oxide-based catalysts [4] which is in full accord with the present findings.

The activity of these oxide catalysts was found to become enhanced by the addition of alkali metal compounds as promoters which was attributed to their ability to create ionic centers of the type M^+O^- on the surface responsible for methane activation [4]. In the present work NaH_2PO_4 was chosen as promoter because it was speculated that well-dispersed polyphosphates formed at high temperatures might block particularly active surface sites and thus suppress non-selective reactions [14].

Fig. 3 shows the variation of C_2 selectivity and methane conversion with promoter "loading" (defined as the molar ratio of NaH_2PO_4 content over the total Ag amount of the catalyst) for fixed conditions of CH_4 : O_2 ratio and temperature. If compared with the data of figs. 1 and 2, the presence of the promoter causes a dramatic improvement of the selectivity, albeit higher promoter concentrations decrease the activity substantially. Because of the rather small specific surface area of the silver powder (only about 0.1 m^2/g as estimated from BET measurements)

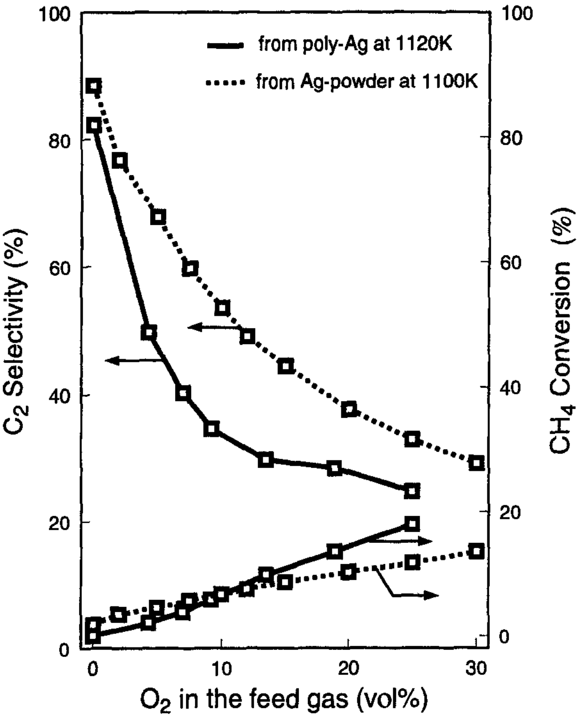

Fig. 2. Variation of activity and C_2 selectivity with O_2 content of the feed gas at fixed temperatures.

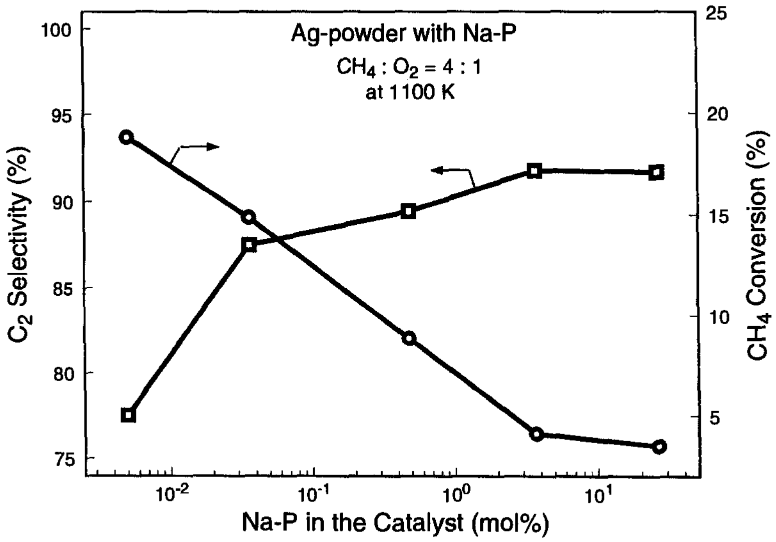

Fig. 3. Variation of activity and selectivity at fixed temperature and CH_4 : O_2 ratio with loading of the catalyst with NaH_2PO_4 as promoter.

already small NaH_2PO_4 concentrations will largely cover the surface if uniformly distributed. For example, a promoter content of 3.7% would be sufficient to coat the Ag surface by more than 100 monolayers, and the application of SEM and EDX (energy dispersive analysis of X-rays) indicated indeed that in this case only a very small fraction of the exposed surface area consists of Ag. As can be seen from fig. 3, lowering of the promoter loading was associated with a continuous increase of the activity, albeit also weak decrease of selectivity. The lowest applied promoter concentration of $5 \times 10^{-3}\%$ corresponds to approximately 0.2 monolayers and is characterized to have 77% C_2-selectivity and 18% conversion. This is equivalent to a C_2-yield of about 14% which has to be compared with the value of about 4% reached with the unpromoted catalyst under identical conditions. In addition, less than 1% of the methane was converted into oxygenated products such as methanol, formaldehyde etc. as identified by infrared spectroscopy.

Usually the reaction is operated under oxygen-limited conditions since excess of oxygen would favour total oxidation. As mentioned above, with the unpromoted Ag catalyst the optimum conditions are found for an oxygen content of about 10% in which case total consumption of gaseous O_2 is reached at about 1000 K. With promoted catalysts this optimum is shifted to higher oxygen concentrations. Figs. 4 and 5 display the CH_4 conversion and C_2 selectivity as well as the C_2 yield, respectively, for a Ag catalyst promoted by $5 \times 10^{-3}\%$ NaH_2PO_4 and operated at 1100 K as a function of the O_2 content in the feed gas. As with the unpromoted catalyst (cf. fig. 2) the reactivity increases continuously with oxygen concentration; however, the C_2 selectivity decreases less rapidly. As a consequence, the yield increases to a maximum value of 10% which reaches a plateau for O_2 concentra-

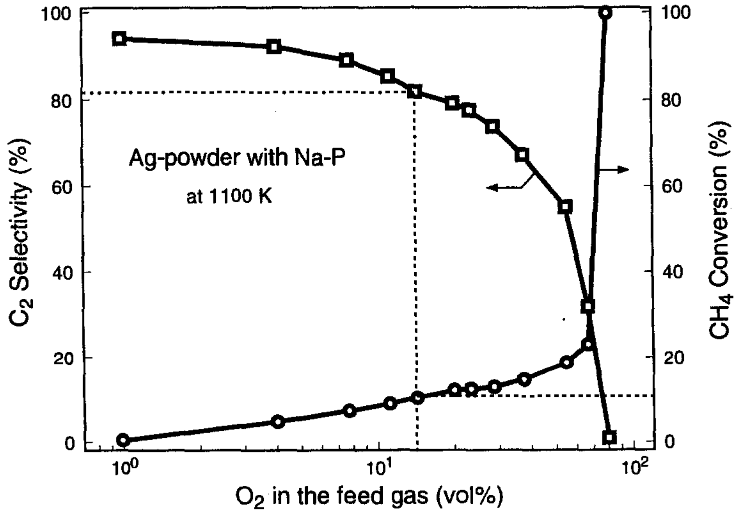

Fig. 4. Activity and selectivity of a promoted Ag catalyst ($5 \times 10^{-3}\%$ NaH_2PO_4) at 1100 K as a function of O_2 content in the feed gas (defined as the percentage of O_2 with respect to CH_4).

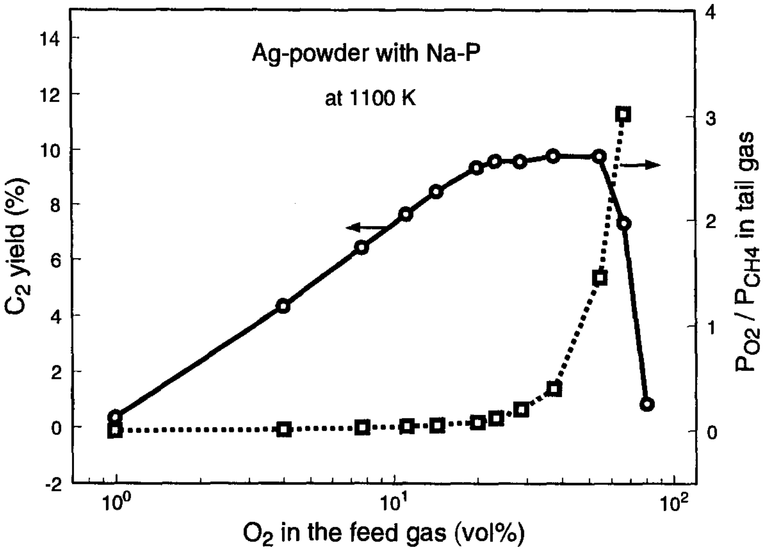

Fig. 5. C_2 yield and O_2 : CH_4 ratio of the outflowing gas as a function of the feed gas composition for a promoted Ag catalyst (5×10^{-3}% NaH_2PO_4) at 1100 K.

tions between 25 and 50%, where still appreciable amounts of oxygen remain unreacted in the tail gas (fig. 5). The fact that the optimum yield (at still rather high selectivity) is reached for such conditions suggests that the generation of CO_x products is not solely due to homogeneous reaction in the gas phase [2], but is also affected by heterogeneous reaction steps at the surface where the promoter possibly eliminates sites with high activities for non-selective oxidation.

The long-term stability of the catalyst is not noticeably affected by presence of low promoter concentrations. As can be seen from fig. 6 the C_2 yield of a catalyst promoted by 5×10^{-3}% NaH_2PO_4 operated at 1120 K remained practically constant over a period of 70 h, such as did the unpromoted catalyst. However, with high promoter concentrations the activity continuously degraded, presumably due to ongoing dispersion and diffusion of the promoter material across the catalyst until the whole surface is uniformly coated with an inactive layer.

Even with promoted Ag catalysts operated under optimum conditions, with the present experimental arrangement the yields rarely exceeded values of about 10%. Without entering detailed discussion of the underlying reaction mechanism it appears to be obvious that oxygen will attach C_2H_4 and C_2H_6 more readily than CH_4, and hence the desired products should be removed from the reacting zone as rapidly as possible. This requires special efforts in reactor design as was recognized in the quoted recent work of refs. [9,10], where yields of up to 88% could be reached, even with pure Ag catalysts. The present work demonstrates that considerable improvement can already be reached on the side of the catalyst by promotion with proper additives.

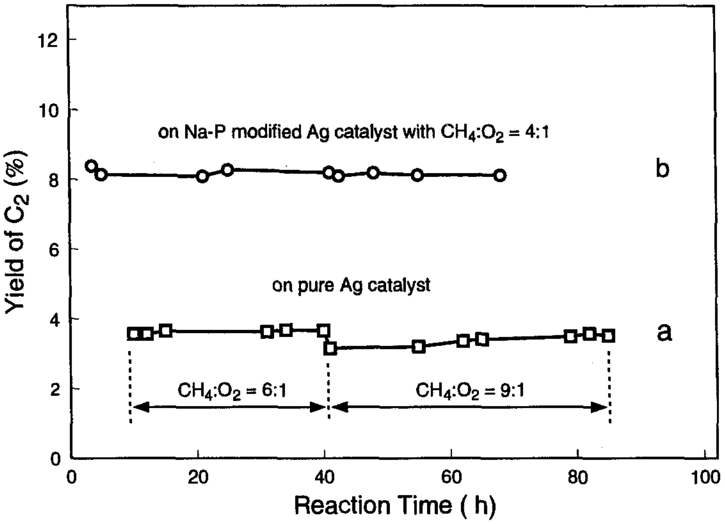

Fig. 6. Long-time stability of pure and NaH_2PO_4-promoted (5×10^{-3}%) Ag catalysts at 1120 K.

4. Conclusions

(1) At temperatures exceeding 1020 K bulk silver catalysts were found to be active in methane conversion to ethane, ethylene and small amounts of oxygenated hydrocarbons.

(2) Promotion with small amounts of NaH_2PO_4 causes a pronounced (i.e. up to threefold) increase of the C_2 selectivity and yield.

(3) The kinetic data suggest that undesired total oxidation is not dominated by homogeneous reaction in the gas phase but by surface processes.

(4) Further improvements of the selectivity and yield are to be expected by optimizing the reactor design.

Appendix

A.1. IDENTIFICATION OF REACTION PRODUCTS

The specific activity and selectivity of the catalysts were determined by analysing the MS intensities of the corresponding components at their characteristic peaks which were chosen to avoid possible overlaps in the signals of ion fragments of different molecules. The relative distributions of the MS intensities (ion currents) at the major fragments of the reactants and possible products are listed in table 1.

The relative partial pressure (P_n) of the component n was calculated by

$$P_n = \frac{I_n^+}{S_n} \tag{1}$$

Table 1
Relative ion currents of the fragments of the components relating to the experiment

m/e	H_2	CH_4	H_2O	CO	C_2H_4	C_2H_6	O_2	Ar	CO_2
2	100								
15		85							
16		100	1.8				18		
18			100						
27					51.8	33.4			
28				100	100	100			13
29					5	20.0			
30						22.0			
32							100		
40								100	
44									100

I_n^+ is the measured ion current of the component n at its characteristic peak and S_n is the corresponding sensitivity factor. The S_n values given by Balzers for the QMS120 mass spectrometer are listed in table 2. Due to an inevitable overlap at $m/e = 27$ for C_2H_4 and C_2H_6, the relative partial pressure of C_2H_4 was determined by subtracting the total intensity from the contribution of C_2H_6 at the $m/e = 27$ peak.

The conversion of methane, expressed as the fraction of methane reacted, was calculated using two different methods: one with respect to the direct measurement of the change in the partial pressure of methane during the reaction and the other with the total carbon balance in the tail gas.

Method 1:

$$\text{methane conversion (\%)} = \frac{P_{CH_4}^{in} - P_{CH_4}^{out}}{P_{CH_4}^{in}} \times 100\% . \tag{2}$$

Method 2:

$$\text{methane conversion (\%)} = \frac{(2P_{C_2}^{out} + P_{CO_2}^{out})}{P_{CH_4}^{out} + (2P_{C_2}^{out} + P_{CO_2}^{out})} \times 100\% . \tag{3}$$

Table 2
Relative sensitivity factors of the related components at these characteristic peaks

Related molecule	Mass of characteristic peak	Rel. sensitivity factor
H_2	2	1.3
CH_4	15	2.40
C_2H_4	27	1.05
C_2H_6	30	0.75
O_2	32	1.4
Ar	40	2.4
CO_2	44	1.3

Both methods yielded essentially identical data.

The C_2 selectivity, defined as the ratio of the number of moles of methane converted to C_2 to the total number of moles of methane reacted, is given by

$$C_2 \text{ selectivity } (\%) = \frac{2P_{C_2}^{\text{out}}}{(2P_{C_2}^{\text{out}} + P_{CO_2}^{\text{out}})} \times 100\% . \tag{4}$$

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