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OXIDATIVE DIMERISATION OF METHANE ON A SUPPORTED Pd-Ag CATALYST USING A DIFFUSION CONTROLLED CERAMIC WALL REACTOR

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Supported palladium-silver oxides were used as catalysts for the partial oxidation of methane by molecular oxygen in a tubular reactor with ceramic wall separation. The ceramic wall controls the O_2 supply in the catalyst bed. The results indicate that the reactor configuration can play an important role in methane oxidation. C_2H_6, C_2H_4, CO_2 and H_2O were obtained at temperatures less than 300 ° C. At this temperature any contribution from homogeneous gas phase reaction can be ruled out.

1. Introduction

Coupling methane oxidatively to form ethane and ethene is currently the subject of considerable research interest. Several research groups have concentrated their efforts in this area after the first report of Keller and Bhasin [1]. Lunsford et al. [2–4] have demonstrated that MgO and CaO, when promoted with alkali salts, oxidatively couple methane to ethane in the presence of oxygen. The Union Carbide work [1] describes a broad screening program involving single metal oxides. The Exxon work [5] investigated a multimetal oxide catalyst system containing a noble metal. The more promising catalysts include some members of the lanthanide oxides series [6,7] as well as a number of metal oxides promoted with group IA elements [8–10]. A major feature of these oxides is that they only became active for carbon-carbon bond formation reaction at high temperatures (> 700 ° C), and at such temperatures contribution from homogeneous gas phase reaction becomes significant [11,12]. Therefore fundamentally it is important to find a catalytic system capable of achieving considerable conversion and selectivity to C_2 hydrocarbons under moderate conditions. Recently Thampi et al. [13] have used a supported Pd catalyst and showed that it was able to catalyse this reaction at moderate temperatures like 315–400 ° C.

The present work is concerned with the use of supported noble metal and bimetallic catalysts such as Pd-M (where M = Cu, Rh, Mn or Ag). O_2 was used as the oxidant. A microporous membrane reactor wall was used to control the O_2 diffusion to the reaction zone. Such a controlled diffusion was necessary to inhibit the total oxidation of CH_4 to CO_2. A similar approach has been tried before by Stoukides et al. [14,15] by employing solid ion conducting oxides as a membrane wall, where the system functions like a fuel cell and an electrical potential was applied across the wall. The temperature of reaction remains high ($> 700\,^\circ C$) because of the poor ionic conductivity observed at lower temperatures. Therefore development of porous materials which can control O_2 diffusion without an electrical bias applied across the wall is useful for low temperature CH_4 dimerisation. Ionic conductivity is not important in such applications.

2. Experimental

2.1. CATALYTIC EXPERIMENTS

The catalytic experiments have been performed in a fixed bed, feed flow reactor at atmospheric pressure. Figure 1 shows a schematic diagram of the reactor. It consists of an outer quartz tube and an inner ceramic tube (SiO_2-Al_2O_3) with 7 mm internal diameter and 11 mm external diameter. The length of the ceramic tube was 41.5 mm. The catalyst was loaded inside the ceramic tube and retained in position by plugs of quartz wool. Methane was passed through the ceramic tube, while oxygen was passed through the outer quartz tube. The pores (125–300 μm) of ceramic tube allows diffusion of O_2 across the ceramic wall to the catalyst bed. The normal catalyst charge was 0.2 g unless otherwise specified.

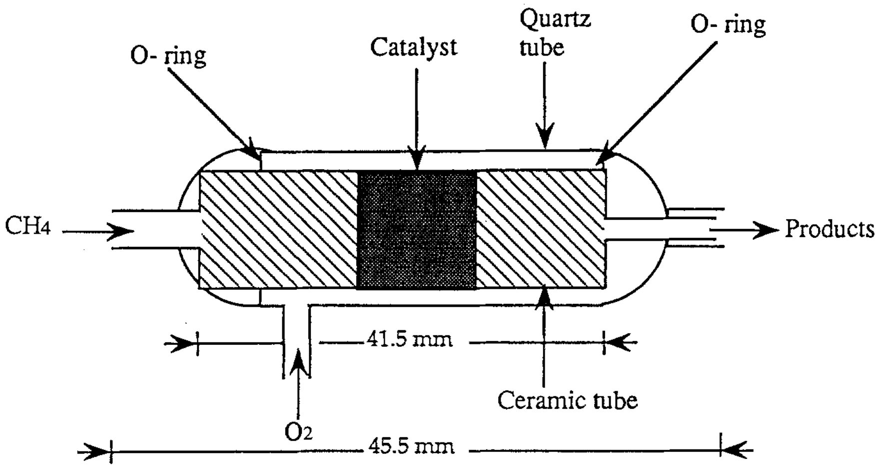

Fig. 1. Reactor configuration.

The catalyst was pretreated in flowing argon for 2 hrs at the reaction temperature. The reactor was heated using an electronically controlled tube furnace.

All the reaction products were analysed using a gas chromatograph equipped with a thermal conductivity detector. For analysing CO_2, CH_4 and C_2H_6 a porapak QS column was employed while for the analysis of CO a molecular sieve 5 Å column was used. Helium was used as the carrier gas (flow 60 ml/min).

2.2. CATALYST PREPARATION

Titania (P25) supplied by Degussa has been used as support. The supported catalysts have been prepared by impregnation with aqueous solutions of the metal nitrates of Pd and Pd-M (M = Mn, Rh or Cu) and dried at 170 ° C for 18 hours and subsequently calcined for 18 hours at 370 ° C.

Pd-Ag catalysts were prepared by a sputtering method in a system described elsewhere [16]. The targets were 80 nm diameter Pd or Ag foils bonded to the copper cathode disks by electrically conductive silver loaded epoxy adhesive. Supported bimetallic catalysts of Pd-Ag were prepared by successive metal deposition on TiO_2 by employing the pure metal targets. The system operated at 20 mA, 550 V.D.C. in an argon plasma at 0.75 mbar. Since there are no subsequent heat treatments or chemical treatments involved, sputtered catalysts are less likely to form Pd-Ag intermetallic compounds.

3. Results and discussion

When the catalysts were studied in a normal flow reactor where the reactant gases ($CH_4 + O_2$) pass in a single stream, only total oxidation was observed. By changing the reactor configuration, i.e, from mixed gas to separate diffusion limited oxygen admission as described in fig. 1, the catalytic properties have changed. In this configuration CH_4 and O_2 are admitted in separate streams but mixing occurs only inside the reactor due to O_2 transfer across the ceramic separator. C_2H_6 was then observed in the product stream. This showed the occurrence of oxygen transfer through the pores of ceramic tube, leading to a partial methane oxidation. Some of the catalysts studies in this work were active for the oxidative dimerisation of CH_4, when the reaction was carried out in a single feed operation mode as reported by Thampi et al. [13]. However the same catalysts were not active for C_2H_6 formation when the reaction was carried out in a reactor with ceramic tube separation. Only total oxidation of CH_4 to CO_2 occurred. These observations suggest that the reactor geometry could play an important role in the oxidative dimerisation of CH_4 and a controlled supply of O_2 alone would not ensure higher C_2 selectivity. The importance of reactor configuration and materials for CH_4 dimerisation have been reviewed extensively [17,18].

Table 1
Conversion and selectivity of different catalysts based on Pd-M/TiO_2. Flow = 12 ml/min, CH_4/O_2 = 5.

Catalysts	T (°C)	Conv. (%)	Selectivity		
			CO_2	% CO	C_2H_6
Pd/TiO_2 [a]	320	0.45	100	–	–
Pd-Cu/TiO_2	354	0.14	100		
	388	1.49	100	–	–
Pd-Rh/TiO_2	300	9.2	100	–	–
	400	11.5	98	2	–
Pd-Mn/TiO_2	295	8.6	100	–	–
	418	12.5	94	6	–
Pd-Ag/TiO_2	348	4.22	85	–	15
	380	10.2	95	–	5
Pd/TiO_2 [b]	380	2.70	100	–	–

[a] Catalyst prepared by impregnation.

[b] Catalyst prepared by sputtering.

$$\text{Selectivity to product\%} = \frac{\text{Conversion of methane to product}}{\text{Total conversion of methane}} \times 100.$$

Yield of C_2H_6% = Total CH_4 conversion(%) × Selectivity (%)/100.

Blank experiments were performed in the absence of the catalysts using an empty reactor. The experimental conditions for the blank experiments were similar to those in the presence of the catalyst. The results showed that no product was observed in the absence of the catalyst.

Oxidative transformation of methane was studied at 250–400 °C in the presence of catalysts. For the temperatures higher than 400 °C only total oxidation of methane was observed. The results in terms of conversion, selectivity and yield of C_2H_6, using different catalysts based on supported Pd-M (M = Mn, Rh, Cu or Ag) are summarized in table 1. With the impregnated catalysts of Pd and Pd-Cu/TiO_2, no C_2 compounds were produced and only total oxidation of methane to CO_2 occurred. The addition of Rh and Mn to Pd/TiO_2 produced small amounts of CO in addition to CO_2. However the Pd-Ag/TiO_2 catalysts showed a remarkable difference in their catalytic abilities by the formation of C_2H_6.

The Pd/TiO_2 without other metals and tested under same conditions showed weak catalytic activity in the total oxidation of methane. The oxidative coupling of methane occurred only on Pd-Ag/TiO_2 at a temperature less than 300 °C. These observations suggest that Pd-Ag/TiO_2 catalyst is the most promising catalyst among the metal oxides tested in this work. Thus we chose Pd-Ag/TiO_2 for detailed studies.

Conversion of methane and selectivity of the products are plotted in fig. 2 as a function of temperature. The experiments were carried out at a ratio CH_4/O_2 = 5,

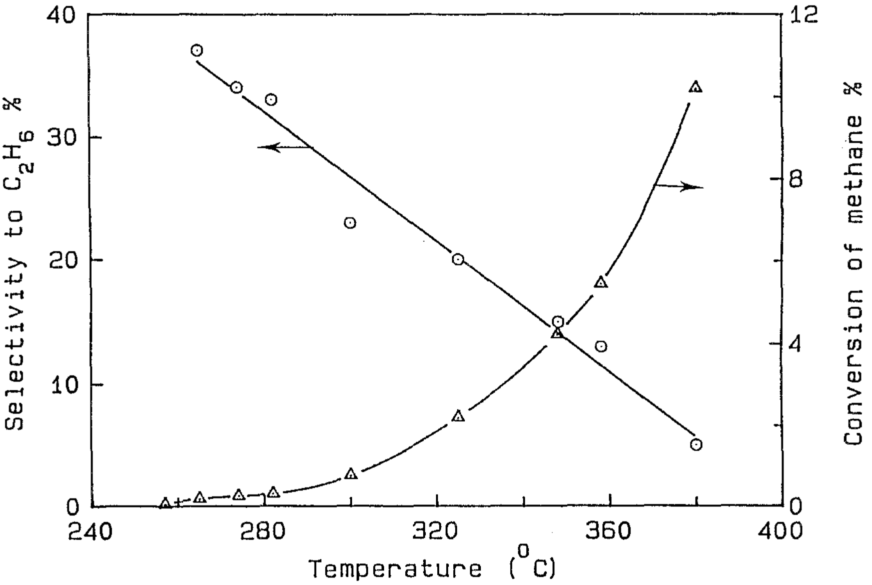

Fig. 2. Conversion and selectivity towards C_2H_6 as a function of temperature, with Pd-Ag/TiO_2 (0.58%-0.82%). $CH_4/O_2 = 5$, Flow = 12 ml/min.

with a total flow rate of 12 ml/min using 0.2 g of Pd-Ag/TiO_2. Conversion was lower for temperatures less than 300 ° C, and increased with increasing temperature, but the selectivity to ethane decreased as conversion increased. Consequently CO_2 selectivity increased. The highest yield of ethane was achieved with a temperature of about 358 ° C. The minimum temperature required to observe C_2H_6 was 260 ° C under the conditions quoted before.

The contact time has been reported to have important roles in catalytic oxidative coupling of methane due to the secondary oxidation of the hydrocarbon products [19–21]. In this work, the influence of residence time was investigated on Pd-Ag/TiO_2 (0.58%–0.80%) by varying the feed flow rate. The results are reported in terms of the inverse volumetric feed flow rate. Figure 3 displays conversion and products selectivity at 350 ° C using a CH_4/O_2 flow ratio of 5. Conversion of methane and yield of ethane increase with increasing residence time (decreasing feed flow rate). When methane was fed without oxygen, no reaction was observed for temperatures studied in this work, which is consistent with studies on methane pyrolysis where methane is converted to acetylene only at high temperatures ($T > 1000$ ° C) [22].

To obtain the optimum condition for C_2H_6 yield for Pd-Ag/TiO_2 (0.58%–0.80%), the influence of the methane to oxygen ratio during the oxidative coupling of methane has been investigated. The results are summarized in table 2. A feed flow rate of 12 ml/min and temperature of 350 ° C have been maintained during the experiment. The conversion decreased when the ratio increased, and

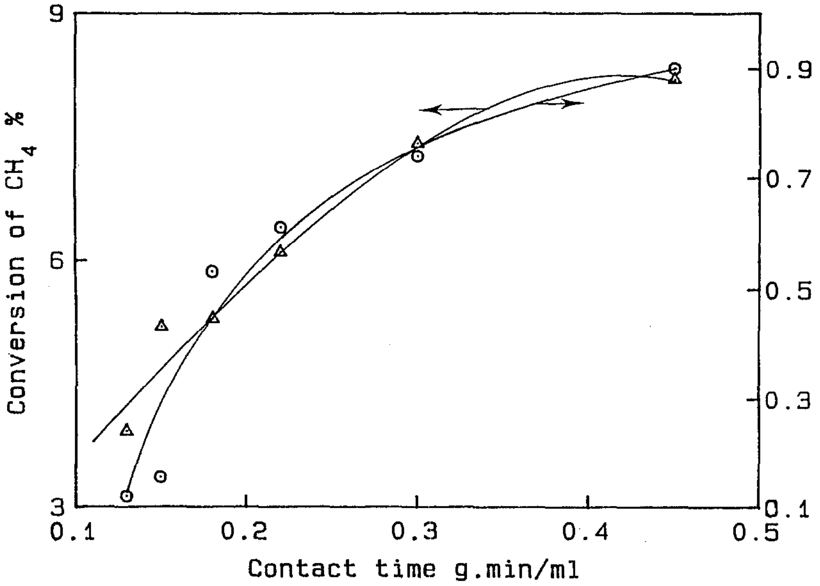

Fig. 3. Contact time dependance for methane conversion and C_2H_6 yield at 350 ° C.

the C_2H_6 selectivity registered only a marginal increase. CO_2 selectivity also decreased a little with increasing CH_4/O_2 ratio. Better yield of C_2H_6 was attained at lower CH_4/O_2 ratios. This indicates that smaller ratios are preferable for oxidative coupling of methane.

To examine the effect of silver loading on the catalytic properties, catalytic runs were carried out at different loading levels of Ag by changing the sputtering time (4 h for Pd; 2 h, 4 h and 6 h for Ag). The amount of Pd and Ag were estimated by elemental analysis. The results are reported in table 3. In the absence of Ag no C_2 compound was produced, and the amount of CH_4 converted over Pd/TiO_2 was less than that obtained over $Pd-Ag/TiO_2$. Among this set of catalysts the maximum methane conversion was achieved over the Pd-Ag (0.86%–

Table 2
Effects of ratio CH_4/O_2 over $Pd-Ag/TiO_2$ (0.58%–0.82%). Reaction conditions: $T = 350$ ° C, $P = 1$ atm, Flow = 12 ml.min^{-1}

Ratio CH_4/O_2	Conv. CH_4 (%)	S_{CO_2} (%)	$S_{C_2H_6}$ (%)	Yield C_2H_6 (%)
2	9.79	95	5	0.5
4	3.91	88	12	0.47
8	2.57	86	14	0.37
10	2.18	85	15	0.33
12	2.61	84	16	0.41
15	2.51	84	16	0.40
20	2.35	85	15	0.35

Table 3
Effects of Ag loading on supported Pd. Reaction condition: Mass of catalyst = 0.15 g, Flow = 12 ml/min, $CH_4/O_2 = 5$.

Catalysts	T (°C)	Conv. (%)	S_{CO_2} (%)	$S_{C_2H_6}$ (%)	Yield C_2H_6 (%)
Pd/TiO_2	300	0.07	100	–	–
2.17%	360	4	100	–	–
Pd-Ag	300	0.44	82	18	0.08
0.62%–0.73%	350	2.37	88	12	0.28
Pd-Ag	300	0.77	77	23	0.18
0.59%–0.82%	348	4.22	85	15	0.63
Pd-Ag	295	4.35	87	13	0.57
0.86%–2.82%	352	13.56	98	2	0.29

2.82%) catalyst, but the maximum yield of C_2H_6 with relatively high selectivity was obtained over Pd-Ag (0.59%–0.80%) catalyst. At temperature less than 300 ° C in the case of Pd-Ag (0.86%–2.82%) catalyst, ethylene was also detected in trace amounts. These results suggest that some amount of silver is required for selective methane oxidation. One reason for this can be the mediating role played by silver atoms by first adsorbing oxygen and then desorbing it as a suitable species for selective oxidation of methane.

4. Conclusion

The operating parameters were found to be critical in the conversion of methane. The reactor configuration, methane-to-oxygen ratio, residence time and temperature were each found to influence methane conversion and product selectivity. Residence time has a significant effect on the conversion of methane, but little effect on product selectivities. Another critical operating parameter for the oxidative coupling of CH_4 is the methane-to-oxygen ratio. Increasing the CH_4/O_2 ratio can produce a small increase in the production of C_2H_6, but a decreased methane conversion. It is clear that the catalysts tested here do not show high methane conversion and C_2-hydrocarbon selectivity as reported in the literature. However the most important conclusion of this study is that the oxidative dimerisation of methane can occur at very low temperatures such as 260 ° C. This is even less than reported by Thampi et al., [13] earlier. At these temperatures the homogeneous reaction of methane leading to products was never observed. This study also proves that the reactor configuration can be a critical parameter in the oxidative dimerisation of methane.

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