OXIDATIVE DIMERISATION OF METHANE ON SUPPORTED PALLADIUM OXIDE CATALYSTS

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Supported palladium oxide catalysts are able to convert CH_4 to C_2H_6, CO, CO_2, H_2 and H_2O at temperatures $\geq 315\,^\circ C$. Catalysts did not show any support effect when TiO_2, Al_2O_3, ZrO_2, La_2O_3 and MgO were used as supports. With sequential O_2 pulsing the catalyst showed long term activity when used at temperatures below 400 ° C. Addition of Pt increased selectivity whereas with Ga it decreased. Results indicate participation of lattice O_2 from catalyst in the reaction pathway.

1. Introduction

In the last few years oxidative dimerisation of CH_4 has become one of the frontier areas of catalytic research [1]. After a detailed scanning of several oxides as catalysts by Keller and Bhasin [2] a series of papers have appeared in this field. Several promising catalysts were discovered such as alkali metal doped alkaline earth oxides [3,4], promoted and unpromoted transition metal oxides [5,6], alkali and alkaline earth compounds [7], several lead compounds [7,8], rare earth oxides [9,10], perovskite oxides [11], layered oxyhalides [12], heteropolyoxometallates [13], etc. To our knowledge, no noble metal containing catalysts have been reported for this reaction. Keller and Bhasin [2] have used platinum oxide on alumina but found little activity at 800 ° C. Almost all the catalysts require severe operating conditions such as temperatures in the range of 700–900 ° C to gain meaningful CH_4 conversions and C_2^+ selectivity. This is a major disadvantage for its practical application. CH_4 conversion was very small when N_2O or O_3 was used as oxidants at moderate temperatures (350 to 700 ° C) [14,15]. In this case CH_2O and CH_3OH are often produced as products. Therefore there is a scope to look for alternate catalysts which can oxidatively dimerise CH_4 at rather mild conditions without using N_2O or O_3. While using severe temperatures or when starting with oxidants like N_2O or O_3, it is difficult to estimate the relative

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contribution of heterogeneous vs homogeneous reactions leading to products. Questions have been asked about the relative importance of these two widely different reaction schemes during Ch_4 oxidation [15–18]. The prevailing view is that the heterogeneous catalyst is mostly a source of radicals providing reactive species for gas phase homogeneous reactions [19]. Therefore it is also fundamentally important to search for new catalysts operating at lower temperatures where the contribution from gas phase homogeneous reactions is small. In this paper we are reporting on noble metal catalysts useful for CH_4 oxidation.

2. Experimental

For all experiments a supported catalyst was used. Following were the supports: TiO_2 (P25), ZrO_2, Al_2O_3, La_2O_3 and MgO (all oxides except MgO were supplied by Degussa A.G., W. Germany; MgO was obtained from Fluka). Catalysts were prepared by impregnation or deposition-precipitation or exchange. For impregnation, required amounts of Pd ions in the form of $Pd(NO_3)_2$ (Fluka) in aqueous solution was impregnated over the support and the resulting powder was dried at 120 °C for 16 hours and subsequently calcined for 10 hours at 370 °C. For deposition-precipitation, $PdCl_2$ hydrate (K&K Labs., USA) was used as the starting material. The support oxide was dispersed in a solution containing $PdCl_2$ in 0.1N HCl at 70 °C and then the pH of the solution was slowly raised to 10.6 by the progressive but slow addition of 0.1N NaOH. After evaporating off water, the powder was calcined to 180 °C for 18 h and 370 °C for another 18 h. The powder was then dialysed for 4 days to remove the NaCl. The catalyst was dried and stored. This procedure was followed to get relatively uniform particle dispersion of palladium oxide on the support.

Catalytic experiments were carried out in a fixed bed quartz reactor at atmospheric pressure. The reactor was a quartz U-type (65 cm × 1 cm I.D). The catalyst (100 mg) was held in place by plugs of quartz-wool. The catalysts were pre-treated in O_2 free Ar (purified and passing through oxisorb; pure Ar was obtained from Carbagas, Switzerland) for 2 h at the initial reaction temperature. However the reaction temperature was varied afterwards while CH_4 was on stream to study reactions at higher temperatures without further pre-treatments. All gas flows were measured through pre-calibrated rotameters before entering the reactor. Analysis was carried out by using gas chromatographs equipped with thermal conductivity detectors. For CO analysis a molecular sieve 5 Å column and for CO_2, CH_4, C_2H_6 and other hydrocarbons a porapak QS column were used with He carrier gas. For analysing H_2, a molecular sieve 5 Å column with Ar carrier gas was employed.

For allowing pulses of O_2 in between catalytic runs when necessary, a six port injection valve having a loop of 2 ml per pulse was used. The reactor was externally heated using a furnace fitted with an electronic controller.

Elemental analysis was carried out to determine the level of impurities like C and Cl^-. The level of these impurities on a fresh catalyst was always below 0.3%. Unless and otherwise mentioned, all experiments were carried out under pure CH_4 (99.99% Carbagas) stream without simultaneous feeding of O_2 or any other diluents.

3. Results and discussions

Preliminary data on oxidative dimerisation of CH_4 over supported Pd catalysts show that the conversion does not depend on the nature of catalyst preparation in any significant manner. All Pd supported catalysts showed similar behaviour independent of the nature of support on its metal dispersion. Main products of reaction were CO_2, CO, H_2, H_2O and C_2H_6. At temperatures above 450 ° C, C_2H_4 was also a product. The presence of oxygen containing compounds indicate the involvement of lattice oxygen from the catalyst with simultaneous reduction of the metal oxide. The minimum temperature required to observe C_2H_6 was 315–320 ° C under the present experimental conditions. To our knowledge this is the minimum temperature ever reported for oxidative dimerisation of CH_4 without the use of oxidants like N_2O. Figure 1 shows a plot of % conversion and % selectivity of C_2H_6 as a function of temperature for a 4.4% palladium oxide/ZrO_2 catalyst. The WHSV of the reaction was 4.7 (CH_4 flow = 12 ml/min.). As the temperature was raised from 320 ° C to 405 ° C, the % conversion increased by two-fold, but selectivity goes up by a factor of more than 5. It was noticed that

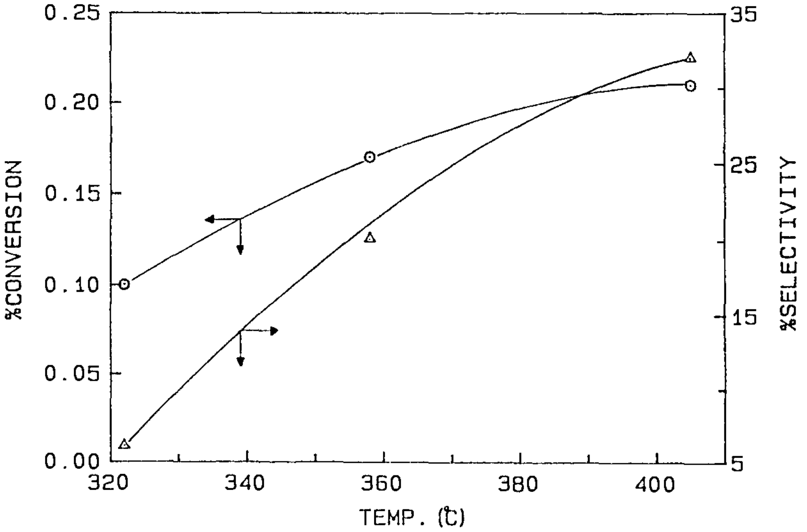

Fig. 1. Conversion and selectivity as a function of temperatures when the system is in Phase II. Above 410 ° C, the system is not in steady state sufficiently long. See text for more details. Catalyst: 4.4% palladium oxide/TiO_2 (100 mg). CH_4 flow = 12 ml/min (WHSV = 4.7).

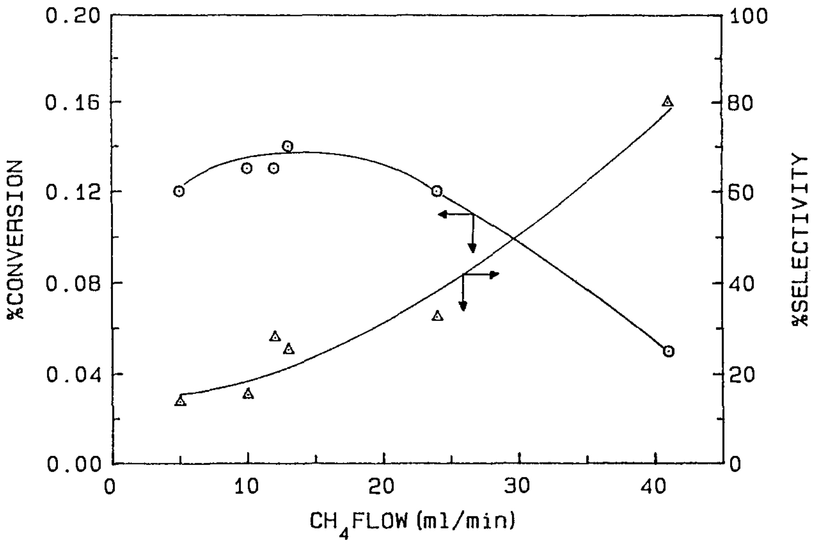

Fig. 2. Conversion and selectivity as a function of CH_4 flow for 100 mg 4.4% palladium oxide/ZrO_2 catalyst. $T = 358\,°C$.

when the catalyst was operated at temperatures above 400 °C, the deactivation was quick and the selectivity dropped from 68% to 40% and conversion from 0.2% to 0.1% by 3 h. At lower temperatures the catalytic deactivation was relatively slower and all the values plotted in figs. 1–4 remained steady for at least 2 hours. In the first 1 h (Phase I), CO_2 and CO levels were high followed by a steady conversion level for ca. 2–10 h (Phase II, data points in figs. 1–4) depending on

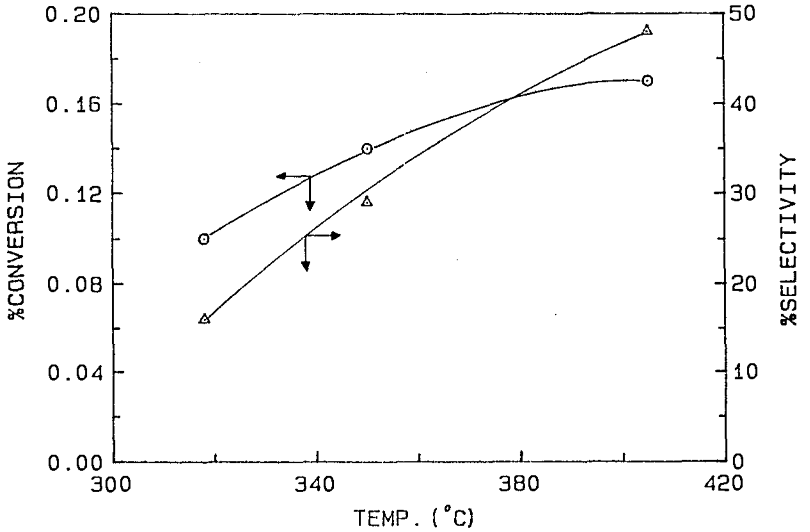

Fig. 3. Conversion and selectivity as a function of temperature for 100 mg (4.4%Pd +1% Pt) oxide/TiO_2. All other conditions are the same as that of fig. 1.

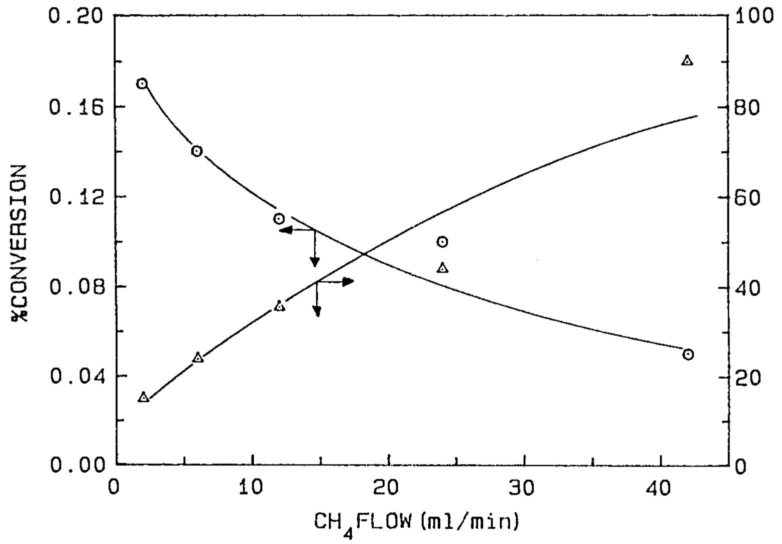

Fig. 4. Conversion and selectivity as a function of CH_4 flow for 100 mg (4.4% Pd+1% Pt) oxide/TiO_2 catalyst. $T = 350\,^{\circ}C$.

the reaction temperature after which the catalyst begins to deactivate (Phase III). When the catalyst becomes totally inactive, 2–3 pulses of O_2 at the reaction temperature completely regenerate the catalyst back to Phase I. By this sequential pulse operation, the useful life of the catalyst remained for several weeks without any loss in activity. Simultaneous feeding of CH_4 and O_2 leads to low C_2 selectivity but high conversion. Keller and Bhasin also observed this behaviour with their oxide catalysts [2]. A 4.4% palladium oxide supported catalyst when operated at temperatures above 450 ° C, showed conversion levels similar to that of 350 ° C, but with $> 95\%$ C_2 selectivity where C_2H_4 (25% of C_2 products) was also detected. Such catalysts degraded quickly and frequent O_2 pulses were necessary to regenerate the material. However, these catalysts did not produce any C_2 hydrocarbons when operated afterwards at temperatures below 420 ° C showing that the catalyst was irreversibly damaged at high temperature and lost its selectivity. This is understandable since at ca. 500 ° C, most of these oxide supports (especially TiO_2 and ZrO_2) get reduced in the presence of H_2 (a product of the reaction). When CH_4 was mixed with 0.1% or 0.2% O_2, the minimum temperature required to produce C_2H_6 went up to 385 ° C with better conversions. For instance at 420 ° C with 0.2% O_2 in the feed, a conversion of 0.12% and C_2 selectivity exceeding 75% was registered after an hour of reaction (phase II). In 3 h, the conversion was only 0.05% with 50% selectivity. After 16 h, conversion was 0.05% and selectivity was 20%.

Figure 2 is a plot of % conversion and selectivity vs. CH_4 flow. It shows that higher conversions were achieved with $CH_4 = 12$ ml/min. (WHSV = 4.7), but better selectivities were attained at higher flow rates.

When 1% Pt was added to 4.4% palladium oxide/TiO_2 catalyst, the degree of conversion did not improve, but selectivity improved a little (fig. 3). The behaviour of this catalyst towards the variation of WHSV was also different when compared to Pt free palladium oxide catalyst (fig. 4). Other elements like Ga when added increased the conversion but decreased the C_2 selectivity. At 410 ° C and WHSV 4.7, % conversion was 0.40, but selectivity was only 9.2%.

The catalyst sample did not show any increase in C content after the reaction. This suggests that catalyst deactivation is not due to coking. In fact, several catalyst samples after the reaction registered a net decrease in the C level showing that during the reaction, a part of the chemisorbed or physisorbed impurities (notably CO_2 and CO_3^{2-}) were removed.

Another possible route to loss of activity is the removal of lattice O_2 from catalyst. CH_4 reacts with O_2 from the lattice ($O_{2(s)}$) producing CO, CO_2 and other products.

$$CH_4 + 2O_{2(s)} \rightarrow CO_2 + 2H_2O \tag{1}$$

$$2CH_4 + 3O_{2(s)} \rightarrow 2CO + 4H_2O \tag{2}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{3}$$

$$H_2 + \tfrac{1}{2}O_{2(s)} \rightarrow H_2O \tag{4}$$

$$2CH_4 + \tfrac{1}{2}O_{2(s)} \rightarrow C_2H_6 + H_2O \tag{5}$$

A high level of H_2 generation was observed during the initial stages of reaction. During the first 2 h, the rate of H_2 production was of the order of 2.5 μmol/min. The loss of O_2 from the lattice reduces the catalyst, ie., palladium oxide to Pd. In fact reduction of palladium oxide was noticed when XPS measurements were carried out on a spent catalyst after reaction with methane. This data will be presented in a separate manuscript [20].

4. Conclusions

Oxidative dimerisation of CH_4 was hitherto achieved at severe operating conditions in the presence of non-noble metal catalysts. The present study shows for the first time that a noble metal oxide is able to catalyse this reaction at $T \geqslant 315\,°C$ without using oxidants like N_2O or O_3. The authors are confident that the present low level of conversion can be improved with noble metal catalysts along the same lines used in this work.

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