Selective oxidation of methane to carbon monoxide on supported palladium catalyst


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Abstract

Partial oxidation of methane by oxygen has been studied on a number of supported palladium catalysts in the temperature range of 373-1023 K at GHSV's ranging from 5000 to 20,000 h⁻¹ and with CH₄:O₂ ratio range from 4:1 to 8:1. The supports studied included oxides of metals belonging to Group IIIa and IVa of the periodic table, oxides of representative metals belonging to the lanthanide series, γ-Al₂O₃ and SiO₂. CO, CO₂, H₂O and H₂ were the only detectable reaction products on all the catalysts. The CO selectivity on all catalysts increases with an increase in reaction temperature, a decrease in GHSV and an increase in the CH₄:O₂ ratio. Carbon monoxide is formed with greater than 90% selectivity on palladium support on all the oxides, excepting SiO₂, studied here at a temperature of 1023 K, GHSV of 5000 h⁻¹ and with a feed composition of 40% CH₄, 5% O₂ and 55% Ar.

Keywords: carbon monoxide, methane selective oxidation, palladium.

INTRODUCTION

Methane is the principal constituent of natural gases. Most of this gas is currently being burnt in the absence of economic processes for converting this gas into useful products. A considerable amount of effort is, therefore, being given by researchers to convert methane to chemical feedstocks such as methanol, C₂-hydrocarbons and syngas.

This note deals with selective oxidation of methane by oxygen to carbon monoxide on palladium supported on oxides of metals in the Group IIIa and IVa of the periodic table, CeO₂, γ-Al₂O₃ and SiO₂.
EXPERIMENTAL

Sample preparation

Specpure $\text{Sc}_2\text{O}_3$, $\text{Y}_2\text{O}_3$, $\text{La}_2\text{O}_3$, $\text{TiO}_2$, $\text{ZrO}_2$, $\text{HfO}_2$, $\text{CeO}_2$ and $\gamma$-$\text{Al}_2\text{O}_3$ used as supports were obtained from Johnson-Matthey. $\text{SiO}_2$ was supplied by Uni-lever. Each of these supports was loaded with 1% Pd by weight. A few drops of water were added to the required amount of specpure $\text{Pd(NO}_3\text{)}_2$ (Johnson-Matthey) and a support to form an homogeneous paste. The paste was then calcined at 823 K in air to produce the unreduced catalyst.

Surface area measurement

The surface area of the samples was determined by the single point BET method using a Micromeritics pulse chemisorb apparatus (Model 2700).

Catalytic activity measurements

Catalytic studies were carried out in a quartz fixed bed microreactor operated at a pressure of 1 atm. Catalyst particles (200–400 $\mu$m) were packed up to a length of 30 mm inside a 20 cm long quartz reactor tube which had an internal diameter of 1–1.2 mm. The reactor tube was singly placed inside a bore cut out from a cylindrical stainless steel block heated by cartridge heaters. All gases (99.99% purity) used in the present investigation were obtained from BOC. Appropriate amounts of methane, oxygen and argon were admitted separately using Brooks mass flow controllers and were pre-mixed before entering the reactor. The products were analysed by a Hewlett-Packard gas chromatograph (series 5890) coupled with a multichannel mass spectrometer (series 5970). The gases were eluted through a poraplot Q column in the GC.

Catalytic studies were carried out on both the unreduced catalysts as well as on catalysts obtained by heating in-situ each catalyst in a flow of hydrogen at 673 K for one hour.

RESULTS AND DISCUSSION

$\text{CO}_2$, $\text{CO}$, $\text{H}_2\text{O}$ and $\text{H}_2$ were the only detectable products of oxidation of methane on all the catalysts studied in the present investigation. The variation of the rates of carbon monoxide and carbon dioxide produced on a reduced Pd/ $\text{CeO}_2$ catalyst at varying reactor temperatures using a feed of 40% $\text{CH}_4$, 5% $\text{O}_2$ and 55% $\text{Ar}$ at a GHSV of 5000 h$^{-1}$ (293 K and 1 atm) is shown in Fig. 1. For comparison the product distribution obtained with $\text{CeO}_2$ catalyst under the same conditions are also shown in the same figure.

Oxidation of methane on $\text{CeO}_2$ results in the formation of carbon dioxide at
Temperature, K  

Fig. 1. Rates of carbon monoxide (▲ △) and carbon dioxide (● ○) produced on (a) reduced Pd/CeO₂ (open symbols) and (b) CeO₂ (filled symbols) at different reaction temperatures using a feed consisting of 40% CH₄: 5% O₂: 55% Ar at a GHSV of 5000 h⁻¹ (293 K and 1 atm).

all temperatures above 573 K and this is found to be in agreement with previously reported results [1]. In contrast, carbon dioxide produced with a reduced Pd/CeO₂ catalyst passes through a maximum at a temperature ca. 773 K. At higher temperatures the amount of carbon dioxide formed decreases and carbon monoxide produced rapidly increases. At a temperature of 1023 K, carbon monoxide is produced with 99.6% selectivity whilst on CeO₂ catalyst carbon dioxide is produced with 99% selectivity. Mass spectroscopic analysis of the reaction product at this temperature showed that hydrogen was the other major product on reduced Pd/CeO₂.

Oxidation of methane by oxygen on an unreduced Pd/CeO₂ catalyst shows a similar trend in variations of carbon dioxide and carbon monoxide with the reactor temperature; but their selectivities were found to be different from those observed on a reduced catalyst, for example, at 1023 K the percentage carbon monoxide and carbon dioxide selectivities were 68 and 32% respectively.

The variation in percentage carbon monoxide and carbon dioxide selectivities of a reduced Pd/CeO₂ catalyst with a change in GHSV at 1023 K using feed compositions of (a) 40% CH₄, 10% O₂ and 50% Ar and (b) 40% CH₄, 5% O₂ and 55% Ar is shown in Fig. 2. It is seen that both an increase in contact
Fig. 2. Percentage carbon monoxide (▲ △) and carbon dioxide (● ○) selectivities of a reduced Pd/CeO$_2$ catalyst at 1023 K for different GHSV using feed compositions of (a) 40% CH$_4$: 10% O$_2$: 50% Ar (open symbols) and (b) 40% CH$_4$: 5% O$_2$: 55% Ar (filled symbols).

TABLE 1

Catalytic activity of palladium supported on different oxides at 1023 K

<table>
<thead>
<tr>
<th>Support</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>CH$_4$ conversion (%)</th>
<th>Rate of conversion of CH$_4$ per unit BET area (μmol s$^{-1}$ m$^{-2}$)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc$_2$O$_3$</td>
<td>12.1</td>
<td>39</td>
<td>0.66</td>
<td>99.6</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>14.39</td>
<td>66.9</td>
<td>1.53</td>
<td>99.3</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>14.37</td>
<td>49.3</td>
<td>0.44</td>
<td>99.5</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>50.2</td>
<td>33.4</td>
<td>0.13</td>
<td>92.3</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>4.0</td>
<td>36.7</td>
<td>1.10</td>
<td>98.3</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>4.2</td>
<td>53.2</td>
<td>1.56</td>
<td>99.3</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>1.8</td>
<td>35</td>
<td>1.80</td>
<td>99.4</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>14.8</td>
<td>58.0</td>
<td>0.90</td>
<td>99.5</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>99.27</td>
<td>23.2</td>
<td>0.16</td>
<td>63.7</td>
</tr>
</tbody>
</table>
time with the catalyst and an increase in CH₄:O₂ ratio, favour carbon monoxide formation.

One possible mechanism that may explain the above results involves adsorption of methane to form a surface \( \text{CH}_x \) species which desorbs to form carbon dioxide in the gas phase \([2]\). The \( \text{CH}_3 \) species in parallel undergoes a surface reaction probably via intermediate formation of other \( \text{CH}_x \) species to form carbon monoxide. At higher temperatures the surface reaction rate exceeds desorption rate of the \( \text{CH}_3 \) species thus at temperatures of 1023 K or above only carbon monoxide is produced. It is also possible that at temperatures above 923 K (Fig. 1) the carbon dioxide initially produced reacts with surface \( \text{CH}_x \) species to form carbon monoxide and hydrogen.

It is well known that underlying supports, as used in the present investigation, show varying catalytic activities for the oxidation of methane by oxygen (for example, see ref. 3). In contrast to the pure supports only, the supported palladium catalysts show high carbon monoxide selectivities at temperatures above 923 K and no \( \text{C}_x \)-hydrocarbons were observed at any of the temperatures studied here. At a temperature of 1023 K, a GHSV of 5000 h⁻¹ (293 K and 1 atm) and a feed composition of 40\%, \( \text{CH}_4 \), 5\% \( \text{O}_2 \) and 55\% \( \text{Ar} \), it was found that palladium supported on all the oxides excepting on \( \text{SiO}_2 \) show more than 90\% carbon monoxide selectivity. The rate of conversion of methane was, on the other hand, found to be strongly dependent on the support used. The results are summarised in Table 1. The results on reduced Pd/\( \gamma \)-Al₂O₃ catalysts obtained in the present investigation are in agreement with those reported earlier \([4]\).

Detailed characterisation and chemisorption studies are therefore necessary in order to explain the observed variation in the catalytic activity of palladium dispersed on different supports.

REFERENCES