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Dry reforming of methane to synthesis gas over supported molybdenum carbide catalysts

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The dry reforming of methane at elevated pressure over supported molybdenum carbide catalysts, prepared from oxide precursors using ethane TPR, has been studied. The relative stability of the catalysts is $Mo_2C/Al_2O_3 > Mo_2C/ZrO_2 > Mo_2C/SiO_2 > Mo_2C/TiO_2$, and calcination of the oxide precursor for short periods was found to be beneficial to the catalyst stability. Although the support appears to play no beneficial role in the methane dry reforming reaction, the alumina-supported material was stable for long periods of time; this may be important for the production of pelletised industrial catalysts. The evidence suggests that the differences in the stabilities may be due to interaction at the precursor stage between MoO_3 and the support, while catalyst deactivation is due to oxidation of the carbide to MoO_2, which is inactive for methane dry reforming.

Keywords: supported molybdenum carbide, methane dry reforming, syngas

1. Introduction

Recently, it was reported that under certain conditions the carbides of molybdenum and tungsten are active catalysts for the reforming of methane to synthesis gas, using steam (1), carbon dioxide (2) or air (3) as the oxidants under stoichiometric conditions, and with no carbon deposition [1–3]:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad \Delta H^0_{298} = +206\ \mathrm{kJ\,mol^{-1}}, \quad (1)$$

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \quad \Delta H^0_{298} = +247\ \mathrm{kJ\,mol^{-1}}, \quad (2)$$

$$CH_4 + \tfrac{1}{2}O_2 \rightleftharpoons CO + 2H_2 \quad \Delta H^0_{298} = -38\ \mathrm{kJ\,mol^{-1}}. \quad (3)$$

These three reactions are extremely important for the utilisation of natural gas, and the eventual production of synfuels (e.g., by Fischer–Tropsch synthesis or via methanol). The conventional supported nickel catalysts used for methane reforming are active for carbon formation, which leads to reactor plugging, while non-coking alternatives are usually based on expensive and rare noble metals, such as ruthenium, rhodium or iridium. The early transition metals, on the other hand, are abundant and relatively cheap, and many methods exist for the synthesis of their carbides with high surface areas suitable for catalysts [4]. It has been suggested that they can replace the scarce and expensive noble metals for a number of catalytic applications [5].

The molybdenum and tungsten carbides were found to have a comparable activity to some noble metal catalysts (e.g., 5% Ir/Al_2O_3) and were extremely stable at elevated pressure, with no deactivation observed over the duration of an experiment (>3 days); the catalysts deactivated at atmospheric pressure, due to oxidation of M_xC to MO_2. The success of their application to methane reforming has been associated with there being similarities between these carbides and Ru and Pt [6].

To date the majority of research on the application of early transition metal carbides to methane reforming has concentrated on the bulk carbides. In this paper we have explored the use of supported molybdenum carbide as a catalyst for methane dry reforming to synthesis gas, and have studied the effect of the support on the stability of the catalysts.

2. Experimental

2.1. Catalyst preparation and characterisation

The following procedure, which was used to prepare the precursor supported MoO_3 materials, is based on that of Xie and Tang [7]. A colourless solution of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ – Fisons, mw = 1235.86) was stirred with the appropriate amount of support material (γ-Al_2O_3, Akzo, high purity, 250–355 μm; SiO_2, Grace, acid washed, 250–355 μm; TiO_2, Norton, high purity, 250–355 μm; ZrO_2, Norton, XZ 16052, 250–355 μm). This slurry was dried for 12 h at 423 K and calcined for either 4 or 24 h at 723 K in air. Due to the variability in surface areas and characteristics displayed by different support materials two series of materials were prepared. In the first a theoretical monolayer dispersion of catalyst precursor was prepared on each support in an attempt to provide

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consistent surface characteristics, although as the surface areas of each support are different this resulted in disparate quantities of active catalyst. The monolayer capacity can be estimated by using the simple close-packed monolayer model [7]. Assuming that O^{2-} ions from the MoO_3 form a close-packed layer on the surface of the support, the Mo^{6+} ions occupy the interstices formed by O^{2-} ions and, taking 1.4 Å for the atomic radius, the weight of MoO_3 required to achieve a monolayer was calculated. In the second catalyst series, a constant amount of molybdenum oxide (3.8 wt%) was loaded onto each support.

The supported Mo_2C methane reforming catalysts were prepared by the temperature-programmed reaction (TPRe) of the supported MoO_3 precursor under a flowing ethane/hydrogen mixture. This allowed lower catalyst synthesis temperatures to be employed than with the more common TPRe method using methane [8–11]. Catalyst synthesis involved heating the precursor materials, under 10% v/v C_2H_6/H_2, from room temperature to 900 K, at a heating rate of 1 $K\,min^{-1}$. Normally the catalysts were prepared *in situ* and tested immediately. For characterisation studies, the carbide materials were passivated under flowing 1% O_2/N_2 for 12 h, since these materials are readily oxidised in air.

Support surface areas were determined using an all-glass high vacuum line, and calculated from the N_2 BET isotherms. X-ray diffraction (XRD) was carried out using a Philips PW1710 diffractometer with Cu Kα radiation.

2.2. Catalyst testing and product analysis

The apparatus used in this investigation was a modified version of the commercial Labcon microreactor described previously [3]. The catalyst sample was placed between two quartz wool plugs in the centre of a 4 mm i.d. silica tube and inserted into a vertical Severn Science tube furnace. Calibration of the furnace allowed accurate and reproducible reaction temperatures to be used in the experiments, and no significant cooling or heating effects due to reaction endothermicity were observed. The exit gas stream from the reactor passed through a Tescom two-stage back-pressure regulator, which provided a smooth pressure drop across the reactor bed. All the pipework was heated to prevent condensation of the products.

Product analysis was carried out using a Hewlett–Packard 5890II gas chromatograph, fitted with both a thermal conductivity detector, and a methanator/flame ionisation detector. Separation of the products was achieved using a 3 m Porapak Q packed column, with argon carrier gas. Reference data and pure component injections were used to identify the major peaks, and response factors for the products and reactants were determined and taken into account in the calculation of the conversion and product distribution. In all cases carbon balances were better than 97%. Slight deviation in the expected conversions and selectivities at the start of the reactions is attributed to the large dead volume of the reactor and the time taken for the reactions to reach equilibrium at elevated pressure.

3. Results and discussion

3.1. Characterisation of supported MoO_3 and Mo_2C

Figure 1 depicts the XRD patterns of the SiO_2 support material, and the theoretical monolayer MoO_3 supported on SiO_2 before and after ethane carburisation. All the peaks due to MoO_3 in pattern (2) have disappeared, and new peaks assignable to β-Mo_2C are seen; this phase is similar to that observed in the bulk carbide samples used in the earlier studies on methane oxyreforming [3]. None of the starting orthorhombic MoO_3, or reduced oxide, MoO_2, can be seen in the pattern for Mo_2C/SiO_2, and no MoC was observed. The broadening and weakening of the peaks after carburisation indicate that the highly crystalline MoO_3 present on the support was converted to molybdenum carbide with a relatively high surface area. The sample probably consists of discrete regions of Mo_2C crystallites dispersed over SiO_2, or in other words this sample is made up of small areas of bulk Mo_2C. The other supported systems of Mo_2C/Al_2O_3, Mo_2C/TiO_2 and Mo_2C/ZrO_2 exhibited closely analogous results, and the XRD data are not shown.

3.2. Dry reforming over the supported molybdenum carbide catalysts

The catalysts which were prepared with a theoretical monolayer loading were tested for the stoichiometric dry reforming of methane with carbon dioxide, at 1220 K, 8 bar and at a GHSV of 2.6×10^3 h^{-1}; all the MoO_3 precursor materials used in this section were calcined for a period of 4 h. Earlier work had shown that kinetic parameters are very difficult to obtain with the carbides due to fast deactivation of the catalysts under the differential conditions needed for kinetic measurements, and therefore lifetime studies were carried out as described elsewhere [1–3].

The lifetime studies for Mo_2C/SiO_2, Mo_2C/Al_2O_3 and Mo_2C/ZrO_2 are shown in figure 2. Data for Mo_2C/TiO_2 is not shown as its activity was very low (see table 1). The initial conversion values for the three catalyst sys-

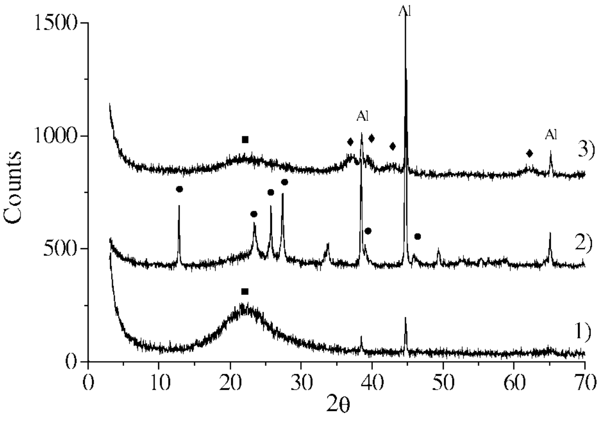

Figure 1. XRD pattern of (1) SiO_2, (2) MoO_3/SiO_2 and (3) Mo_2C/SiO_2 formed by C_2H_6 TPRe of MoO_3/SiO_2 ((■) SiO_2, (●) MoO_3, (◆) Mo_2C; Al = aluminium sample holder).

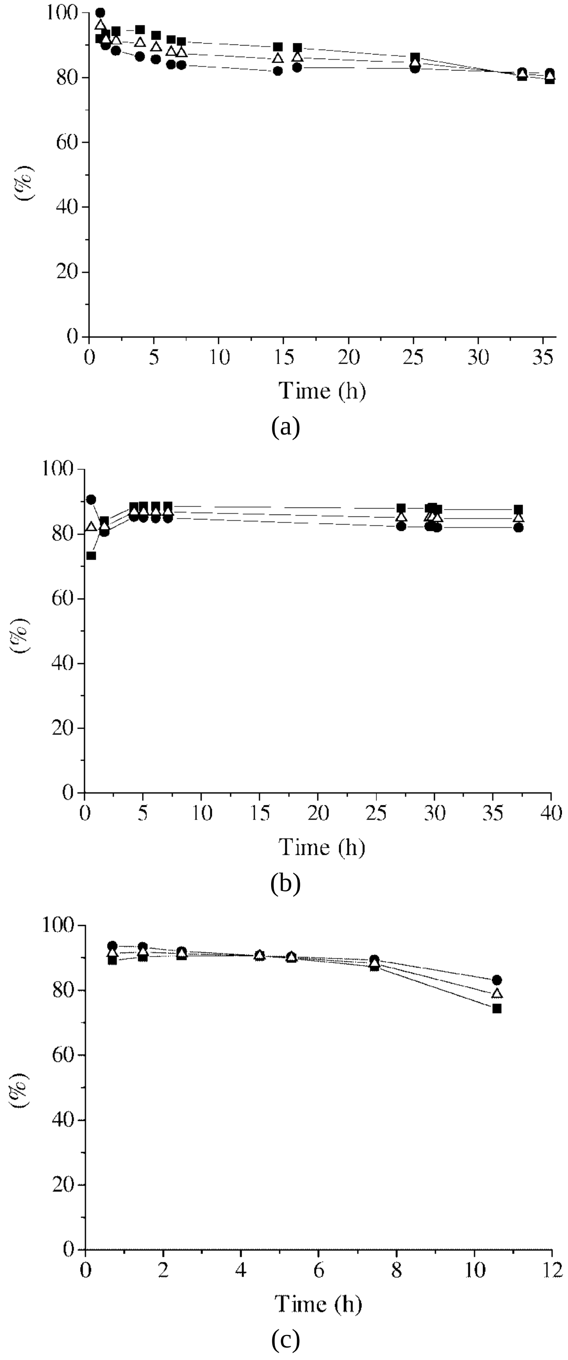

Figure 2. Lifetime study for methane dry reforming over monolayer-Mo_2C catalysts: (a) SiO_2, (b) Al_2O_3 and (c) ZrO_2 (1220 K, 8 bar, $CH_4/CO_2 = 1$ GHSV = $2.6 \times 10^3\ h^{-1}$); (■) C_{CH_4}, (•) C_{CO_2} and (△) Y_{CO}.

Table 1
Initial values for the dry reforming of methane over the supported monolayer-Mo_2C catalysts.[a]

Catalyst (monolayer loading Mo_2C (wt%))	Support BET surface area ($m^2\,g^{-1}$)	C_{CH_4} (%)	C_{CO_2} (%)	Y_{CO} (%)	H_2/CO
SiO_2 (18.3)	320	91	86	89	0.95
γ-Al_2O_3 (12.5)	194	89	86	87	0.97
ZrO_2 (6.5)	90	90	93	92	0.96
TiO_2 (10.1)	150	31	27	29	–
Thermodynamic eqm.	–	92.7	96.8	94.7	0.92

[a] Reaction conditions: 1220 K, 8 bar, $CH_4/CO_2 = 1$, GHSV = $2.6 \times 10^3\ h^{-1}$.

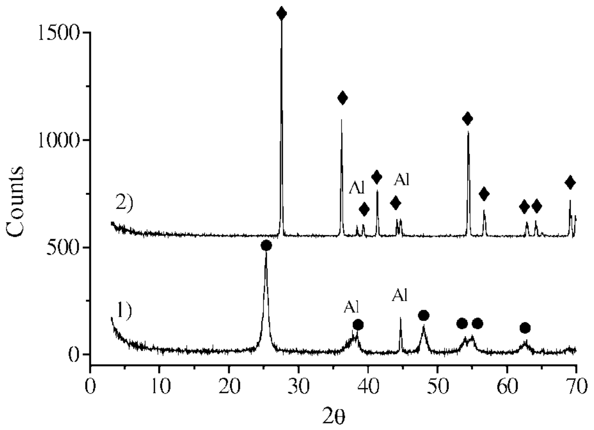

Figure 3. XRD patterns obtained from: (1) MoO_3 supported on high surface area TiO_2 prepared and calcined in the standard manner and (2) TiO_2-supported system after heating at 1220 K for 10 h ((♦) rutile TiO_2, (•) anatase TiO_2).

tems in figure 2 approach those expected from thermodynamic equilibrium calculations (table 1). Figure 2 shows that the Mo_2C/Al_2O_3 catalyst system was stable for longer than 40 h, while the SiO_2-supported system exhibited clear signs of deactivation after only 5 h. The relative order of stability, within the molybdenum carbide monolayer systems, was $Al_2O_3 > SiO_2 > ZrO_2 > TiO_2$. This stability order closely mirrors those obtained from activity studies of supported noble metal catalysts. Thus, Nakamura and co-workers [12–14] and Erdőhelyi et al. [15] observed both a significant effect on catalytic activity from the supports and an activity order of $Rh/Al_2O_3 > Rh/TiO_2 > Rh/SiO_2$. The reason for the admirable performance of TiO_2 in these publications may be associated with the lower temperatures (600–800 K) of the reactions and the much shorter experiment times (generally under an hour), whereas under the conditions used in this study XRD showed that a phase change from anatase to rutile occurs, accompanied by sintering of the material, as shown in figure 3. This behaviour has been previously observed by Zhang et al. for dry reforming reaction over Rh/TiO_2 at 973 K. They found a dramatic drop in conversion from approximately 90 to 75% in the first hour followed by a steady significant decrease in activity of the catalyst, leading to complete deactivation after about 40 h [16].

From our results for the monolayer systems, it can be argued that no simple correlation exists between the surface area of the support and the corresponding catalyst stability. For example, Al_2O_3 possesses 60% of the surface area of SiO_2 and yet the Mo_2C supported catalyst exhibits a significantly longer lifetime. In addition, the large differences in surface areas between some of the catalysts mean that the loading of the active catalyst varies from system to system; e.g., at monolayer loadings the amount of Mo_2C present on SiO_2 (18.3% based on Mo, 320 $m^2\,g^{-1}$) is much higher than for ZrO_2 (6.5% Mo, ZrO_2 90 $m^2\,g^{-1}$). Therefore, the performance superiority of Mo_2C/SiO_2, evident in figure 2, may be a function of the higher quantity of active catalyst present. For a further comparison, new catalysts were prepared with a constant Mo_2C loading, and were tested for dry reforming under the same conditions as the monolayer catalysts.

The XRD patterns of the four supported catalyst systems (constant 3.8% Mo_2C loading) after dispersion and calcination of MoO_3, but before carburisation were obtained. They exhibited only peaks corresponding to the support materials themselves, and for this reason are not shown here; the absence of peaks for MoO_3 indicates a high MoO_3 dispersion. The results for methane dry reforming using the Al_2O_3-, SiO_2- and ZrO_2-supported catalysts are presented in figure 4. All four catalyst systems deactivated much faster than the monolayer systems, but the lifetime studies again demonstrated a difference in catalytic lifetimes, with Mo_2C/Al_2O_3 exhibiting the longest lifetime and Mo_2C/TiO_2 the shortest. In addition, the 3.8% Mo_2C/ZrO_2, although it deactivated slowly, was now significantly more stable than Mo_2C/SiO_2. As with the monolayer systems the Mo_2C/TiO_2 catalyst deactivated very rapidly, and therefore the data for this catalyst material are not presented in figure 4. For the lower loading molybdenum carbide catalysts the stability order was as follows: $Al_2O_3 > ZrO_2 > SiO_2 > TiO_2$. Al_2O_3 still retains its superiority as a catalyst support, but the behaviour exhibited by ZrO_2 is now more comparable.

Thus it can be seen that a large amount of supported molybdenum carbide is needed to obtain a stable and active dry reforming catalyst, and it appears that the support plays no positive role in the reaction.

3.3. Effect of catalyst precursor calcination time

A theoretical monolayer quantity of MoO_3 was dispersed on each of two supports, Al_2O_3 and SiO_2, in accord with the method described earlier. Half of each sample was then calcined for 4 h and the other half was calcined for 24 h. Each sample was then carburised by ethane TPRe and the resulting materials evaluated for dry reforming under the same conditions as used previously.

Figure 5 shows the comparison of methane conversions for the catalysts, and demonstrates there is a significant difference in behaviour between the samples calcined for 4 h and those calcined for 24 h, with the latter samples exhibiting much shorter lifetimes. Clearly, longer calcination times for the precursor materials have a deleterious effect on the molybdenum carbide dry reforming catalysts, illustrating the importance of choosing the correct parameters for the catalyst preparation.

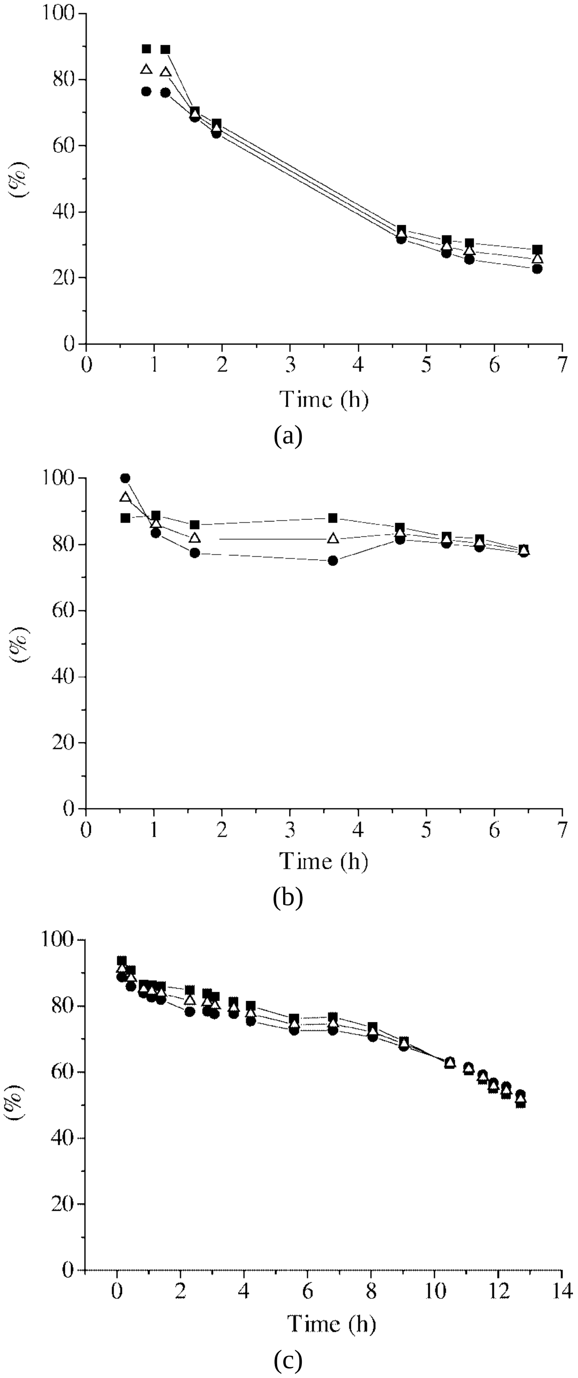

Figure 4. Lifetime study for methane dry reforming over less-than-monolayer (3.8%) Mo_2C catalysts: (a) SiO_2, (b) Al_2O_3 and (c) ZrO_2 (1220 K, 8 bar, $CH_4/CO_2 = 1$, GHSV $= 2.6 \times 10^3$ h^{-1}); (■) C_{CH_4}, (●) C_{CO_2} and (△) Y_{CO}.

The most likely explanation for the substantial differences in catalyst lifetimes is increased dispersion of the MoO_3 over the support with time. While the loading of MoO_3 has been designed to achieve monolayer dispersion, an ideal single atom coverage was almost certainly not achieved. Indeed, the presence of peaks for MoO_3 in the XRD patterns (e.g., figure 1) demonstrates that a true monolayer was not attained. BET surface area measurements of γ-Al_2O_3 show no significant change in surface area between samples calcined for 4 and 24 h, the surface areas being 196 and 189 $m^2\,g^{-1}$, respectively. It has been well established [16–18], that the longer a MoO_3/support system is calcined, the higher the dispersion achieved, since MoO_3 thermodynamically favours the formation of a mono-

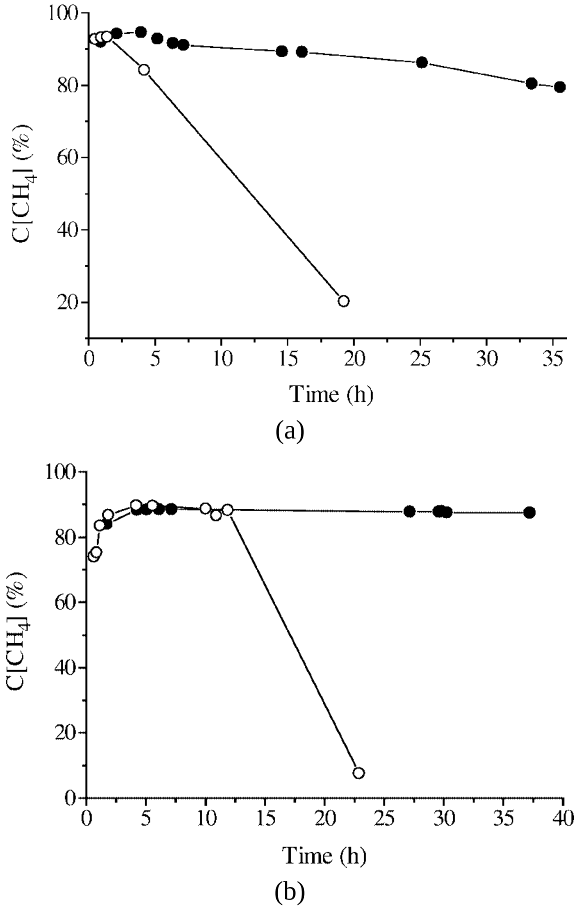

Figure 5. Effect of calcination time on the catalyst lifetime, shown as methane conversion, for methane dry reforming over: (a) monolayer-Mo_2C/SiO_2 and (b) monolayer-Mo_2C/Al_2O_3; catalysts were calcined for 4 (●) or 24 h (○) (1220 K, 8 bar, $CH_4/CO_2 = 1$, GHSV $= 2.6 \times 10^3$ h^{-1}).

layer [16]. Many authors have described strong interactions between MoO_3 and SiO_2, and particularly Al_2O_3 [17–20]. It is likely that on systems of low dispersity such interactions are of little consequence as the bulk of the MoO_3 is removed from the surface and almost unaffected. However, as the dispersity increases, the MoO_3 layer would become substantially thinner, thereby increasing the proportion of MoO_3 in contact with support. There are many possible consequences of the interaction between MoO_3 and the support:

(i) reaction may occur between the oxide and the support to give a composite at the surface (e.g., $Al_2(MoO_4)_3$) which could be more difficult to convert to the carbide;

(ii) the carbide layer which is formed may be very thin, such that if deactivation occurs there is no further bulk carbide carbon to move to the surface and thereby stabilise the catalyst;

(iii) the surface MoO_3 most immediate to the surface may interact with the support, such that the transition from MoO_3 to Mo_2C is rendered more difficult, or alternatively the oxidation of Mo_2C to MoO_2 more facile.

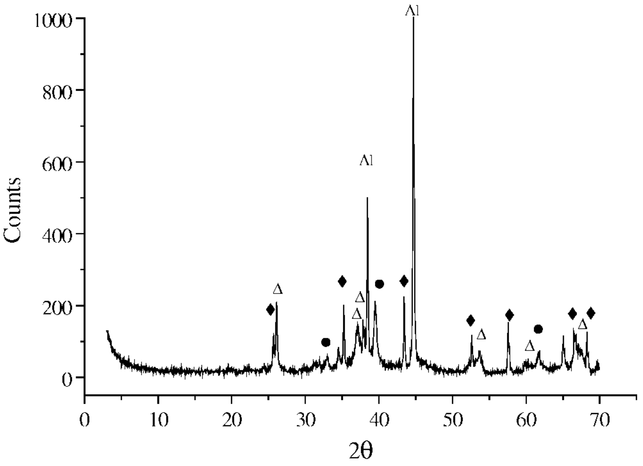

Figure 6. XRD pattern of post-dry reforming deactivated monolayer-Mo_2C/Al_2O_3 (precursor calcination time = 24 h). (●) γ-Al_2O_3, (♦) α-Al_2O_3, (Δ) MoO_2.

3.4. Characterisation of deactivated post-reaction dry reforming Mo_2C/Al_2O_3

Previous studies on the bulk group VI transition metal carbides as catalysts for methane reforming have demonstrated that the main route for catalyst deactivation was oxide formation; thus XRD showed that the active Mo_2C was converted to inactive MoO_2. The XRD pattern of the monolayer Mo_2C/Al_2O_3 (precursor which was calcined for 24 h) catalyst post-dry reforming and after the onset of deactivation is shown in figure 6. As before, with the bulk materials, the XRD pattern has peaks attributable to MoO_2, indicating that the main deactivation route is again likely to be oxidation. However, figure 6 also shows evidence of a phase change in the support material; the prepared γ-alumina has changed to α-alumina which has a lower surface area. It is well known that γ-alumina is unstable at the high temperatures used in this study [21], and the conversion to α-alumina may well be a contributing factor to catalyst deactivation. Nevertheless, it is thought probable that the predominant mechanism for the deactivation process is via oxide formation.

4. Conclusion

In conclusion, the stoichiometric carbon free reforming of methane over supported molybdenum carbide, prepared by C_2H_6 TPRe, has been demonstrated. As before, the carbide catalysts were more stable at elevated pressures, close to those desired by industry. It has been shown that the choice of the support for the molybdenum carbide dry reforming catalysts is crucial to catalyst stability, and the order of catalyst stability found in this study was: $Mo_2C/Al_2O_3 > Mo_2C/ZrO_2 > Mo_2C/SiO_2 > Mo_2C/TiO_2$. The MoO_3/support precursor calcination time was also found to be important, with the most stable catalysts being formed from only short calcination times; this is attributed to MoO_3 dispersion being lower. Finally, we conclude that molybdenum carbides supported on Al_2O_3 or

ZrO_2 are promising systems for methane dry reforming, with the monolayer Mo_2C/Al_2O_3 showing no appreciable sign of deactivation after dry reforming for 40 h.

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