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Characterisation of $Co/Mg/Al_2O_3$ high pressure partial oxidation catalysts

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Abstract

Coprecipitated $Co/Mg/Al_2O_3$ catalysts were synthesised (Mg/Co/Al ratio 1:1:2 and 1:3:4) and characterised by TPR, TEM, XRD and BET. The materials catalysed the partial oxidation of methane to CO and H_2 (1:2 ratio) at 20 bar pressure (conversions of 75–95%). The catalyst deactivated with time on line (20% reduction in conversion in 150 min). BET analysis revealed that sintering of the catalyst occurred during the catalytic reaction. Further, large quantities of carbon were formed in the post bed part of the reactor. TEM analysis of the carbon revealed cobalt embedded carbon rods. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Partial oxidation reaction; Deactivation; Carbon rods; Cobalt

1. Introduction

Synthesis gas, an important source of hydrogen, is largely produced in industry from the steam reforming of methane over an Al_2O_3 supported Ni catalyst [1]. Other catalysts based on Rh, Ru, Pd, Pt and Co are also known to show some activity for this reaction [2,3]. The reaction is highly endothermic and produces a mixture of H_2 and CO in a 3/1 ratio. The partial oxidation of methane is suggested to be an alternative and favoured option to steam reforming since the reaction is exothermic and produces a syngas ratio of H_2 to CO of 2 to 1. Here energy costs are lowered considerably and the H_2 to CO ratio is suitable for the Fischer–Tropsch synthesis reaction [2–4]. Since the partial oxidation reaction is a two-stage process [5,6] consisting of both the oxidation and the reforming of methane, most of the steam reforming catalysts mentioned above have also been used for the partial oxidation reaction. The reaction scheme for this process is shown below:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \text{(combustion)} \qquad (1)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \text{(reforming)} \qquad (2)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \text{(reforming)} \qquad (3)$$

Recently, it was proposed that Ru supported on TiO_2 can be used to bring about the reaction in a single step, with methane directly converted to syngas ($CH_4+0.5O_2 \rightarrow CO+2H_2$) [5]. This suggests that similar findings may be possible for Co based catalysts.

Supported Co catalysts have been reported to bring about a two-step low pressure methane partial oxidation reaction [6], and these Co/Al_2O_3 catalysts were found to deactivate due to solid state transformations,

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sintering, and carbon deposition that take place during the reaction [1,6]. Recently, Co catalysts have been prepared by coprecipitation procedures to try and eliminate/minimise the rate of sintering, solid-state transformations (mainly aluminate formation) and carbon deposition; while at the same time maintaining the high activities and selectivities of the catalyst towards syngas formation [7].

This paper reports a study of related new coprecipitated $Co/Mg/Al_2O_3$ catalysts. The activity of these catalysts for the partial oxidation reaction at *high pressure* is reported. The reducibility and morphology (including surface area studies) of the catalysts before reaction, after reduction and after the reaction, have been investigated. The analysis of the carbon that deposited below the catalyst bed after activity evaluation is also reported.

2. Experimental

2.1. Preparation of catalysts

Stoichiometric amounts of $Mg(NO_3)_2$, $Co(NO_3)_2$, and $Al(NO_3)_3$ were coprecipitated with NaOH and the gel was aged for 12 h. The mixture was then washed for three days after which the catalyst was filtered under vacuum. This was followed by overnight drying at 120°C and calcination at 800°C for 8 h. Two types of catalysts with different mole ratios of $Mg(NO_3)_2$ to $Co(NO_3)_2$, were prepared: catalysts $MgAl_2O_4\cdot CoAl_2O_4$ and $MgAl_2O_4\cdot 3CoAl_2O_4$ with ratios of $Co(NO_3)_2$ to $Al(NO_3)_3$ of 1:3:4 and 1:1:2, respectively. A Graphite lubricant was added to the catalyst powder to assist with pellet formation. The pellets were crushed and the required particles ($300\,\mu m < x < 500\,\mu m$) were used in the partial oxidation reaction.

2.2. Characterisation of catalysts

XRD measurements of the catalysts were performed using two different diffractometers. A Rigaku diffractometer with a high temperature sample chamber was used for an in situ reduction measurements. Hydrogen gas (1 bar) was passed over the catalyst at 600°C, 700°C and 800°C and a scan taken after 30 min of reduction. The samples were analysed over 30 min between $2\theta=5^\circ$ and 68°. For post-reaction samples/catalysts, a Phillips PW 1820 was used to determine XRD patterns. The samples were analysed over 30 min between $2\theta=5^\circ$ and 100°. In both diffractometers, finely ground samples were used for analysis.

Temperature programmed reduction (TPR) studies were performed on a home-built installation. The catalyst (100 mg) was dried at 150°C for 1 h under flowing nitrogen. After cooling the catalyst to room temperature, the catalyst was heated to 950°C over a period of 90 min under flowing hydrogen at a heating rate of 10°C/min.

BET analysis was performed on a known mass of catalyst which had been dried in situ at 150°C for 1 h.

For the partial oxidation reaction studies, 200 mg of catalyst was loaded into a conventional stainless steel continuous flow microreactor (i.d. and o.d. of 4 mm and 6 mm, respectively). Before the reaction, the catalyst was reduced in situ at 600°C in a flow of H_2 ($120\ cm^3/min$) for 30 min. CH_4 ($120\ cm^3/min$) and O_2 ($60\ cm^3/min$) were then introduced and the gaseous products analysed by means of an on-line chromatograph. The total pressure of the gases was set at 20 atm.

The carbon generated in the reaction, found below the catalyst bed, was analysed on a JEM 100 C TEM. A finely ground catalyst sample deposited on a thin carbon film supported on a standard copper grid was used in the determination.

3. Results and discussion

Fig. 1 shows the performance of both $MgAl_2O_4\cdot CoAl_2O_4$ and $MgAl_2O_4\cdot 3CoAl_2O_4$ catalysts in the partial oxidation reaction (20 bar). Catalyst $MgAl_2O_4\cdot 3CoAl_2O_4$ was more active initially showing 95% conversion which gradually dropped to 80% in 150 min of reaction. Catalyst $MgAl_2O_4\cdot CoAl_2O_4$ was less active with the conversion gradually dropping from 75% to 55% under a comparable reaction time. This phenomenon could be directly related to the relative amounts of cobalt in the catalysts, with $MgAl_2O_4\cdot 3CoAl_2O_4$ having more cobalt than $MgAl_2O_4\cdot CoAl_2O_4$ [6]. The H_2/CO ratio in the product stream from both reactions was found to be 2.1. Both catalysts gradually lost activity with time on line until an apparent steady state was achieved after 60 min of reaction.

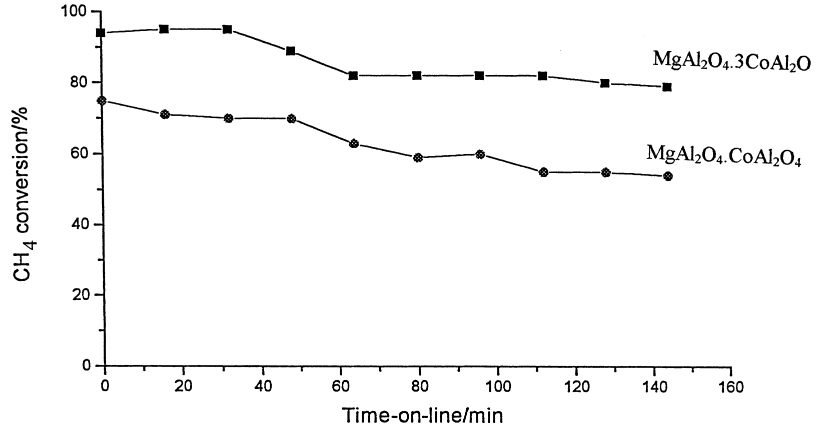

Fig. 1. Partial oxidation reaction performance of both $MgAl_2O_4{\cdot}3CoAl_2O_4$ and $MgAl_2O_4{\cdot}CoAl_2O_4$.

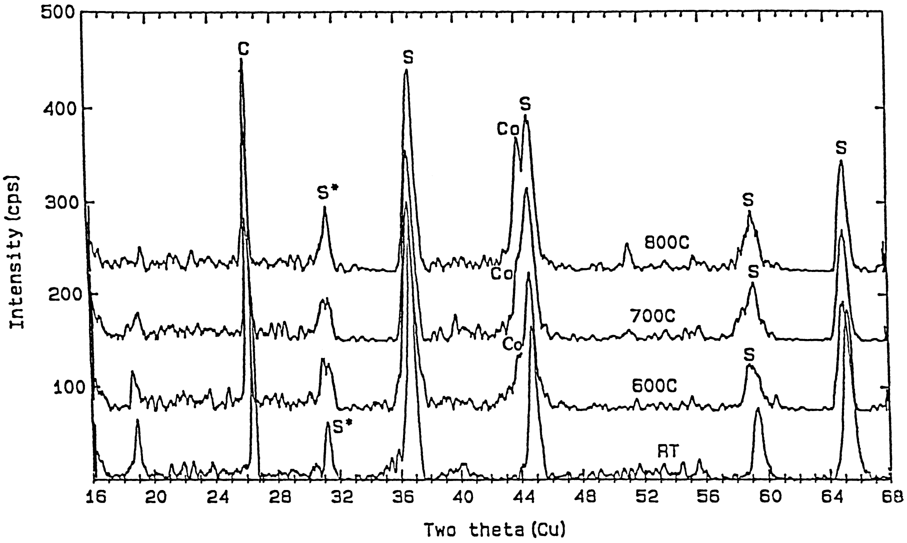

Fig. 2. In situ XRD Patterns for $MgAl_2O_4{\cdot}CoAl_2O_4$ after reduction at various temperatures.

Figs. 2 and 3 show the in situ XRD patterns of catalysts $MgAl_2O_4{\cdot}CoAl_2O_4$ and $MgAl_2O_4{\cdot}3CoAl_2O_4$ after reduction at room temperature, 600°C, 700°C and 800°C. The XRD patterns of the fresh catalyst after high temperature reduction revealed the presence of $MgAl_2O_4$ and $CoAl_2O_4$ spinels and the graphite lubricant. The formation of spinels was expected because of the high calcination temperature (800°C) which causes diffusion of MgO and CoO into Al_2O_3 to form $MgAl_2O_4$ and $CoAl_2O_4$, respectively [6,8–10]. This high calcination temperature also leads to the formation of Co_3O_4 that is known to form only at high Co loadings [9,11]. Co metal as expected was not observed after reduction at room temperature, largely due to the stability of CoO, Co_3O_4 and $CoAl_2O_4$ at low temperatures [6,7,9,10]. It was only at elevated reduction temperatures that Co metal appeared and its amount increased with temperature.

Fig. 4 shows the XRD pattern of the catalysts after the high pressure partial oxidation reaction. It seems that during the reaction, some of the Co reoxidised to Co_3O_4 as the Co peaks clearly became reduced in size (compare with the XRD patterns in Figs. 2 and 3).

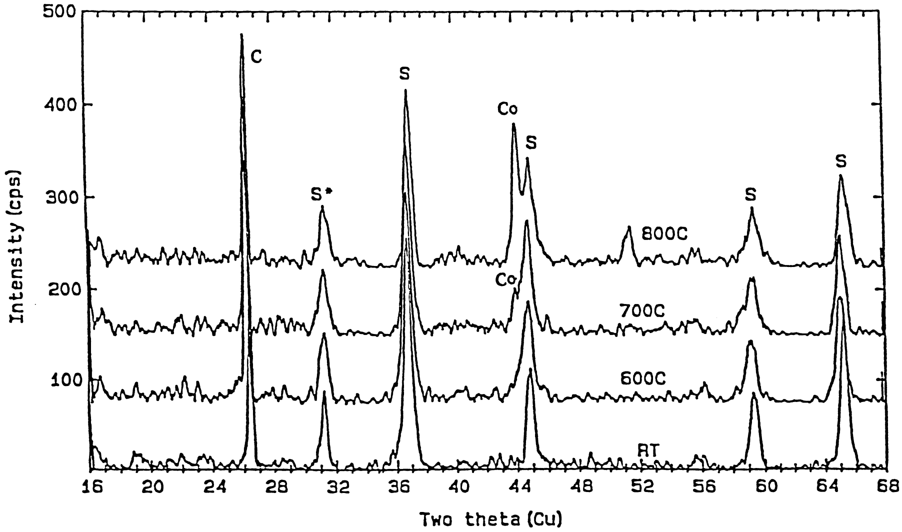

Fig. 3. In situ XRD Patterns for $MgAl_2O_4{\cdot}CoAl_2O_4$ after reduction at various temperatures.

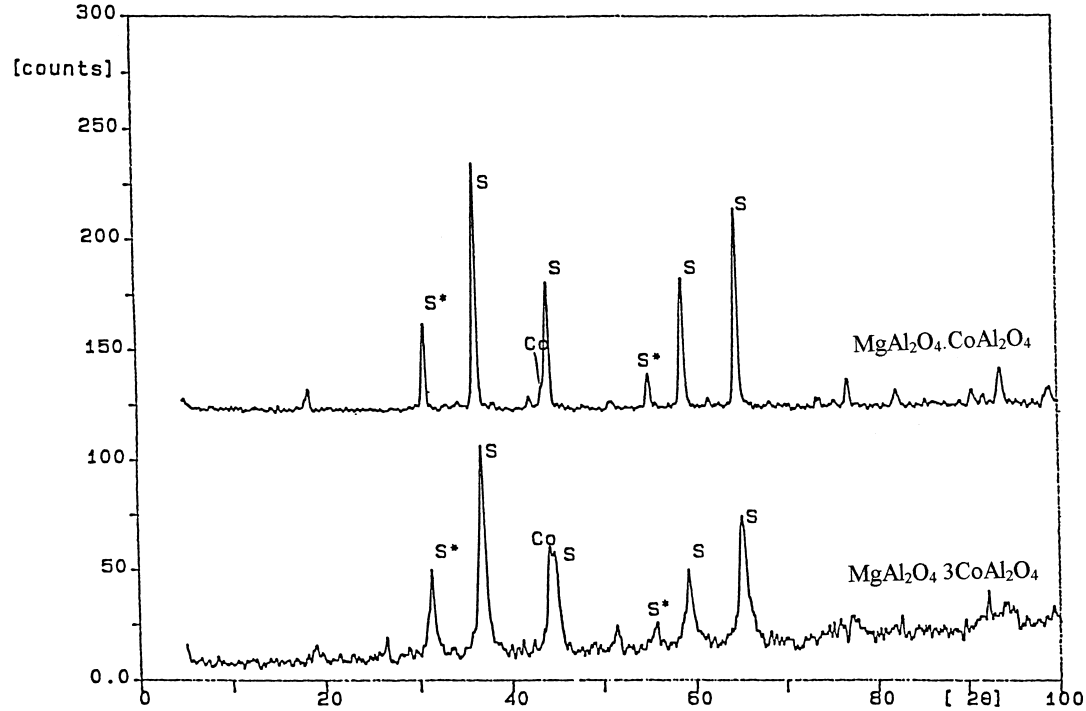

Fig. 4. XRD Patterns for $MgAl_2O_4{\cdot}CoAl_2O_4$ and $MgAl_2O_4{\cdot}3CoAl_2O_4$ after partial oxidation reaction.

Figs. 5 and 6 show the TPR profiles of both $MgAl_2O_4{\cdot}CoAl_2O_4$ and $MgAl_2O_4{\cdot}3CoAl_2O_4$, respectively. The profiles are similar, with the reduction peaks of $MgAl_2O_4{\cdot}CoAl_2O_4$ occurring at a slightly higher temperature than those for $MgAl_2O_4{\cdot}3CoAl_2O_4$. The first two peaks (550–750°C) relate to the reduction of

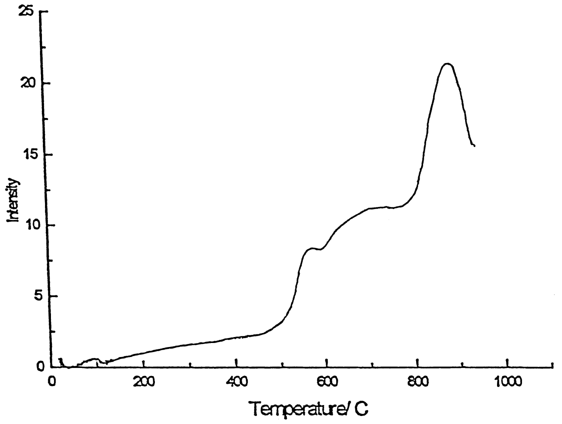

Fig. 5. Temperature programmed reduction of $MgAl_2O_4 \cdot CoAl_2O_4$.

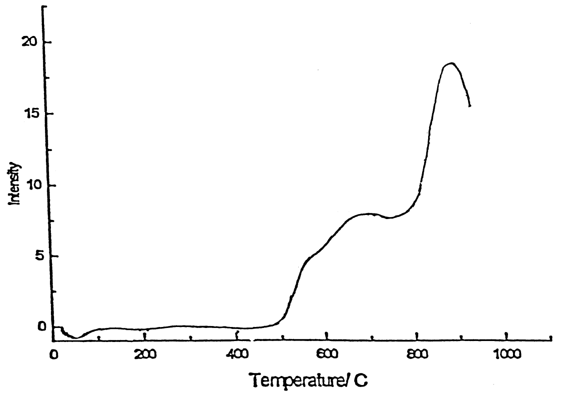

Fig. 6. Temperature programmed reduction of $MgAl_2O_4 \cdot CoAl_2O_4$.

Co_3O_4 and CoO, respectively; while the peak at the highest temperature (>800°C) relates to the reduction of both $MgAl_2O_4$ and $CoAl_2O_4$.

Table 1 shows the BET surface areas for $MgAl_2O_4 \cdot CoAl_2O_4$ and $MgAl_2O_4 \cdot 3CoAl_2O_4$, and reveals that catalyst $MgAl_2O_4 \cdot 3CoAl_2O_4$ has a higher surface area than $MgAl_2O_4 \cdot CoAl_2O_4$ under all conditions. It can also be seen that the increase in surface area is in the order: post-reaction < calcined < reduced catalyst. The carbon that was formed during the partial oxidation reaction (see below) could have contributed to the decrease in surface area of the post-reaction catalyst. Another factor could have been sintering due to the high reaction temperature (850°C), even though aluminates are known to slow down this phenomenon [8].

After the high pressure reaction, an examination of the catalyst revealed that it had two distinct colours; deep blue colour found in the material at the *top* of the reactor bed and a grey colour found in the material at the end of the reactor bed. The grey colour is due to metallic Co while the blue colour is due to the $CoAl_2O_4$ [6]. Similar results were obtained from a low pressure study. In this study, it was proposed that combustion occurred on $CoAl_2O_4$ while a reforming reaction took place on Co [6].

Table 1
BET catalyst surface areas

Catalyst state	Surface area ($m^2 g^{-1}$)	
	N1	N2
Calcined (fresh)	46.79	70.05
Reduced	48.51	73.11
Post-reaction	43.86	44.89

It is believed that the role of the spinel is two fold. It acts (i) as a source of cobalt metal which is required for the oxidation reaction and (ii) as a matrix to hold the cobalt in a cubic geometry [6,7]. The magnesium is required to stabilise the spinel at the high temperatures of the reaction [9]. Transition metal spinels are unstable at high temperatures and reduction would lead to the collapse of the structure to α-Al_2O_3 [6–10].

Copious deposits of carbon were formed under the high atmospheric reaction conditions. TEM micrographs of the carbon that was found below the catalyst bed are shown in Figs. 7 and 8; both tubular filamentous carbon and carbon rods are to be seen (rod widths of about 105 nm). Many of the rods and filaments encapsulate black solids at their ends which are assigned to Co metal particles. Other authors have

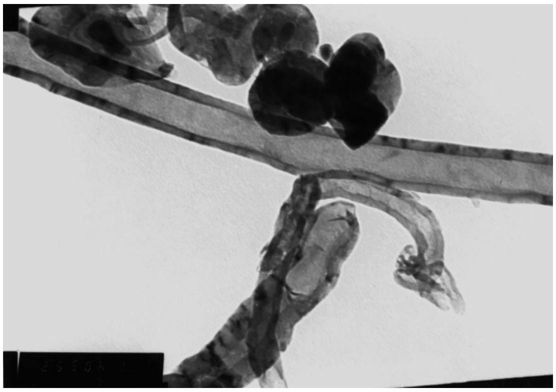

Fig. 7. Co embedded in carbon nanotubes: N1.

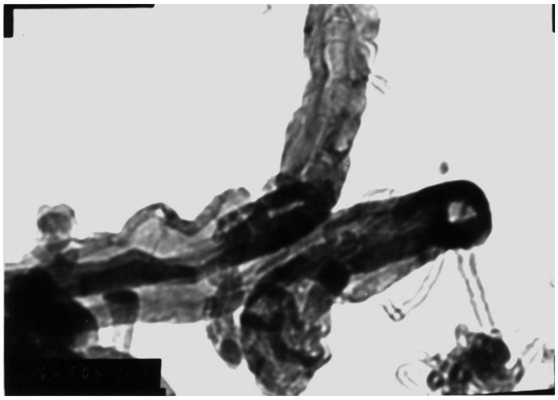

Fig. 8. Co embedded in carbon nanotubes: N2.

observed the same phenomenon with encapsulated metals such as Ni and Fe [12] even though the carbon deposits were formed from 1,3 butadiene and not CH_4 in these latter instances. The loss in activity as shown in Fig. 1 is related to the loss of Co metal (in the carbon deposits), the active component in the catalyst. However, this is not the only method for catalyst deactivation (loss of surface area) and hence no direct correlation between the amount of carbon formed and catalyst activity is possible [13].

4. Conclusion

The $Co/Mg/Al_2O_3$ catalysts catalyse the partial oxidation of methane at high pressures (20 bar) and high temperature (600–800°C). The reduction reaction transforms the catalyst bed into two distinct coloured regions (corresponding to the presence of Co and $CoAl_2O_4$, respectively) that continue to exist even after the partial oxidation reaction. The new catalysts were observed to deactivate with time, and this phenomenon was related to loss of pore volume and surface area, as well as the formation of carbon deposits that removed metal from the catalyst. Indeed, the partial oxidation reaction indirectly provides a high yield route to cobalt encapsulated nanotubes/rods [14].

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