A novel catalyst $Pt/CoAl_2O_4/Al_2O_3$ for combination CO_2 reforming and partial oxidation of CH_4

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$Pt/CoAl_2O_4/Al_2O_3$, $Pt/CoO_x/Al_2O_3$, $CoAl_2O_4/Al_2O_3$ and CoO_x/Al_2O_3 catalysts were studied for combination CO_2 reforming and partial oxidation of CH_4. The results indicate that $Pt/CoAl_2O_4/Al_2O_3$ is the most effective, and XRD results indicate that Pt species are well dispersed over the $Pt/CoAl_2O_4/Al_2O_3$. High dispersion is related to the presence of $CoAl_2O_4$, formed during calcining at high temperature before Pt addition. In the presence of Pt, $CoAl_2O_4$ in the catalyst could be reduced partially at 973 K. Based on these results, it appears that zerovalent platinum with high dispersion and zerovalent cobalt resulting from $CoAl_2O_4$ reduction are responsible for high activity in the $Pt/CoAl_2O_4/Al_2O_3$ catalyst.

KEY WORDS: combination CO_2 reforming and partial oxidation of CH_4; synthesis gas; $Pt/CoAl_2O_4/Al_2O_3$ catalyst.

1. Introduction

Methane is the most abundant component of natural gas although it is also produced in a variety of petrochemical and waste treatment operations. Presently, about 1% of the natural gas produced worldwide is used in chemical industries, while the rest is burned as fuel for heating and power generation [1]. The growing importance of environmental protection coupled with the need for a more effective use of the enormous natural gas reserves have stimulated research in methane conversion to feedstock and chemicals of commercial importance [2]. Natural gas is mainly used in industry for the manufacture of synthesis gas (CO/H_2). Synthesis gas is a versatile feedstock for methanol and ammonia synthesis processes and also for a number of Fischer–Tropsch synthesis processes for the production of liquid fuels, olefins and oxygenates. Synthesis gas is produced at present by steam reforming of methane. However, this process is highly endothermic and, hence, highly energy intensive. Moreover, it typically produces synthesis gas with high H_2/CO ratio (>4.0) due to the water–gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$), resulting in low selectivity and yield for carbon monoxide. In recent years, research to produce synthesis gas from methane has centered on two other processes: catalytic CO_2 reforming of CH_4 [3–8] and the catalytic partial oxidation of methane [9–12]. Both processes produce synthesis gas with more useful H_2/CO ratios. However, the catalytic partial oxidation of methane to synthesis gas may lead to a "hot-spot" which is hazardous and/or difficult to control particularly for large-scale operations. Because the CO_2 reforming of methane is an endothermic process, its coupling with the catalytic partial oxidation of methane can overcome the overheating hazard. In addition, by combining the two reactions, one can control the ratio H_2/CO and thus the selectivity for various Fischer–Tropsch synthesis products. This coupling was studied over noble-metal-based catalysts [13,14], and nickel-based catalysts [15–17]. Here, we report on studies using a novel catalyst $Pt/CoAl_2O_4/Al_2O_3$ which is highly active for combination of CO_2 reforming and partial oxidation of CH_4.

2. Experimental

2.1. Catalyst preparation

CoO_x/Al_2O_3 and $CoAl_2O_4/Al_2O_3$ catalysts were prepared by the wet-impregnation method, using nitrate salt as the metal precursor and γ-Al_2O_3 as support. After drying at 393 K, the resulting material was then calcined in air at 923 K and 1473 K for 5 h, respectively. The Co loading was 4 wt%. $Pt/CoO_x/Al_2O_3$ and $Pt/CoAl_2O_4/Al_2O_3$ catalysts were prepared by impregnating CoO_x/Al_2O_3 and $CoAl_2O_4/Al_2O_3$ with a solution of H_2PtCl_6 and calcined at 923 K for 5 h. For reference, Pt/Al_2O_3 catalysts were also prepared according to the procedure for $Pt/CoAl_2O_4/Al_2O_3$ catalysts, but the carrier (γ-Al_2O_3) was calcined at 1473 K for 5 h before use.

2.2. Catalytic reaction

The catalytic reaction was carried out in a tubular fixed-bed flow reactor made of quartz (i.d. = 4 mm)

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under atmospheric pressure. Prior to reaction, the catalyst was reduced at 973 K in H_2 for 1 h (unless otherwise stated), followed by Ar purge and heating under Ar flow to the reaction temperature (1023 K). The reactant gas stream consisted of methane, carbon dioxide and oxygen with a molar ratio of 1 : 0.4 : 0.3, controlled by mass flow controller, with GHSV = 24 000 h^{-1}. After condensing and drying, the reaction effluents were analyzed using the TCD of a gas chromatograph equipped with a TDX-01 column.

2.3. Catalyst characterization

Surface area of the support as well as the catalysts were determined by adsorption at 77 K using the BET method in an OMNISORP 100CX apparatus.

XRD data were obtained using a Rigaku-D/max-B automated power X-ray diffractometer (Cu K_α, 45 kV, 40 mA).

In TPR experiments, 50 mg of catalyst was charged in a quartz microreactor (i.d. = 4 mm). After purging with N_2 at room temperature, the sample was reduced in a 5% H_2/N_2 stream (30 ml/min). The reaction temperature was uniformly raised with ramp of 20 K/min from room temperature to a holding temperature of 1173 K, which was held for 13 min. The H_2 consumption was monitored by a TCD connected to a PC data station.

3. Results and discussion

3.1. Catalytic activity measurements

Table 1 reports the results obtained over various CoO_x/Al_2O_3 catalysts after a reaction time of 0.5 h. It shows that the CoO_x/Al_2O_3 catalyst has poor activity and low selectivity. $CoAl_2O_4/Al_2O_3$ showed only total oxidation of CH_4 until the prereduction temperature was increased to 1123 K. Interestingly, when $CoAl_2O_4/Al_2O_3$ catalyst was reduced at 1123 K, the catalytic activity increased remarkedly. This is attributed to the Co metal produced by partial reduction of $CoAl_2O_4$ [18]. Carbon is not formed on the active catalysts, and the selectivity of CO is almost 100%. From table 1, it is also found that with promotion by a small amount of Pt, $Pt/CoAl_2O_4/Al_2O_3$ catalyst showed significant improvement in activity.

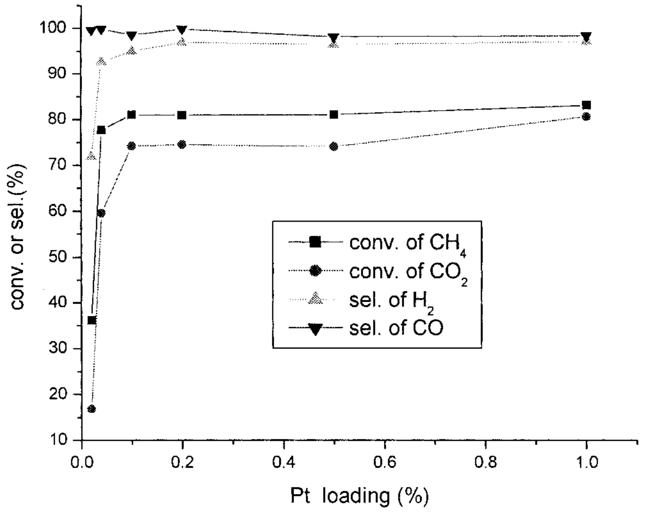

Figure 1. Effect of Pt content on catalytic activity of $Pt/CoAl_2O_4/Al_2O_3$. Reaction conditions: $T = 1023$ K, GVSV = 24 000 h^{-1}, $CH_4 : CO_2 : O_2 = 1 : 0.4 : 0.3$.

Figure 1 shows the effect of Pt content on the activities of $Pt/CoAl_2O_4/Al_2O_3$ catalysts. $Pt/CoAl_2O_4/Al_2O_3$ catalysts increase in activity with Pt low loadings, but above 0.1%, increasing Pt loading has little effect on the activity.

Catalyst stability was also examined. Figure 2 shows that a rapid decline in CH_4 conversion is observed for the 0.2%Pt/Al_2O_3 catalyst. During 2 h of reaction, the conversion of methane decreased from 40.1% for the initial reaction to 31.2%. However, 0.2%$Pt/CoAl_2O_4/Al_2O_3$ catalyst maintained high activity during 30 h on stream without coke formation, showing superior stability.

3.2. XRD study

Figure 3 shows XRD spectra of CoO_x/Al_2O_3 catalysts and $CoAl_2O_4/Al_2O_3$ which were calcined at 923 and

Table 1
Catalytic activities of CoO_x/Al_2O_3, $CoAl_2O_4/Al_2O_3$, 0.2%$Pt/CoO_x/Al_2O_3$ and 0.2%$Pt/CoAl_2O_4/Al_2O_3$

Catalyst	Conversion (%)		Selectivity (%)	
	CH_4	CO_2	H_2	CO
CoO_x/Al_2O_3	32.5	8.0	56.5	98.8
$CoAl_2O_4/Al_2O_3$ [a]	–	–	trace	trace
$CoAl_2O_4/Al_2O_3$ [b]	53.8	35.0	85.4	100
0.2%$Pt/CoO_x/Al_2O_3$	52.1	30.5	82.7	100
0.2%$Pt/CoAl_2O_4/Al_2O_3$	80.9	74.5	96.7	99.9

Note: Reaction conditions: $T = 1023$ K, GHSV = 24 000 h^{-1}, $t = 0.5$ h, $CH_4 : CO_2 : O_2 = 1 : 0.4 : 0.3$.

[a] CH_4 combustion primary reaction.

[b] Reduced at 1123 K for 1 h before reaction.

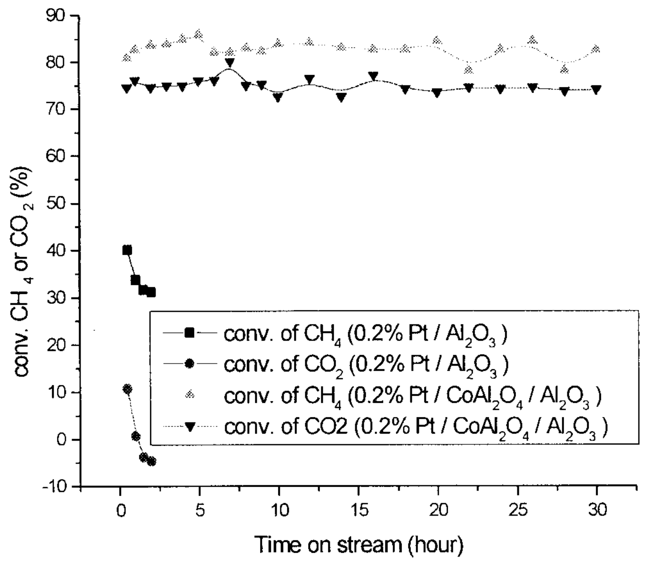

Figure 2. Stability of catalysts for combination of CO_2 reforming and partial oxidation of CH_4. Reaction conditions: $T = 1023$ K, GHSV = 24 000 h^{-1}, $CH_4:CO_2:O_2 = 1:0.4:0.3$.

Table 2
Color and surface area of catalysts

Catalyst	Color	BET area (m^2/g)
Al_2O_3 [a]	White	162.9
Pt/Al_2O_3 [b]	White	8.8
CoO_x/Al_2O_3	Black	162.9
$CoAl_2O_4/Al_2O_3$	Sky blue	8.6
0.2%$Pt/CoO_x/Al_2O_3$	Black	153.1
0.2%$Pt/CoAl_2O_4/Al_2O_3$	Sky blue	9.9

[a] Calcined at 923 K.
[b] Al_2O_3 was precalcined at 1473 K.

1473 K, respectively. For CoO_x/Al_2O_3 catalysts, three peaks are observed at $d = 0.244$, 0.286 and 0.467 nm (2θ values 36.8, 31.3 and 19.0°, respectively). Considering that the diffraction lines characteristic of CO_3O_4 and $CoAl_2O_4$ blend together at $d = 0.244$ and 0.286 nm, except for a line of CO_3O_4 at 0.476 nm which is absent from the XRD pattern of $CoAl_2O_4$ [18], the presence of CO_3O_4 is suggested for the CoO_x/Al_2O_3 catalyst. With $CoAl_2O_4/Al_2O_3$, however, the peak at 0.467 nm disappears and several sharp peaks clearly exhibit the presence of $CoAl_2O_4$ and α-Al_2O_3, agreeing with the literature [4]. This is also supported by the results in table 2. When the calcination temperature was increased from 923 to 1473 K, the catalyst experienced pronounced changes in color and surface area, indicating phase transformations of CO_3O_4 to $CoAl_2O_4$ and γ-Al_2O_3 to α-Al_2O_3. The effect of platinum addition on XRD patterns for CoO_x/Al_2O_3 and $CoAl_2O_4/Al_2O_3$ catalysts is shown in figure 4. When the Pt content is 1%, crystalline PtO_2 is clearly dectected for Pt/Al_2O_3 and $Pt/CoO_x/Al_2O_3$ catalysts. However, no distinct XRD peaks of Pt species are detected for $Pt/CoAl_2O_4/Al_2O_3$ catalysts at 1%Pt, although weak peaks of PtO_2 are observed at 2%Pt. These findings suggest that Pt species are highly dispersed in the $Pt/CoAl_2O_4/Al_2O_3$ catalyst.

3.3. *TPR results*

From figure 5, it can be seen that the reduction behaviors of $CoAl_2O_4/Al_2O_3$ with and without Pt are very different. On $CoAl_2O_4/Al_2O_3$ catalyst a peak due to the reduction of $CoAl_2O_4$ [19] appears above 1173 K. On Pt/Al_2O_3 catalyst three peaks appear at 423, 493 and 713 K, respectively. The former two peaks could be assigned to a two-step reduction of "free" PtO_2 [20], *i.e.* $Pt^{4+} \rightarrow Pt^{2+} \rightarrow Pt^0$, and the last peak probably indicates stronger interaction with the support.

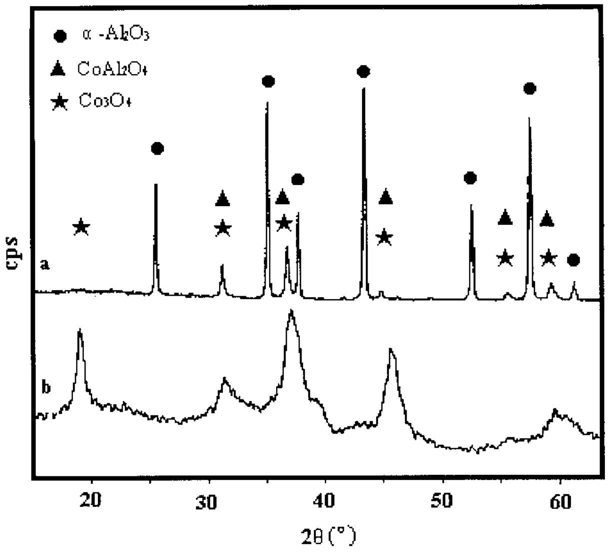

Figure 3. Patterns of (a) $CoAl_2O_4/Al_2O_3$ and (b) CoO_x/Al_2O_3.

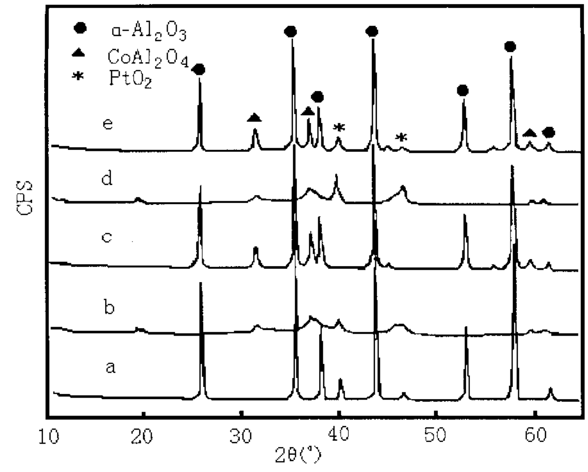

Figure 4. XRD patterns of $Pt/CoAl_2O_4/Al_2O_3$. (a) 1%Pt/Al_2O_3; (b) 1%$Pt/CoO_x/Al_2O_3$; (c) 1%$Pt/CoAl_2O_4/Al_2O_3$; (d) 2%$Pt/CoO_x/Al_2O_3$; (e) 2%$Pt/CoAl_2O_4/Al_2O_3$.

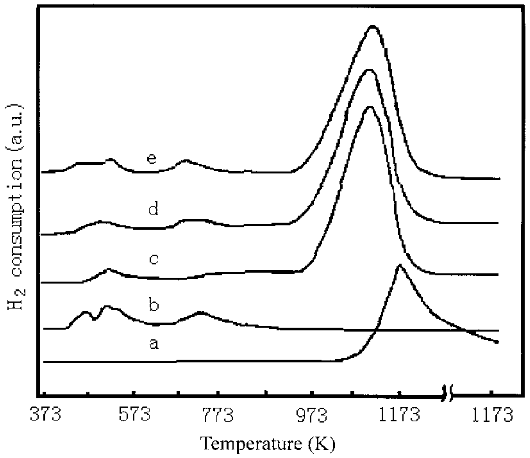

Figure 5. TPR profiles of (a) $CoAl_2O_4/Al_2O_3$; (b) 1%Pt/Al_2O_3; (c) 0.2%$Pt/CoAl_2O_4/Al_2O_3$; (d) 0.6%$Pt/CoAl_2O_4/Al_2O_3$; (e) 1%$Pt/CoAl_2O_4/Al_2O_3$.

These peaks are also observed for $Pt/CoAl_2O_4/Al_2O_3$ catalysts. However, due to Pt addition, the peak of CoO_x/Al_2O_3 reduction shifts to about 1100 K and its intensity is greatly increased. This clearly demonstrates that Pt promotes reduction of $CoAl_2O_4$. The Pt-assisted process could be attributed to hydrogen spillover, which facilitates $CoAl_2O_4$ reduction. Relating results of TPR and activity measurements listed in table 1, it seems that the zerovalent platinum and zerovalent cobalt resulting from $CoAl_2O_4$ reduction promoted by Pt are responsible for the high activity of $Pt/CoAl_2O_4/Al_2O_3$ catalysts for combination of CO_2 reforming and partial oxidation of CH_4 to synthesis gas.

As shown in figure 6, the Pt-assisted reduction of Co species is also observed for $Pt/CoO_x/Al_2O_3$ catalysts. On CoO_x/Al_2O_3 catalysts, two peaks appear at 863 and 1173 K, which are ascribed to the reduction of CO_3O_4 and cobalt surface phase, respectively. With addition of a small amount of Pt, the peaks shift to lower temperature. However, it can be seen from table 2 that, in the case of catalytic performance, the effect of Pt addition is very different for CoO_x/Al_2O_3 and $CoAl_2O_4/Al_2O_3$ catalysts.

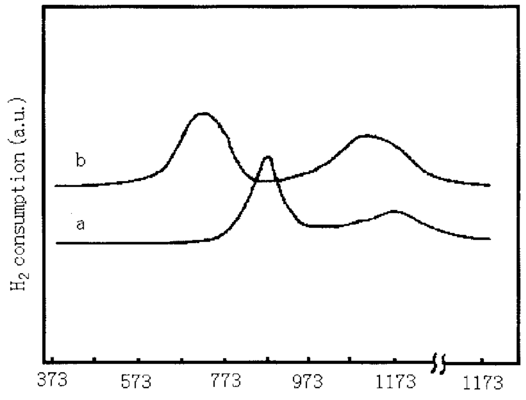

Figure 6. TPR profiles of (a) CoO_x/Al_2O_3; (b) 0.2%$Pt/CoO_x/Al_2O_3$.

As to the great difference in activity between 0.2%$Pt/CoO_x/Al_2O_3$ and 0.2%Pt $CoAl_2O_4/Al_2O_3$ catalysts (see table 1), the other clue probably lies in the different dispersion of PtO_2, the precursor of Pt^0, over the two catalysts suggested by the XRD results shown in figure 4. It is probable that a higher dispersion of PtO_2 is likely to result in a higher dispersion of Pt^0, which is responsible for higher activity. This is supported by literature for $Pt\text{-}Co/Al_2O_3$ catalyst [21].

4. Conclusions

The combination of CO_2 reforming and partial oxidation of CH_4 has been investigated on $Pt/CoO_x/Al_2O_3$ and $Pt/CoAl_2O_4/Al_2O_3$ catalysts by comparing with CoO_x/Al_2O_3, $CoAl_2O_4/Al_2O_3$ and Pt/Al_2O_3 catalysts. Among the catalysts investigated, $CoAl_2O_4/Al_2O_3$ calcined at 1473 K and promoted by a small amount of Pt is the most effective for the combination of CO_2 reforming and partial oxidation of methane, in terms of high activity, optimal stability and excellent resistance to carbon deposition. At lower metal content, the activity order for the catalysts is $Pt/CoAl_2O_4/Al_2O_3 > Pt/CoO_x/Al_2O_3 > Pt/Al_2O_3 \gg CoAl_2O_4/Al_2O_3$. Due to Pt addition, $CoAl_2O_4$ in the catalyst can be reduced partially under H_2 at 973 K.

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