Catalytic Performance and Characterization of Pt-Co/Al$_2$O$_3$ Catalysts for CO$_2$ Reforming of CH$_4$ to Synthesis Gas

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Pt-Co/Al$_2$O$_3$ catalyst has been studied for CO$_2$ reforming of CH$_4$ to synthesis gas. It was found that the catalytic performance of the catalyst was sensitive to calcination temperature. When Co/Al$_2$O$_3$ was calcined at 1473 K prior to adding a small amount of Pt to it, the resulting bimetallic catalyst showed high activity, optimal stability and excellent resistance to carbon deposition, which was more effective to the reaction than Co/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ catalysts. At lower metal loading, catalyst activity decreased in the following order: Pt-Co/Al$_2$O$_3$ > Pt/Al$_2$O$_3$ $\gg$ Co/Al$_2$O$_3$. With 9% Co, the Co/Al$_2$O$_3$ calcined at 923 K was also active for CO$_2$ reforming of CH$_4$, however, its carbon formation was much more fast than that of the Pt-Co/Al$_2$O$_3$ catalyst. The XRD results indicated that Pt species well dispersed over the bimetallic catalyst. Its high dispersion was related to the presence of CoAl$_2$O$_4$, formed during calcining of Co/Al$_2$O$_3$ at high temperature before Pt addition. Promoted by Pt, CoAl$_2$O$_4$ in the catalyst could be reduced partially even at 923 K, the temperature of pre-reduction for the reaction, confirmed by TPR. Based on these results, it was considered that the zerovalent platinum with high dispersion over the catalyst surface and the zerovalent cobalt resulting from CoAl$_2$O$_4$ reduction are responsible for high activity of the Pt-Co/Al$_2$O$_3$ catalyst, and the remain CoAl$_2$O$_4$ is beneficial to suppression of carbon deposition over the catalyst.

Keywords   Synthesis gas, Pt-Co/Al$_2$O$_3$ catalyst, activity, carbon deposition

Introduction

The catalytic reforming of CH$_4$ with CO$_2$, rather than H$_2$O, for the production of synthesis gas is attractive industrially because it yields low H$_2$/CO product ratios which are preferable as feeds for Fischer-Tropsch synthesis reaction.[1] This reaction has also important environmental implications because both CH$_4$ and CO$_2$ are regarded as the main factors leading to the green house effect. Furthermore, this process exhibits certain potential to be used as thermochemical heat-pipe for recovery, storage and transmission of solar and other renewable energy sources.[2,3] One of the major problems encountered in the application of this process is catalyst deactivation, mainly by carbon deposition *via* the Boudouard reaction and/or CH$_4$ cracking, which are favorable under reaction conditions.[4-6]

During the past decades, the process of CO$_2$ reforming of CH$_4$ has received considerable attention, and efforts have focused on development of catalysts which show high activity towards synthesis gas formation, and are also resistant to carbon deposition, thus displaying stable long-term operation. Numerous nickel-based catalysts[1,6,7-10] and supported noble metal catalysts[4,5,11-18] have been tested for this process. However, there have been relatively few investigations of CO$_2$-CH$_4$ reforming over cobalt-based catalysts, and, especially, the uses of supported noble metal-cobalt bimetal as catalysts for the process have scarcely been reported.

In this paper, catalytic performance of Pt-Co/Al$_2$O$_3$ catalyst was examined for the reaction and a preliminary characterization for the catalyst was also per-

formed by X-ray diffraction (XRD) and temperature-programmed reduction (TPR) techniques. From this work, some interesting results have been obtained.

Experimental

Catalyst preparation

Co/Al$_2$O$_3$ catalysts were prepared by the wet-impregnation method, using nitrate salt as the metal precursor and γ-Al$_2$O$_3$ (S_{BET} = 220 m^2/g), sieved to a 20/40-mesh fraction, as the support. After dried at 393 K, the resulting material was then calcined in air at 923 K or 1473 K for 5 h. Pt-Co/Al$_2$O$_3$ catalysts were prepared by impregnating Co/Al$_2$O$_3$ with a solution of H$_2$PtCl$_6$ and calcining at 923 K for 5 h. The above catalysts were denoted as xPtyCoT in which x (or y) and T refer to the metal loading in mass percentage and calcining temperature of Co/Al$_2$O$_3$, respectively. For reference, Pt/Al$_2$O$_3$ catalysts were also prepared according to the procedure for Pt-Co/Al$_2$O$_3$ catalysts, but the carrier (γ-Al$_2$O$_3$) was calcined at 1473 K for 5 h before used.

Catalytic reaction

The catalytic reaction was carried out in a fixed bed flow reactor made of quartz tube (4 mm i.d.) under atmospheric pressure. Prior to reaction, the catalyst was reduced at 923 K in H$_2$ for 1 h (unless otherwise stated), followed by Ar purge and heating under Ar flow to the reaction temperature (973 K). A CH$_4$ + CO$_2$ (nCH$_4$/nCO$_2$ = 1.07) gas mixture, with a GHSV = 4100 h^{-1}, was used as feed gas. After condensed and dried, the reaction effluents were analyzed using the TC detector of a gas chromatography equipped with a TDX-01 column. The amount of carbon deposition on catalyst was measured by temperature programmed oxidation (TPO).[19]

Catalyst characterization

Surface area of the support as well as the catalysts were determined by N$_2$ adsorption at 77 K using the BET method in an OMNISORP 100CX apparatus.

XRD data were obtained on a Rigaku-D/max-B automated power X-ray diffractometer. Anode Cu K_α (45 kV, 40 mA) was used as the X-ray source.

In TPR experiments, 50 mg of catalyst was charged in a quartz microreactor (4 mm i.d.). After purged with N$_2$ at room temperature (RT) for 1 h, 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 RT to a holding temperature of 1173 K, which was held for 13 min. The H$_2$ consumption was monitored by a TC detector connected to a PC data station.

Results and discussion

Activities of Co/Al$_2$O$_3$ catalysts

Table 1 reports the results obtained over various Co/Al$_2$O$_3$ catalysts after a reaction time of 100 min. It demonstrates that the activity of Co/Al$_2$O$_3$ catalysts depends on both Co loading and calcining temperature. The methane reforming activity is in the following order: 9Co923 ≫ 4Co923 > 9Co1473 ~ 4Co1473. 9Co923 catalyst shows optimal activity, but presents notable carbon deposition. 4Co923 catalyst is much less active than 9Co923 catalyst. Furthermore, a rapid deactivation is also observed for the catalyst. CH$_4$ conversion over 4Co923 sharply decreases from 68.1% to 3.0% during 100 min of the reaction. The deactivated catalyst displays a pronounced change from black to gray blue in color, indicating that a phase transformation, probably such as Co^0→CoAl$_2$O$_4$ occurred during the reaction. For 4Co1473 and 9Co1473 catalysts, no activity is measured unless a pre-reduction at higher temperature (about 1073 K) is performed. This is attributed to the inactive CoAl$_2$O$_4$ species formed during calcining Co/Al$_2$O$_3$ at high temperature.[20]

Activities of Pt-Co/Al$_2$O$_3$ catalyst

Table 2 compiles activities of Pt-Co/Al$_2$O$_3$ catalysts. Comparing Table 2 with Table 1, it is found that promoted by a small amount of Pt, both 4Co1473 and 9Co1473 catalysts show significant improvement in activity, and display excellent resistance to carbon deposition. On the other hand, the addition of Pt results in negligible improvement in activity for 4Co923 catalyst and a notable increase in carbon formation for 9Co923

catalyst, respectively. These results demonstrate that the addition of Pt to Co/Al_2O_3 catalyst could affect greatly its catalytic performance and the effect is sensitive to catalyst preparation conditions. Among the catalysts list-ed in Table 1 and Table 2, the Co/Al_2O_3 catalyst calcined at 1473 K and promoted by Pt is the most effective for CO_2 reforming of CH_4.

Table 1   Catalytic performance of Co/Al_2O_3 catalysts (GHSV = 4100 h^{-1}, T = 973 K, t = 100 min)

Catalyst	Conversion (%)		$(CO + H_2)$ (%)	CO/H_2	Formed[a] carbon (%)
	CH_4	CO_2			
4Co923	3.0	8.1	5.4	8.41	Trace
4Co1473	~0	~0	Trace	—	Trace
9Co923	82.2	88.9	86.0	1.13	2.07
9Co1473	~0	~0	Trace	—	Trace
9Co1473[b]	76.2	90.4	83.1	1.18	1.815

[a] The carbon amount on catalysts was defined as percentage of weight of catalyst.

[b] The catalyst was reduced at 1073 K for 1 h before reaction.

Table 2   Catalytic performance of Pt-Co/Al₂O₃ catalysts (GHSV = 4100 h^{-1}, T = 973 K, t = 100 min)

Catalyst	Conversion (%)		$(CO + H_2)$ (%)	CO/H_2	Formed[a] carbon (%)
	CH_4	CO_2			
0.2Pt4Co923	6.5	7.6	7.1	5.29	Trace
0.2Pt4Co1473	80.8	88.3	83.1	1.08	0.024
0.2Pt9Co923	82.0	88.5	85.0	1.08	6.012
0.2Pt9Co1473	81.8	89.6	85.6	1.07	0.081

[a] The carbon amount on catalysts was defined as percentage of weight of catalyst.

Fig. 1 shows effect of Pt content on activities of Pt-Co1473 and Pt/Al₂O₃ catalysts. In a certain range of Pt content, all catalysts present increase in activity with Pt loading, but PtCo1473 catalysts are more active than Pt/Al₂O₃ catalyst. The optimum Pt contents are 0.04% and 0.2% for the PtCo1473 catalysts at 9% and 4% Co,
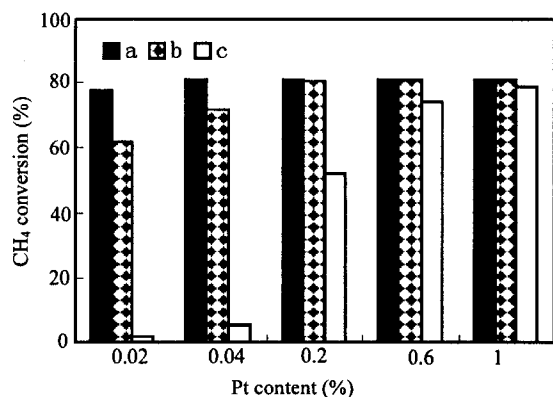
respectively. Above the content, an increase in Pt load-ing does not produce any further significant increase in activity. However, when Pt content is below 0.2%, Pt/Al₂O₃ catalyst exhibits negligible activity, although its CH_4 conversion reaches the value of PtCo1473 catalysts when Pt content increases to 1%.

The catalyst stability was also examined. As shown in Fig. 2, a linear decline in CH_4 conversion is observed
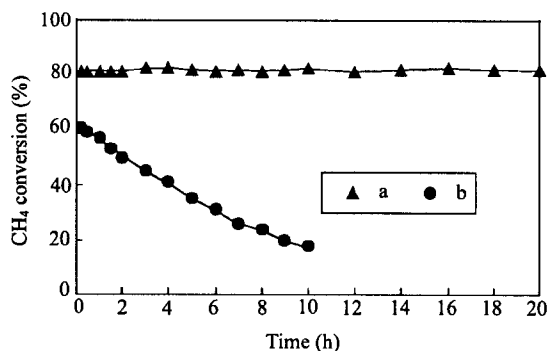

Fig. 1   Effent of Pt content on catalytic activity of different cata-lysts (a) Pt9Co1473; (b) Pt4Co1473; (c) Pt/Al₂O₃ (Reaction conditions: T = 973 K, GHSV = 4100 h^{-1}, t = 100 min).

Fig. 2   Stability of catalysts for CO_2 reforming of CH_4. (a) 0.2Pt4Co1473; (b) 0.2% Pt/Al₂O₃ (Reaction condi-tions: T = 973 K, GHSV = 4100 h^{-1}).

for the $0.2\% Pt/Al_2O_3$ catalyst, presumably due to accumulation of carbonaceous species on the catalyst surface.[18] During 10 h of reaction, the conversion decreases from 59.8% for the initial reaction to 18.7%. By contrast, 0.2Pt4Co1473 catalyst maintains its high activity during 20 h of reaction without significant coke formation, showing optimal stability and excellent resistance to carbon deposition.

XRD *study*

Fig. 3 gives XRD spectra of Co/Al_2O_3 catalysts calcined at 923 and 1473 K. For Co/Al_2O_3 catalysts calcined at 923 K, three peaks are observed at $d = 0.244$, 0.286 and 0.467 nm (2θ-value: 36.8, 31.3 and 19.0°, respectively), in which the intensities increase toward higher cobalt loading. 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 0.467 nm which is absent from XRD pattern of $CoAl_2O_4$,[20] the presence of Co_3O_4 can be inferred for 4Co923 and 9Co923 catalysts. On 4Co1473 and 9Co1473 catalysts, however, the peak of 0.467 nm disappears and several sharp peaks clearly exhibit the presence of crystalline $CoAl_2O_4$ and α-Al_2O_3 in both the catalysts, agreeing with the literature results.[21] This is also supported by the results showed in Table 3. When

calcination temperature increases from 923 to 1473 K, the catalysts experienced pronounced changes in color and surface area, indicating such phase transformations as Co_3O_4 to $CoAl_2O_4$ and γ-Al_2O_3 to α-Al_2O_3 caused by calcination of Co/Al_2O_3 at high temperature.

The effect of platinum addition to Co/Al_2O_3 catalysts on their XRD patterns is shown in Fig. 4. When Pt content is 1%, the crystalline PtO_2 is clearly detected for Pt/Al_2O_3 and PtCo923 catalysts. However, no distinct XRD peaks of Pt species are detected for PtCo1473 catalyst at 1%Pt, the XRD pattern of which is the same as 4Co1473 catalyst's shown in Fig. 3, although weak peaks of PtO_2 are observed at 2% Pt. These findings suggest that Pt species well dispersed over $Pt-Co/Al_2O_3$ catalyst when Co/Al_2O_3 is calcined at 1473 K before platinum addition. During calcining at high temperature, support γ-Al_2O_3 is transformed into α-Al_2O_3 and $CoAl_2O_4$ spinel is formed. On the other hand, comparing XRD intensities of PtO_2 over Pt/Al_2O_3, the catalyst with α-Al_2O_3 as the support confirmed by profile a in Fig. 4, with that over PtCo923, the catalyst with γ-Al_2O_3 as the support, it is obvious that α-Al_2O_3 can not be considered as a better carrier for dispersing PtO_2. Consequently, the higher dispersion of Pt species over PtCo1473 catalyst than over Pt/Al_2O_3 and PtCo923 catalysts might be related to the presence of $CoAl_2O_4$. It is presumable that the Pt species disperse preferably over surface phase of $CoAl_2O_4$ rather than over Al_2O_3 support similarly to that demonstrated by Zsoldos *et al*.[22] More detailed studies remain to be done.
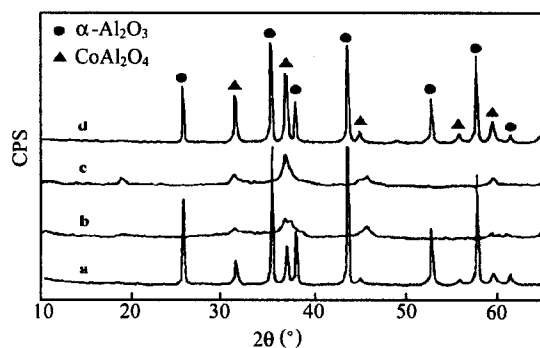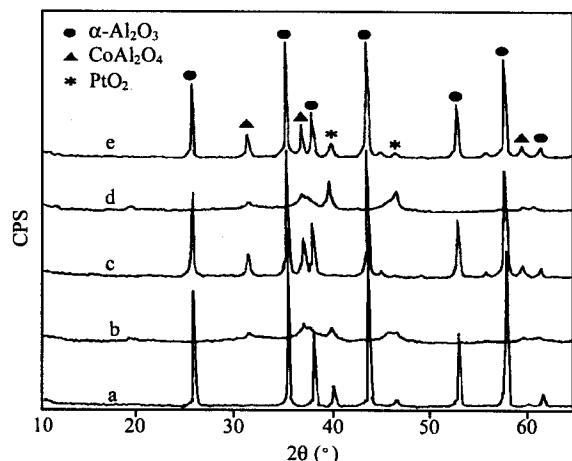

Fig. 3 XRD patterns of Co/Al_2O_3 catalysts. (a) 4Co1473; (b) 4Co923; (c) 9Co923; (d) 9Co1473.

Table 3 Color and surface area of catalysts

Catalyst	Color	BET area (m^2/g)
4Co923	black	162.9
4Co1473	sky blue	8.6
0.2Pt4Co923	black	153.1
0.2Pt4Co1473	sky blue	9.9

Fig. 4 XRD patterns of $Pt-Co/Al_2O_3$ catalysts. (a) 1% Pt/ Al_2O_3; (b) 1Pt4Co923; (c) 1Pt4Co1473; (d) 2Pt4Co923; (e) 2Pt4Co1473.

TPR *results*

From Fig. 5, it can be seen that the reduction behaviors of Co/Al₂O₃ catalysts calcined at 1473 K with and without Pt are far different. On Co1473 catalyst a peak due to the reduction of $CoAl_2O_4$,[23] appears at above 1173 K, which has not dropped to baseline although the reduction at 1173 K lasts for 13 min. On Pt/Al₂O₃ 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,[24] *i. g.*, $Pt^{4+} \to Pt^{2+} \to Pt^0$, and the last peak probably indicates the reduction of PtO_2 with stronger interaction with support. These peaks are also observed for PtCo1473 catalysts. However, due to Pt addition, the peak of $CoAl_2O_4$ reduction shifts to 1103 K, and its intensity is greatly increased also. This clearly demonstrates that Pt promotes reduction of $CoAl_2O_4$. The Pt-assisted process could be attributed to spillover hydrogen activated on the platinum metal, which facilitates $CoAl_2O_4$ reduction.
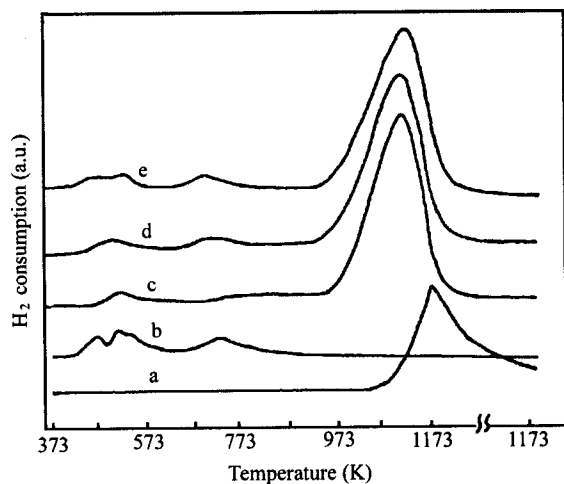

Fig. 5 TPR profiles of PtCo1473 catalysts (a) 4Co1473; (b) 1%Pt/Al₂O₃; (c)0.2Pt4Co1473; (d) 0.6Pt4Co1473; (e) 1Pt4Co1473.

Fig. 6 shows TPR profiles of 4Co1473 and 0.2Pt4Co1473 catalysts that have been reduced at 923 K in H₂ for 1 h and cooled in N₂ flow after the reduction. No effect of the pre-reduction on TPR profile is observed for 4Co1473 catalyst. The profile of reduced catalyst is the same as that of the fresh one, indicating that $CoAl_2O_4$ in the catalyst can not be reduced under the pretreatment conditions. On the other hand, by compar-

ing profile b with profile c in Fig. 6, it is found that in addition to disappearance of the peaks due to platinum reduction, a decrease in the area of the peak due to $CoAl_2O_4$ reduction is also caused by the reduction prior to TPR. The hydrogen consumptions for $CoAl_2O_4$ reduction during the TPR process are 0.797 and 0.524 mmol H₂/gcata. for fresh and reduced 0.2Pt4Co1473 catalyst, respectively. The values indicate that about 34% of the Co, being present as $CoAl_2O_4$ in the catalyst, is reduced to Co^0 by reduction at 923 K for 1 h, the pretreatment employed for the reaction of CO_2-CH_4 reforming. Relating results of TPR and activity measurements listed in Table 1 and Table 2, it is considered that the zerovalent platinum and the zerovalent cobalt resulting from $CoAl_2O_4$ reduction promoted by Pt are responsible for the high activity of PtCo1473 catalysts for CO_2 reforming of CH_4 to synthesis gas. On the other hand, the remained $CoAl_2O_4$ in the catalyst probably plays a role in the suppression of coking during the reaction. This is supported by the results obtained over Ni/Al₂O₃[25] and Co/Al₂O₃[21] catalysts, in which $NiAl_2O_4$ and $CoAl_2O_4$ were found to be beneficial to improve anti-carbon deposition property of the catalysts.
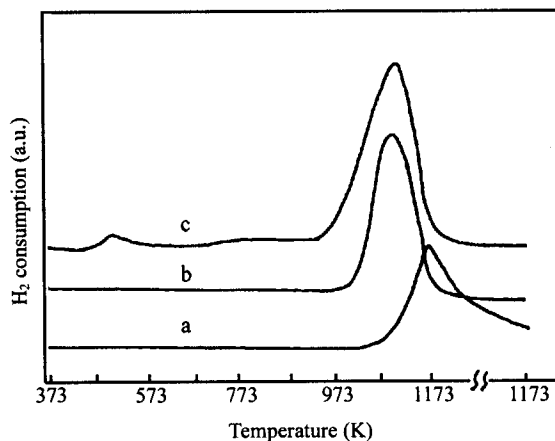

Fig. 6 TPR profiles of 4Co1473 and 0.2Pt4Co1473 catalysts before and after reduction at 923 K for 1 h. (a) 4Co1473 before or after reduction; (b) 0.2Pt4Co1473 after reduction; (c) 0.2Pt4Co1473 before reduction.

As shown in Fig. 7, the Pt-assisted reduction of Co species is also observed for PtCo923 catalysts. On 4Co923 and 9Co923 catalysts, two peaks appear at 863 and 1173 K, which are ascribed to the reduction of Co_3O_4 and $CoAl_2O_4$, respectively. The intensities of the

peaks increase toward high Co content, but the increasing is more notable for the peak at 863 K. This is related to the higher activity of 9Co923 catalyst than 4Co923 catalyst. With addition of small amount of Pt, both the catalysts present shifting of the peaks to lower temperature and increase in peak intensities, similarly to the case of 4Co1473 catalyst. However, in the case of catalytic performance, the effect of Pt addition is far different for Co/Al$_2$O$_3$ catalysts calcined at different temperatures (see Table 2). It is well known that carbon deposition during CO$_2$-CH$_4$ reforming originate from CH$_4$ decomposition and/or CO disproportion reaction. Numerous studies suggest that CO dissociation on transition metal surface is initiated via adsorption at a multiply coordinated site,[26-28] and the higher coordination sites are favorable to CH$_4$ cracking,[29] also. Accordingly, it is considered that the higher coordination of active sites over the catalyst surface due to higher metal loading and higher reducibility is more susceptible to coking. The results of XRD (Fig. 3) and TPR (Fig. 7) show that the Co species over 9Co923 catalyst is present mainly as reducible Co$_3$O$_4$. Promoted by Pt, CoAl$_2$O$_4$ would also be reduced partially under the reaction conditions. This would result in an assembly of "crowed" active sites over the catalyst and thus lead to increase in carbon formation. At lower Co content as the case of 4% Co/Al$_2$O$_3$ catalyst, both poor activity and negligible carbon deposition are observed. The activity can be greatly improved by adding Pt to the catalyst calcined at high temperature. To the great difference in activity between 0.2Pt4Co923 and 0.2Pt4Co1473 catalysts (see Table 2), the 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 Fig. 4. It is a reasonable assumption that a higher dispersion of PtO$_2$ is likely to result in a higher dispersion of Pt^0, which is responsible for higher activity. In addition, another situation demonstrated in literature for Pt-Co/Al$_2$O$_3$ catalyst[30] has to be taken into consideration. After pre-reduction on 0.2Pt4Co923 catalyst with composition of $n_{Co} > n_{Pt}$ (where n_{Co} and n_{Pt} are the moles of metallic cobalt and platinum, respectively), part of Pt^0 sites are possible to be covered by metallic cobalt, and then the catalyst would behave as cobalt-like catalyst. This assumption is supported by the fact that 0.2Pt4Co923 is still less active than 0.2% Pt/Al$_2$O$_3$ catalyst and shows almost the same performance as 4Co923 catalyst. In the case of

0.2Pt4Co1473 catalyst with partially reducible CoAl$_2$O$_4$ as the only cobalt species, the covering extent of metallic cobalt over Pt^0 sites can be considered lower or negligible because of a lower n_{Co}/n_{Pt} ratio and a higher Pt^0 dispersion than 0.2Pt4Co923 catalyst's.
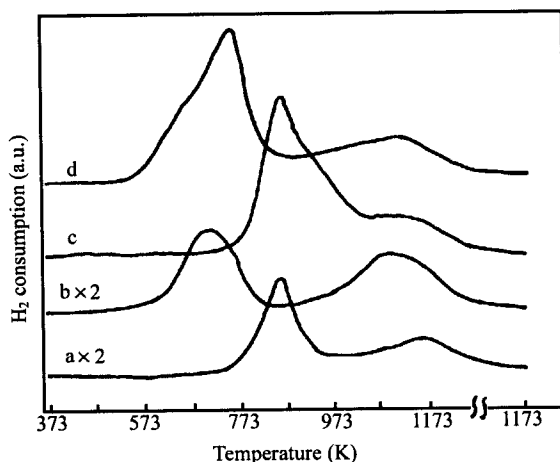

Fig. 7   TPR profiles of PtCo923 catalysts (a) 4Co923; (b) 0.2Pt4Co923; (c) 9Co923; (d) 0.2Pt9Co923.

Conclusions

The CO$_2$ reforming of methane has been investigated on Pt-Co/Al$_2$O$_3$ catalysts by comparison with Co/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ catalysts. The catalytic performance of Pt-Co/Al$_2$O$_3$ is sensitive to calcination temperature. Among the catalysts investigated, Co/Al$_2$O$_3$ calcined at 1473 K and promoted by a small amount of Pt is the most effective to CO$_2$ reforming 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-Co/Al$_2$O$_3$ > Pt/Al$_2$O$_3$ $\gg$ Co/Al$_2$O$_3$. When Co loading is 9%, Co/Al$_2$O$_3$ calcined at 923 K is also active for CO$_2$ reforming of CH$_4$, but its carbon formation is much more fast than Pt-Co/Al$_2$O$_3$ catalyst's.

The Pt species is found to be well-dispersed over the bimetal catalyst, when Co/Al$_2$O$_3$ is calcined at 1473 K prior to adding Pt to it, the calcining resulting in the formation of CoAl$_2$O$_4$. Due to Pt addition, CoAl$_2$O$_4$ in the catalyst presents a notable improvement in reducibility, which can be reduced partially under the reaction conditions. It is deduced that the zerovalent platinum, being present over the catalyst surface with high dispersion, and the zerovalent cobalt resulting from CoAl$_2$O$_4$ reduction are responsible for high activity of the Pt-Co/

Al$_2$O$_3$, and the remain CoAl$_2$O$_4$ is beneficial to suppression of carbon deposition over the catalyst.

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