

## The Dramatic Effect of Metal Precursor on the Catalytic Performance of Co/SiO<sub>2</sub> Catalyst for CO<sub>2</sub> Reforming of CH<sub>4</sub>

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**Abstract:** The cobalt precursor affects the catalytic performance of Co/SiO<sub>2</sub> catalyst remarkably. The catalyst prepared from cobalt acetate exhibits excellent activity, stability and resistance to carbon deposition.

**Keywords:** CO<sub>2</sub> reforming of CH<sub>4</sub>, synthesis gas, Co/SiO<sub>2</sub> catalyst, precursor.

The catalytic reforming of CH<sub>4</sub> with CO<sub>2</sub> over Ni- and Co-based catalysts for the production of synthesis gas with low H<sub>2</sub>/CO ratios is of attraction in industrial Fischer-Tropsch synthesis. One of major problems for this process is catalyst deactivation by carbon deposition and/or active metal sintering. For Co-based catalysts, Co(NO<sub>3</sub>)<sub>2</sub> is generally used as starting salt and much effort was devoted to the effects of promoter, supporter and preparation conditions<sup>1-4</sup>. The effect of cobalt precursor has not been reported. In our work, it is found that the cobalt precursor affects remarkably the catalytic performance of Co/SiO<sub>2</sub> catalyst. The catalyst starting from Co(CH<sub>3</sub>COO)<sub>2</sub> exhibits excellent activity, stability and resistance to carbon deposition.

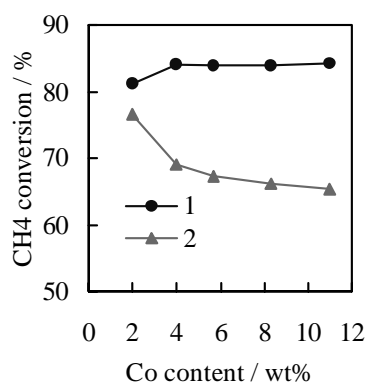
The supported Co/SiO<sub>2</sub> catalysts were prepared by the wet impregnation method, using cobalt nitrate or cobalt acetate as the metal precursor. After being dried overnight at 120°C, the catalyst was then calcined at 600°C in air for 5h. The catalyst prepared from cobalt nitrate and acetate are denoted Co(N)/SiO<sub>2</sub> and Co(A)/SiO<sub>2</sub>, respectively.

The evaluation of catalyst was carried out under atmospheric pressure, at 700°C, using a fixed bed flow reactor. Before reaction, the catalysts were reduced in H<sub>2</sub> at 700°C for 1h. A CH<sub>4</sub>+CO<sub>2</sub> (CH<sub>4</sub>/CO<sub>2</sub>=1.07) gas mixture, with a GHSV=4000cm<sup>3</sup>/g/h, was used as feed gas. The effluents were analyzed in a gas chromatograph equipped with a TDX-01 column. The amount of carbon deposited on catalyst was measured by temperature programmed oxidation (TPO).

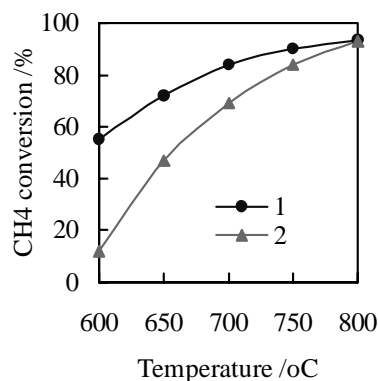
The comparison of activity between Co(N)/SiO<sub>2</sub> and Co(A)/SiO<sub>2</sub> catalysts at different cobalt contents and reaction temperatures were showed in **Figure 1** and **Figure 2**, where CH<sub>4</sub> conversions were measured after 10 min on stream. It is found that the activity of Co(A)/SiO<sub>2</sub> is higher than Co(N)/SiO<sub>2</sub>, especially at high cobalt content and low temperature. The CH<sub>4</sub> conversion over Co(A)/SiO<sub>2</sub> catalyst increases with cobalt

content from 81.2% to 84.1% for the 4wt% cobalt, and then remains invariable above that cobalt content. In contrast, the conversion over  $\text{Co(N)/SiO}_2$  decreases with increasing cobalt content from 76.5% for the 2wt% cobalt down to 65.3% for the 11wt% cobalt. Both the catalysts show an increase in activity with temperature. However, the activity of  $\text{Co(N)/SiO}_2$  catalyst is very poor at low temperature.

**Figure 1.**  $\text{CH}_4$  conversion versus Co content (temperature:  $700^\circ\text{C}$ ; 1:  $\text{Co(A)/SiO}_2$ ; 2:  $\text{Co(N)/SiO}_2$ )

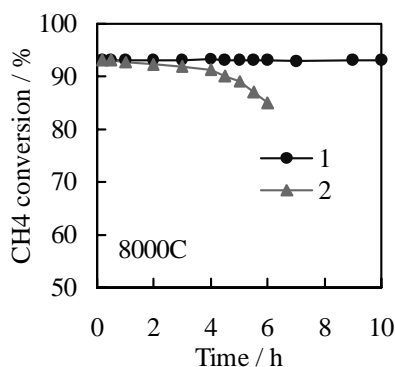
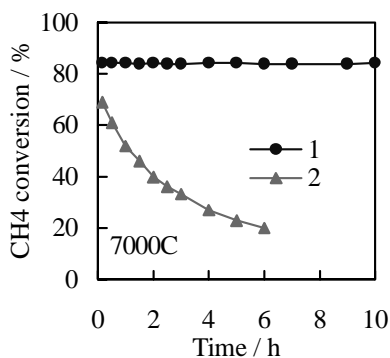


**Figure 2.**  $\text{CH}_4$  conversion versus temperature (Co content: 4wt%; 1:  $\text{Co(A)/SiO}_2$ ; 2:  $\text{Co(N)/SiO}_2$ )



The long-term stability performances of  $4\%\text{Co(A)/SiO}_2$  and  $4\%\text{Co(N)/SiO}_2$  catalysts were examined at  $700$  and  $800^\circ\text{C}$ . The results are given in **Figure 3**. It can be seen that  $4\%\text{Co(A)/SiO}_2$  is extremely stable, exhibiting no deactivation during 10h of reaction. In contrast,  $4\%\text{Co(N)/SiO}_2$  shows poor stability. Its activity is reduced continuously with reaction time at two reaction temperatures. Note that the deactivation rate at  $700^\circ\text{C}$  is faster than that at  $800^\circ\text{C}$ , indicating that the catalyst is not only less active but also less stable at lower temperature.

**Figure 3.** Variation of  $\text{CH}_4$  conversion with time on stream over (1)  $4\%\text{Co(A)/SiO}_2$  and (2)  $4\%\text{Co(N)/SiO}_2$  catalysts at  $700$  and  $800^\circ\text{C}$



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**Table 1** reports the amounts of carbon deposition and cobalt particle sizes determined before and after reaction by XRD. It is found that 4%Co(N)/SiO<sub>2</sub> exhibits a larger initial particle size than 11%Co(A)/SiO<sub>2</sub> and the particle size increases with cobalt content. This can explain the lower initial activity and its decline with increasing cobalt content in the case of Co(N)/SiO<sub>2</sub> catalyst (see **Figure 1**). From the fact that the difference in initial activity between Co(A)/SiO<sub>2</sub> and Co(N)/SiO<sub>2</sub> catalyst increases with decreasing reaction temperature (see **Figure 2**), it can be inferred that this catalytic system exhibits stronger structure sensitivity<sup>5</sup> at low temperature than at high temperature. During 2h of reaction, 11%Co(A)/SiO<sub>2</sub> catalyst presents negligible sintering of the cobalt particles, while the sintering occurred on Co(N)/SiO<sub>2</sub> catalysts obviously. Furthermore, the carbon amounts are much lower for Co(A)/SiO<sub>2</sub> catalysts than for Co(N)/SiO<sub>2</sub> catalysts. On 4%Co(A)/SiO<sub>2</sub> only 0.202% carbon deposits were detected even after 10h of reaction at 700°C, showing an excellent resistance to coking, which is comparable to some noble metal catalysts. Generally, non-noble metal catalysts are deactivated by two factors: sintering of metal particles and formation of carbon deposits on the surface active sites. For 4%Co(N)/SiO<sub>2</sub> catalyst it is interesting to note that as reaction temperature increases from 700 to 800°C, both carbon amount and sintering degree increase while the deactivation rate slows down. This is probably due to the weaker structure sensitivity of the catalyst at higher temperature and/or to the formation of active surface carbide carbons<sup>6</sup>. Thus, we conclude that the deactivation of Co/SiO<sub>2</sub> catalyst starting from Co(NO<sub>3</sub>)<sub>2</sub> is mainly due to sintering of cobalt particles rather than carbon deposition.

**Table 1.** Co Particle size (d) and carbon amount (w)

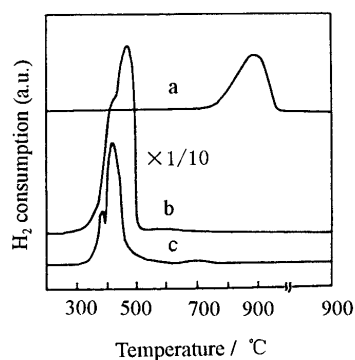
Catalyst	d (nm) <sup>a</sup>	Reaction at 700°C for 2h		Reaction at 800°C for 2h	
		d (nm)	w (%)	d (nm)	w (%)
4%Co(N)/SiO <sub>2</sub>	17.1	21.4	0.041	26.7	2.39
11%Co(N)/SiO <sub>2</sub>	19.5	23.5	0.244	— <sup>b</sup>	— <sup>b</sup>
4%Co(A)/SiO <sub>2</sub>	— <sup>b</sup>	— <sup>b</sup>	~0	— <sup>b</sup>	0.08
11%Co(A)/SiO <sub>2</sub>	7.0	7.9	0.075	— <sup>b</sup>	— <sup>b</sup>

a: Determined after reduction at 700 °C for 1 h; b: Not determined.

The XRD results of unreduced Co/SiO<sub>2</sub> catalysts showed that the dispersion of cobalt species is much higher for Co(A)/SiO<sub>2</sub> than for Co(N)/SiO<sub>2</sub>. Co(N)/SiO<sub>2</sub> clearly exhibited the presence of crystalline Co<sub>3</sub>O<sub>4</sub> even at 2wt% cobalt. However, no distinct XRD peaks due to Co<sub>3</sub>O<sub>4</sub> were detected even for 8.3%Co(A)/SiO<sub>2</sub>, although weak peaks were detected at 11wt% cobalt. **Figure 3** shows the TPR spectra of Co<sub>3</sub>O<sub>4</sub> and 4%Co/SiO<sub>2</sub> starting from Co(NO<sub>3</sub>)<sub>2</sub> and Co(CH<sub>3</sub>COO)<sub>2</sub>. On 4%Co(N)/SiO<sub>2</sub> two peaks due to a two-step reduction of Co<sub>3</sub>O<sub>4</sub><sup>7</sup> appear at 350 and 400°C. The spectrum is similar to that of Co<sub>3</sub>O<sub>4</sub>, showing negligible interaction between supporter and metal. By contrast, on 4%Co(A)/SiO<sub>2</sub> a high-temperature peak appears at about 850°C, which is ascribed to the reduction of well-dispersed surface cobalt silicate species<sup>8</sup>, showing a strong supporter-metal interaction. These results suggest that the cobalt precursor affects

greatly Co/SiO<sub>2</sub> catalyst in many ways such as dispersion and existence of cobalt species and supporter-metal interaction, which lead to a dramatic difference in catalytic performance between the catalysts starting from different precursors.

**Figure 4.** TPR profiles of (a) 4% Co(A)/SiO<sub>2</sub>, (b) Co<sub>3</sub>O<sub>4</sub> and (c) 4% Co(N)/SiO<sub>2</sub> (H<sub>2</sub>/Ar (5% H<sub>2</sub>) 30 ml/min; 50 mg catalyst, 10 mg Co<sub>3</sub>O<sub>4</sub>; β = 20°C/min)



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