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A Novel Catalyst for CO_2 Reforming of CH_4

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Abstract: A novel Ni-Co/SiO_2 catalyst which exhibits high activity and excellent anti-carbon deposition property for CO_2 reforming of CH_4 to synthesis gas is developed.

Keywords: CO_2 reforming of CH_4, synthesis gas, Ni-Co/SiO_2 catalyst.

The reforming of CH_4 with CO_2 into syngas is a very attractive route for the production of energy and chemicals. 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[1~3]. During the past dacades, the process has received attention and nickel and noble metal catalysts have been extensively studied, but few studies were made on cobalt catalysts. Especially, no any studies were made on Ni-Co bimetal catalysts for this reaction. In our earlier studies[4], Co/SiO_2 catalyst prepared from cobalt acetate showed optimal catalytic performance for CO_2 reforming of CH_4. The catalyst, however, had to be reduced at quite high temperature (973K) prior to the reaction. Here, we reports results obtained over Ni-Co/SiO_2 catalyst which exhibits high activity and excellent anti-carbon deposition property even with no pre-reduction.

Co/SiO_2, Ni/SiO_2 and Ni-Co/SiO_2 catalysts were prepared by impregnation and coimpregnation method, respectively. Cobalt or nickel acetate was used as starting salt. After being dried overnight at 393K, the catalyst was then calcined at 873K in air for 5h. Ni or Co loading was 4wt%.

Catalysts were tested in a fixed bed flow reactor without any pre-reduction. All of the tests were conducted under atmospheric pressure in a stream of $CH_4/CO_2=1.07$ and GHSV = 4000cm^3/g/h. 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)[5].

TPR experiments were conducted using 5%H_2 in N_2 (30ml/min) with 20K/min ramp rate in the temperature range between 353 and 1173K. At 1173K, the sample was kept for 13 min. CO_2-TPD was performed at a rate of 20K/min in flowing He. The evolved gases were monitored by on-line mass spectrometry. Before the experiment, the catalyst was reduced in H_2 at 973K for 1h, then flushed with He for 10min and cooled in flowing He to 303K.

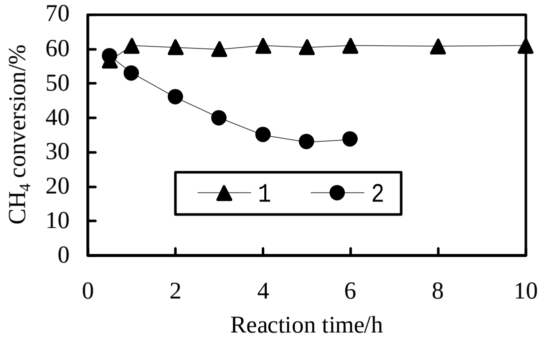
The catalytic results are compared in **Table 1**. Without pre-reduction, the catalytic activity decreased in the order: Ni-Co/SiO_2 > Ni/SiO_2 >> Co/SiO_2. Co/SiO_2 catalyst had no activity, while Ni-Co/SiO_2 was the most active of the three catalysts and much less sensitive to coking than Ni/SiO_2 Catalyst.

Table 1 The results of CO_2 reforming of CH_4 obtained over various catalysts after 2h of reaction

Catalyst	Reaction Temp./K	Products/%			CO/H_2	Carbon Amounts/%
		CH_4	CO_2	CO+H_2		
Co/SiO_2	973	51.5	47.8	Trace	—	—
Ni/SiO_2	873	26.5	21.1	48.5	1.11	8.37
	973	6.37	7.74	85.9	1.07	6.18
Ni-Co/SiO_2	873	21.9	18.3	59.7	1.04	0.64
	973	6.95	3.95	89.1	0.99	0.39

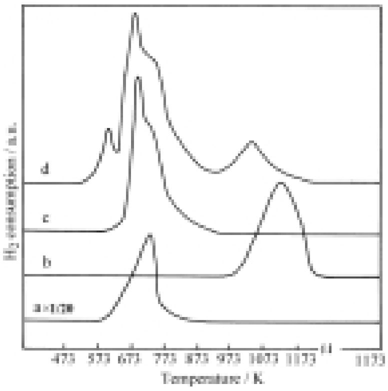
The alteration of CH_4 conversion over Ni/SiO_2 and Ni-Co/SiO_2 catalysts with reaction time at 873K is shown in **Figure 1**. The CH_4 conversion over Ni-Co/SiO_2 catalyst increased with time on stream during the initial 1h of reaction, and then remained invariable with time on stream during 10h of reaction. In contrast, in the case of Ni/SiO_2 catalyst it was found that CH_4 conversion decreased continuously with reaction time and the reaction had to be stopped because of the reactor becoming completely plugged by carbon deposits after 6 h. The activity of Ni/SiO_2 deactivated was renewed by exposure of the catalyst to O_2 at 973K to remove the carbon deposits. This implied that carbon deposition was a main cause for deactivation of the catalyst.

Figure 1 Stability of Ni/SiO_2 (2) and Ni-Co/SiO_2 (1) catalysts (T = 873K)



In **Figure 2** the H_2 TPR data are presented. It is clear that Ni/SiO_2 catalyst was more reducible than Co/SiO_2 catalyst. On the former catalyst two peaks appeared at 681 and 713K, probably due to the reduction of NiO with smaller and larger particle size, respectively[6]. On the latter catalyst, however, only one high-temperature peak (1123K) was measured. The peak, which was characteristic of surface cobalt silicate species[7], diminished and shifted to lower temperature (1028K) in the case of Ni-Co/SiO_2 catalyst. The diminishing of the peak implied that a part of cobalt species was reduced at still lower temperature. Furthermore, differing from Ni/SiO_2 and Co/SiO_2 catalysts further a peak was also observed for the Ni-Co/SiO_2 catalyst. The peak might be ascribed to the reduction of well-dispersed NiO. These results clearly showed improved reducibility for both NiO and cobalt species in Ni-Co/SiO_2. It is inferred that NiO could be reduced under working reaction conditions and the reduction of cobalt species could be promoted by spillover hydrogen activated on the nickel metal. This can account for higher activity of the catalyst than Ni/SiO_2 and Co/SiO_2 catalysts.

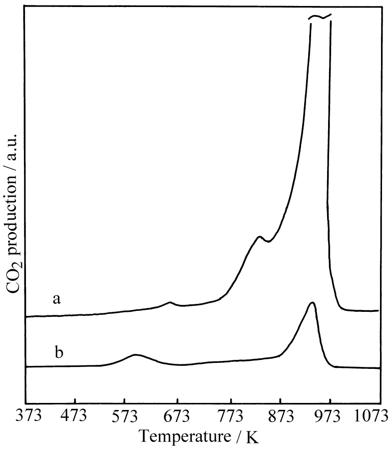
Figure 2 TPR spectra of different catalysts



(a) Pure NiO; (b) Co/SiO_2; (c) Ni/SiO_2; (d) Ni-Co/SiO_2

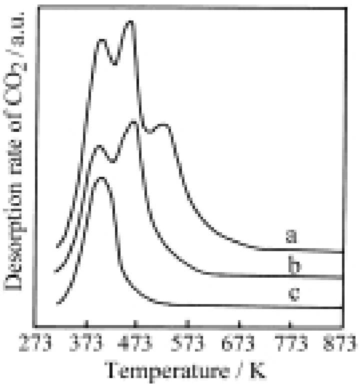
From TPO spectra in **Figure 3**, three type of carbonaceous species are found to exist on Ni/SiO_2 catalyst, designated as C_α at 653K, C_β at 835K and C_γ at 923K. The addition of Co to the catalyst resulted in a disappearance of C_β, a dramatic decrease in C_γ and a shift of the peak of C_α to lower temperature (597K). This implied that Co was responsible for the suppression of less reactive carbon species on Ni-Co/SiO_2 catalyst.

Figure 3 TPO profiles of carbon deposition over (a) Ni/SiO_2 and (b) Ni-Co/SiO_2 catalysts on stream at 973K for 2h



CO_2-TPD profiles are shown in **Figure 4**. On Co/SiO_2 catalyst three peaks, denoted as α, β and γ, appeared at 393, 453 and 513K. They were related to weak, moderate and strong base centers, respectively. The peaks of Ni-Co/SiO_2 catalyst were similar to that of Co/SiO_2 except for peak γ. However, for Ni/SiO_2 catalyst only peak α was observed. From the results, it can be seen that the ability of CO_2 absorption decreased in the order: Co/SiO_2 > Ni-Co/SiO_2 > Ni/SiO_2. In the CH_4/CO_2 reforming reaction, carbon deposits can be eliminated by the gasification reaction, *i.e.*, $CO_2 + C \rightarrow 2CO$. The ability of CO_2 to eliminate carbon will be improved duo to its absorption ability[8]. So it is deduced that the ability of resistance to carbon deposition of the Ni-Co/SiO_2 catalyst might be related to its property of CO_2 absorption.

Figure 5 CO_2-TPD spectra for (a) Co/SiO_2, (b) Co-Ni/SiO_2 and (c) Ni/SiO_2



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