

# Activation and Catalytic Behavior of Several Co/SiO<sub>2</sub> Catalysts for Fischer–Tropsch Synthesis

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Co(A+N)/SiO<sub>2</sub>, Co(N)/SiO<sub>2</sub>, and Co(A)/SiO<sub>2</sub> catalysts prepared by impregnation method with a mixture of cobalt nitrate and cobalt acetate (1:1), cobalt nitrate, and cobalt acetate as precursors, respectively, were reduced by H<sub>2</sub> at 300–700 °C and used for FT synthesis from syngas. For the freshly reduced Co(N)/SiO<sub>2</sub>, Co(A+N)/SiO<sub>2</sub>, and Co(A)/SiO<sub>2</sub> catalysts, H<sub>2</sub> chemisorptions are highest at the reduction temperatures of 300–400 °C, 500 °C, and 600 °C, respectively. For the Co(N)/SiO<sub>2</sub> catalyst reduced at 400 °C, Co(A+N)/SiO<sub>2</sub> catalyst reduced at 500 °C and Co(A)/SiO<sub>2</sub> catalyst reduced at 600 °C, reduction degrees vary as Co(N)/SiO<sub>2</sub> > Co(A+N)/SiO<sub>2</sub> > Co(A)/SiO<sub>2</sub>; cobalt dispersions vary as Co(A)/SiO<sub>2</sub> > Co(A+N)/SiO<sub>2</sub> > Co(N)/SiO<sub>2</sub>. These results suggest that, when oxidized Co/SiO<sub>2</sub> catalysts with various interactions between Co precursor and SiO<sub>2</sub> support are reduced at their optimum reduction temperatures, respectively, the catalyst with stronger interactions between cobalt precursor and SiO<sub>2</sub> support exhibits higher cobalt dispersion but lower reduction degree. The activities of these catalysts for FT synthesis change as Co(A+N)/SiO<sub>2</sub> ≥ Co(A)/SiO<sub>2</sub> > Co(N)/SiO<sub>2</sub>. The activity results also indicate that the well-dispersed cobalt species over the Co(A+N)/SiO<sub>2</sub> and Co(A)/SiO<sub>2</sub> catalysts favor the formation of short chain hydrocarbons to some extent. Turnover rates of the catalysts, which were calculated on the basis of the activity data at steady state and on the H<sub>2</sub> uptakes for the freshly reduced samples, are in a considerably wide range. This may be due to the fact that aggregation of those small cobalt particles by performing FT synthesis gives significant deviations in the turnover rate values. Our catalysts exhibit good stability when they are used for FT synthesis with CO conversion above 80%.

## Introduction

Cobalt-based catalysts have been widely used for Fischer–Tropsch synthesis from syngas.<sup>1–3</sup> It has been generally admitted that on cobalt catalysts the active phase for FT synthesis is cobalt metal and that the activities of Co catalysts depend solely on the number of active sites on the surface.<sup>4–7</sup> Therefore, those Co/SiO<sub>2</sub> catalysts with high reduction degree and cobalt dispersion show high activity for FT synthesis.

When Co/SiO<sub>2</sub> catalysts are prepared by impregnation method using various cobalt salts as precursors, the reduction degrees and cobalt dispersions are greatly changed.<sup>8–12</sup> For example, on the catalysts with cobalt

nitrate as precursor (denoted as Co(N)/SiO<sub>2</sub>), the reduction degrees are high but the cobalt dispersions are low; on the catalysts with cobalt acetate as precursor (denoted as Co(A)/SiO<sub>2</sub>), however, the cobalt dispersions are high but the reduction degrees are low. These results indicate that on the Co(N)/SiO<sub>2</sub> catalysts the interactions between cobalt precursor and SiO<sub>2</sub> are weak but on the Co(A)/SiO<sub>2</sub> catalysts the interactions are very strong. Intermediate interactions can be obtained by using a mixture of cobalt nitrate and cobalt acetate as precursor (denoted as Co(A+N)/SiO<sub>2</sub>).<sup>8,12</sup> After these catalysts were reduced by H<sub>2</sub> at 400 °C, their activities for FT synthesis change as Co(A+N)/SiO<sub>2</sub> ≥ Co(N)/SiO<sub>2</sub> > Co(A)/SiO<sub>2</sub>. However, reduction degrees of the cobalt species on the Co(A+N)/SiO<sub>2</sub> (57%) and Co(A)/SiO<sub>2</sub> catalyst (below 10%) are obviously lower than that of the cobalt species on the Co(N)/SiO<sub>2</sub> catalyst (88%).<sup>8</sup> Effects of reduction temperature for the Co(N)/SiO<sub>2</sub> catalysts have been investigated and highest H<sub>2</sub> chemisorption is obtained at reduction temperatures of

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(1) Ho, S. W.; Houalla, M. D.; Hercules, M. *J. Phys. Chem.* **1990**, *94*, 6396–6399.

(2) Iglesia, E.; Soled, S. L.; Baumgartner, J. E.; Reyes, S. C. *J. Catal.* **1995**, *153*, 108–122.

(3) van de Loosdrecht, J.; van der Haar, M.; van der Kraan, A. M.; van Dillen, A. J.; Geus, J. W. *Appl. Catal. A* **1997**, *150*, 365–376.

(4) Ernst, B.; Bensaddik, A.; Hilaire, L.; Chaumette, P.; Kienemann, A. *Catal. Today* **1998**, *39*, 329–341.

(5) Ernst, B.; Libs, S.; Chaumette, P.; Kienemann, A. *Appl. Catal. A* **1999**, *186*, 145–168.

(6) Huffman, G. P.; Shah, N.; Zhao, J.; Huggins, F. E.; Hoost, T. E.; Halvorsen, S.; Goodwin, J. G., Jr. *J. Catal.* **1995**, *151*, 17–25.

(7) Johnson, B. G.; Bartholomew, C. H.; Goodman, D. W. *J. Catal.* **1991**, *128*, 231–247.

(8) Sun, S.; Tsubaki, N.; Fujimoto, K. *Appl. Catal. A* **2000**, *202*, 121–131.

(9) Tsubaki, N.; Sun, S.; Fujimoto, K. *J. Catal.* **2001**, *199*, 236–246.

(10) Takeuchi, K.; Matsuzaki, H.; Arakawa, H.; Hanaoka, T.; Sugi, Y. *J. Mol. Catal.* **1989**, *55*, 361–370.

(11) Matsuzaki, T.; Takeuchi, K.; Hanaoka, T.; Arakawa, H.; Sugi, Y. *Catal. Today* **1996**, *28*, 251–259.

(12) Sun, S.; Fan, L.; Fujimoto, K. *Chem. Lett.* **1999**, 343–344.

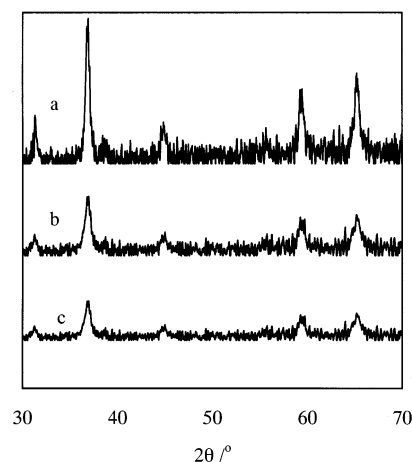
300–400 °C.<sup>13</sup> But for the Co(A+N)/SiO<sub>2</sub> and Co(A)/SiO<sub>2</sub> catalysts, the optimum reduction temperature should be higher. After these oxidized catalysts are reduced at their optimum reduction temperatures, respectively, their activities for FT synthesis may be greatly increased and change in a different sequence. Investigations on which are meaningful for further understanding the effects of the interactions between cobalt precursor and SiO<sub>2</sub> support on preparing high activity cobalt catalysts.

In the present work, oxidized Co(A+N)/SiO<sub>2</sub>, Co(N)/SiO<sub>2</sub>, and Co(A)/SiO<sub>2</sub> catalysts, which were prepared with a mixture of cobalt nitrate and cobalt acetate (mole ratio = 1/1), cobalt nitrate, and cobalt acetate as precursor, respectively, are reduced by H<sub>2</sub> at 300–700 °C and used for FT synthesis with a fixed bed reactor. Different effects of reduction temperatures on activating these catalysts are reported. Since Co(A+N)/SiO<sub>2</sub>, Co(N)/SiO<sub>2</sub>, and Co(A)/SiO<sub>2</sub> catalysts thus prepared are expected to have different dispersions from each other, the present work also aims to make clear the structure sensitivity of Co/SiO<sub>2</sub> catalysts for FT synthesis. Concerning structure sensitivity in the FT synthesis over cobalt-based catalysts, it has been claimed that, when FT synthesis was performed with low CO conversions (10%), the dispersion of cobalt active species has an influence on the chain growth and well-dispersed cobalt on silica favors the formation of short chain hydrocarbons.<sup>1,14</sup> However, Iglesia et al. have shown that with CO conversion ranging between 55 and 65%, turnover rates (site-time yields, moles CO converted/surface g-atom Co-s) vary between  $16 \times 10^{-3} \text{ s}^{-1}$  and  $30 \times 10^{-3} \text{ s}^{-1}$  for various cobalt catalysts. They concluded that, at typical conditions for FT synthesis, support effects disappear and the reaction becomes structure-insensitive.<sup>15,16</sup>

## Experimental Section

**Sample Preparation.** The oxidized Co/SiO<sub>2</sub> catalysts were prepared by incipient-wetness impregnating cobalt nitrate, cobalt acetate, or a mixture of cobalt nitrate and cobalt acetate on a commercial SiO<sub>2</sub> (JRC-SIO-5; BET surface area: 270 m<sup>2</sup> g<sup>-1</sup>, pore volume: 1.22 mL g<sup>-1</sup>), drying in air at 120 °C for 12 h. Then, the obtained samples were calcined in air at 450 °C for 4 h. The atomic ratio of cobalt nitrate and cobalt acetate in the mixture is 1.0. For all samples, weight ratios of cobalt to silica are 0.20. The samples prepared with cobalt nitrate, cobalt acetate, and the mixture of cobalt nitrate and cobalt acetate are referred to as Co(N)/SiO<sub>2</sub>, Co(A)/SiO<sub>2</sub>, and Co(N+A)/SiO<sub>2</sub>, respectively.

**Catalyst Characterization.** Powder XRD patterns of the catalyst samples were obtained on a Miniflex diffractometer (Rigaku) using Cu K $\alpha$  radiation with a Ni filter. Cobalt phases were detected by comparing the diffraction patterns with those in the standard powder XRD file compiled by the Joint Committee on Powder Diffraction Standards published by the International Center for Diffraction Data. The reduced samples were passivated in a stream of 1% O<sub>2</sub>/He at room temperature before being transferred from the reactor for XRD measurements. The average sizes of the particles on the catalysts were calculated using the half-height width of the most intense peak of the diffraction pattern and the Scherrer equation.



**Figure 1.** XRD patterns of the oxidized Co(N)/SiO<sub>2</sub> (a), Co(A+N)/SiO<sub>2</sub> (b), and Co(A)/SiO<sub>2</sub> catalysts.

The amounts of active surface metal on the catalysts were measured by H<sub>2</sub> chemisorption at 100 °C using a conventional volumetric adsorption system. An amount of 0.2 g of catalyst sample was used for each experiment. The catalyst samples were ex-situ reduced at 300–700 °C for 6 h and passivated in a stream of 1% O<sub>2</sub>/He at room temperature and then transferred into the cell. There they were reduced in H<sub>2</sub> at 300 °C for 1 h and followed by evacuation for 3 h before the measurements.

Reduction degrees of the freshly reduced samples were determined by O<sub>2</sub> titration at 400 °C in a flow of helium. The reaction of the reduced cobalt with oxygen was considered to form Co<sub>3</sub>O<sub>4</sub>.<sup>17</sup>

**Activity Test.** Activities of the cobalt catalyst samples for FT synthesis from syngas were measured with a fixed bed reactor. Catalyst sample was in-situ reduced in 30 mL/min flow of H<sub>2</sub> at 300–600 °C for 6 h. Thereafter the reaction was carried out in a 30 mL/min flow of syngas with H<sub>2</sub>/CO/Ar ratios of 62/33/5.0 at 1.0 MPa and 220–240 °C. Each catalyst was tested for over 60 h. Reaction temperatures were measured with a thermocouple inserted into the catalyst bed. Analyses of the gas-phase products were performed by an on-line gas chromatography, which were carried out every 20 min during the reaction. The liquid products were collected in an on-line trap at room temperature and analyzed by an off-line gas chromatograph after the reaction. Anderson-Schultz-Flory (A-S-F) distributions were plotted and the chain growth probability,  $\alpha$ , was calculated using the C<sub>9</sub>–C<sub>22</sub> data.

## Results and Discussion

**Catalyst Characterization.** Bulk cobalt phases of the oxidized and reduced Co(N)/SiO<sub>2</sub>, Co(A)/SiO<sub>2</sub>, and Co(A+N)/SiO<sub>2</sub> catalysts were determined by XRD measurements. The results for the oxidized catalysts are shown in Figure 1. It is found that the patterns of the oxidized catalysts have peaks at 31.3, 36.9, 44.7, 55.9, 59.3, and 65.4°, all of which are characteristics of Co<sub>3</sub>O<sub>4</sub> phase. But the average sizes of the Co<sub>3</sub>O<sub>4</sub> particles on these catalysts change as Co(N)/SiO<sub>2</sub> > Co(A+N)/SiO<sub>2</sub> > Co(A)/SiO<sub>2</sub>. Therefore, on these catalysts the interactions between cobalt precursor and SiO<sub>2</sub> support change as Co(N)/SiO<sub>2</sub> < Co(A+N)/SiO<sub>2</sub> < Co(A)/SiO<sub>2</sub>. Figure 2

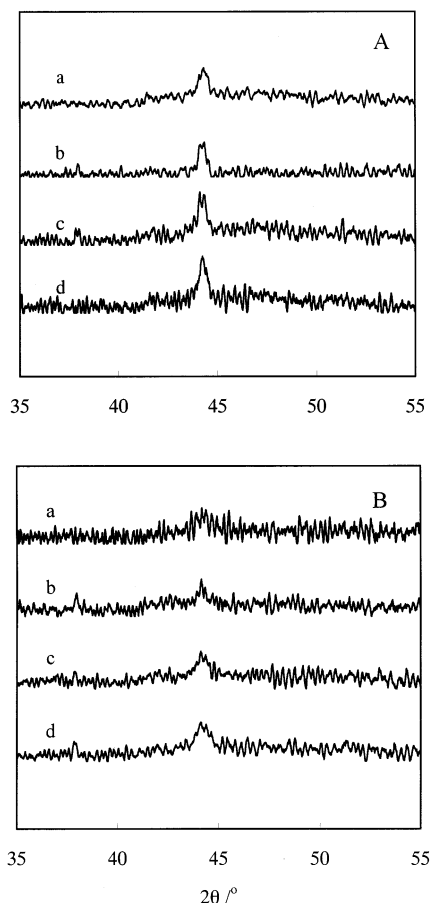
(15) Iglesia, E. *Appl. Catal. A* **1997**, 161, 59–78.

(16) Iglesia, E.; Soled, S. L.; Fiato, R. A. *J. Catal.* **1992**, 137, 212–224.

(17) Chin, R. L.; Hercules, D. M. *J. Phys. Chem.* **1982**, 86, 360–367.

(13) Niemelä, M. K.; Backman, L.; Krause, A. O. I.; Vaara, T. *Appl. Catal. A* **1997**, 156, 319–334.

(14) Reuel, R. C.; Bartholomew, C. H. *J. Catal.* **1984**, 85, 78–88.



**Figure 2.** XRD patterns of the Co(N)/SiO<sub>2</sub> (A) and Co(A+N)/SiO<sub>2</sub> (B) catalysts reduced at 300 °C (a), 400 °C (b), 500 °C (c), and 600 °C (d).

**Table 1.** Characterization Results of the Reduced Co(N)/SiO<sub>2</sub> and Co(A+N)/SiO<sub>2</sub> Catalysts

sample	reduction temp. (°C)	average $d_p$ of Co <sup>0</sup> (nm)	H <sub>2</sub> uptakes (mL H <sub>2</sub> /g)
N	300	19.0	1.05
	400	19.9	1.00
	500	21.6	0.87
	600	23.5	0.65
A+N	300	8.3	1.20
	400	9.9	1.43
	500	10.3	1.65
	600	13.0	1.45
A	400		1.13
	500		1.33
	600		1.48
	700		1.36

shows the patterns for the Co(N)/SiO<sub>2</sub> and Co(A+N)/SiO<sub>2</sub> catalysts reduced at 300–600 °C. Each pattern in Figure 2 includes a small peak at 44.6°, which corresponds to Co<sup>0</sup> phase with fcc structure. The peaks in the patterns of the Co(A+N)/SiO<sub>2</sub> catalysts are broader and weaker than those in the patterns of the Co(N)/SiO<sub>2</sub> catalysts, suggesting that the metallic cobalt particles formed on the reduced Co(A+N)/SiO<sub>2</sub> catalysts are smaller. It is also seen that with increasing reduction temperature the metallic cobalt particles gradually grow. The particle sizes calculated using the XRD data and the Scherrer equation are included in Table 1. The result demonstrates that cobalt particles on all the Co(A+N)/SiO<sub>2</sub> catalysts are significantly smaller than those on the Co(N)/SiO<sub>2</sub> catalysts. The patterns for the reduced Co(A)/SiO<sub>2</sub> catalysts include very weak peaks

**Table 2.** Reduction Degrees and Cobalt Dispersions of the Catalysts Reduced at Their Optimum Reduction Temperatures, Respectively

catalyst	reduction degrees (%)	cobalt dispersions (%)
Co(N)/SiO <sub>2</sub> , 400 °C	95	3.3
Co(A+N)/SiO <sub>2</sub> , 500 °C	71	7.3
Co(A)/SiO <sub>2</sub> , 600 °C	55	8.5

due to the Co<sup>0</sup> phase, indicating that very small particles are formed. They are not shown here.

The amounts of surface cobalt particles on the freshly reduced catalysts are determined by H<sub>2</sub> adsorption at 100 °C. The results are shown in Table 1 as well. Bartholomew et al. pointed out that H<sub>2</sub> chemisorption at 100 °C was most reliable for determining the amount of active surface metal on silica-supported cobalt catalysts.<sup>18</sup> From Table 1, it is seen that H<sub>2</sub> uptakes on the Co(N)/SiO<sub>2</sub> catalysts reduced at 300 and 400 °C are obviously higher than those on the Co(N)/SiO<sub>2</sub> catalysts reduced at 500 and 600 °C. This result indicates that, for the Co(N)/SiO<sub>2</sub> catalyst, H<sub>2</sub> reduction at 500–600 °C leads to significant aggregation of the metallic cobalt particles. On the other hand, H<sub>2</sub> uptake on the Co(A+N)/SiO<sub>2</sub> catalyst reduced at 500 °C is highest among all the H<sub>2</sub> uptakes on the Co(A+N)/SiO<sub>2</sub> catalysts, and H<sub>2</sub> uptake on the Co(A)/SiO<sub>2</sub> catalyst reduced at 600 °C is highest among those on the Co(A)/SiO<sub>2</sub> catalysts. The optimum reduction temperatures for the Co(A+N)/SiO<sub>2</sub> and Co(A)/SiO<sub>2</sub> catalysts are significantly higher than that for the Co(N)/SiO<sub>2</sub> catalyst, which should be due to the fact that on the Co(A+N)/SiO<sub>2</sub> and Co(A)/SiO<sub>2</sub> catalysts the interactions between cobalt with SiO<sub>2</sub> support are stronger. These interactions obviously inhibit the aggregation of the metallic cobalt particles during H<sub>2</sub> reduction at 500–600 °C. When the oxidized catalysts are reduced at their optimum reduction temperatures, respectively, H<sub>2</sub> uptake changes as Co(A+N)/SiO<sub>2</sub> > Co(A)/SiO<sub>2</sub> > Co(N)/SiO<sub>2</sub>.

Table 2 shows the reduction degrees of the above three catalysts measured by O<sub>2</sub> titration. The results indicate that reduction degrees of the catalysts vary as Co(N)/SiO<sub>2</sub> > Co(A+N)/SiO<sub>2</sub> > Co(A)/SiO<sub>2</sub>. This result indicates that, when the oxidized catalysts are reduced at their optimum reduction temperatures, respectively, the catalyst with stronger interactions between the cobalt precursors with SiO<sub>2</sub> support exhibits lower reduction degree. It was reported that highly dispersed CoO<sub>x</sub> particles supported on SiO<sub>2</sub> can be completely reduced at above 800 °C, but it leads to the formation of sintered cobalt metal particles.<sup>10</sup>

Table 2 also shows the cobalt dispersions of the above three catalysts calculated on the basis of the H<sub>2</sub> uptakes and the reduction degrees. Those unreduced cobalt species are not included in the cobalt dispersion calculation. The cobalt dispersions of these catalysts are changed as Co(A)/SiO<sub>2</sub> > Co(A+N)/SiO<sub>2</sub> > Co(N)/SiO<sub>2</sub>. Therefore, when the oxidized catalysts are reduced at their optimum reduction temperatures, respectively, the catalyst with stronger interactions between the cobalt precursor with SiO<sub>2</sub> support exhibits higher cobalt dispersion. However, because reduction degree of the cobalt species on the catalyst with strongest interactions



**Table 3. Activity Data of Various Co(N)/SiO<sub>2</sub>, Co(A+N)/SiO<sub>2</sub>, and Co(A)/SiO<sub>2</sub> Catalysts for FT Synthesis ( $P = 1.0$  MPa,  $T = 220$  °C,  $W/F = 5.0$  g h/mol)**

sample	reduction temp.	CO conv. (CO%)	yields of CO <sub>2</sub> & HC			
			CO <sub>2</sub>	C <sub>1</sub>	C <sub>2-4</sub> (CO%)	$\alpha$
Co(N)/SiO <sub>2</sub>	300 °C	42.8	0.11	2.86	2.07	0.89
	400 °C	42.3	0.12	2.86	2.08	0.88
	500 °C	37.9	0.10	2.85	2.08	0.87
	600 °C	29.2	0.08	2.92	2.83	0.87
Co(A+N)/SiO <sub>2</sub>	300 °C	37.4	0.13	2.88	2.14	0.85
	400 °C	54.2	0.19	4.62	3.55	0.87
	450 °C	63.6	0.24	4.47	3.39	0.87
	500 °C	64.9	0.24	4.71	3.18	0.87
	550 °C	61.0	0.22	4.80	3.70	0.86
Co(A)/SiO <sub>2</sub>	600 °C	57.7	0.19	5.18	4.05	0.86
	400 °C	41.2	0.15	4.01	3.07	0.85
	500 °C	51.3	0.20	5.24	4.03	0.86
	600 °C	57.0	0.20	5.90	4.43	0.86
	700 °C	54.0	0.19	5.81	4.41	0.84

between the cobalt precursor and SiO<sub>2</sub> support may be rather low, the catalyst with largest amount of surface metallic cobalt particles may be that with intermediate interactions.

For the Co(A+N)/SiO<sub>2</sub> and Co(A)/SiO<sub>2</sub> catalysts, reduction degrees become significantly increased by increasing the reduction temperature and, when they are reduced at their optimum reduction temperature, respectively, the cobalt dispersions are still high. The amounts of active surface cobalt become higher than the similar catalyst systems in the literature.<sup>8</sup> However, the cobalt dispersions are still slightly lower than the Co catalysts prepared by using carbonyl precursors or by impregnation with concentrated nitrate solutions, followed by direct reduction of nitrate precursors using slow-temperature ramping protocols.<sup>15</sup>

**Catalytic Activity.** The Co(N)/SiO<sub>2</sub>, Co(A+N)/SiO<sub>2</sub>, and Co(A)/SiO<sub>2</sub> catalysts reduced at 300–700 °C were used for FT synthesis with a fixed bed reactor at the conditions of  $P = 1.0$  MPa,  $T = 220$  °C, and  $W/F = 5.0$  g h/mol. Each catalyst was tested for above 60 h. After FT synthesis for over 10 h, the reaction becomes stable. Table 3 shows the activity data when the reaction was performed for 12 h. It is seen that, for the Co(N)/SiO<sub>2</sub> catalysts, highest CO conversions are those on the catalysts reduced at 300–400 °C. However, for the Co(A+N)/SiO<sub>2</sub> catalysts, highest CO conversion is that on the catalyst reduced at 500 °C; and for the Co(A)/SiO<sub>2</sub> catalysts, highest CO conversion is that on the catalyst reduced at 600 °C. For the catalysts obtained by H<sub>2</sub> reductions of the oxidized catalysts at their optimum reduction temperatures, respectively, CO conversions vary as Co(A+N)/SiO<sub>2</sub>  $\geq$  Co(A)/SiO<sub>2</sub> > Co(N)/SiO<sub>2</sub>.

It is also seen that chain growth probabilities,  $\alpha$ , are weakly affected by the reduction temperature; however, the chain growth probabilities on the Co(A)/SiO<sub>2</sub> and Co(A+N)/SiO<sub>2</sub> catalysts are slightly but significantly lower than those on the Co(N)/SiO<sub>2</sub> catalysts. These results suggest that the well-dispersed cobalt species over the Co(A)/SiO<sub>2</sub> and Co(A+N)/SiO<sub>2</sub> catalysts favor the formation of short chain hydrocarbons to some extent.<sup>1,14</sup> Chain growth probabilities on all the catalysts are in the range of 0.84–0.89, which indicate that our Co/SiO<sub>2</sub> catalysts have the advantage of performing FT synthesis with high contents of liquid hydrocarbons (C<sub>5</sub>–C<sub>20</sub>).

**Table 4. Turnover Rates of Various Co(N)/SiO<sub>2</sub>, Co(A+N)/SiO<sub>2</sub>, and Co(A)/SiO<sub>2</sub> Catalysts (reaction conditions:  $P = 1.0$  MPa,  $T = 220$  °C,  $W/F = 5.0$  g h/mol)**

sample	reduction temp.	CO conv. (CO%)	turnover rates (10 <sup>-3</sup> s <sup>-1</sup> )
Co(N)/SiO <sub>2</sub>	300 °C	42.8	90
	400 °C	42.3	93
	500 °C	37.9	96
	600 °C	29.2	99
Co(A+N)/SiO <sub>2</sub>	300 °C	37.4	69
	400 °C	54.2	83
	500 °C	64.9	87
	600 °C	57.7	89
Co(A)/SiO <sub>2</sub>	400 °C	41.2	79
	500 °C	51.3	86
	600 °C	57.0	86
	700 °C	54.0	89

Turnover rates (site-time yields) of various Co(N)/SiO<sub>2</sub>, Co(A+N)/SiO<sub>2</sub>, and Co(A)/SiO<sub>2</sub> catalysts were calculated on the basis of the activity data shown in Table 3, which are obtained after reaction for 12 h, and of the H<sub>2</sub> uptakes for the freshly reduced catalysts, as shown in Table 1. The results are shown in Table 4. The amounts of active sites on cobalt catalysts are usually determined by H<sub>2</sub> chemisorptions on the freshly reduced samples, because of the obvious difficulty in measuring cobalt dispersions of the wax-filled catalysts after reaction. Because the activities of these catalysts were measured with various CO conversions, before comparing the turnover rates of various catalysts, we investigate the influence of CO conversion, which varied by changing bed-residence time, on turnover rate values for both Co(N)/SiO<sub>2</sub> catalyst reduced at 400 °C and Co(A+N)/SiO<sub>2</sub> catalyst reduced at 500 °C. The results indicate that when CO conversion increases from below 20% to above 40%, turnover rate decreases slightly (below 10%); but when CO conversion increases from about 40% to 70%, turnover rate decreases rapidly (about 25%).

As shown in Table 4, for the Co(N)/SiO<sub>2</sub> catalysts reduced at 300–700 °C, turnover rates vary in a relatively narrow range and increase with reduction temperature. However, if the Co(N)/SiO<sub>2</sub> catalysts are used for FT synthesis at the same CO conversion, turnover rates of the catalysts may show the same value, because turnover rate slightly increases with decreasing CO conversion. This result indicates that the structure changes on the Co(N)/SiO<sub>2</sub> catalyst by increasing reduction temperature show very small effects on the turnover rates.

On the other hand, turnover rates of the Co(A)/SiO<sub>2</sub> and Co(A+N)/SiO<sub>2</sub> catalysts are affected by the reduction temperature; they are obviously lower than those of the Co(N)/SiO<sub>2</sub> catalysts as well. It is noticed that the activities of the Co(A+N)/SiO<sub>2</sub> catalysts reduced at 500–600 °C and the Co(A)/SiO<sub>2</sub> catalysts reduced at 500–700 °C are measured with CO conversions at above 50%; if they are measured with CO conversions at about 40%, turnover rates of the catalysts may increase and become similar to that of the Co(N)/SiO<sub>2</sub> catalyst reduced at 400 °C. These results suggest that the changes in particle size and in reduction degree in our experimental ranges have little effects on the turnover rates.

However, turnover rates of the Co(A+N)/SiO<sub>2</sub> catalysts reduced at 300 °C and of the Co(A)/SiO<sub>2</sub> catalyst

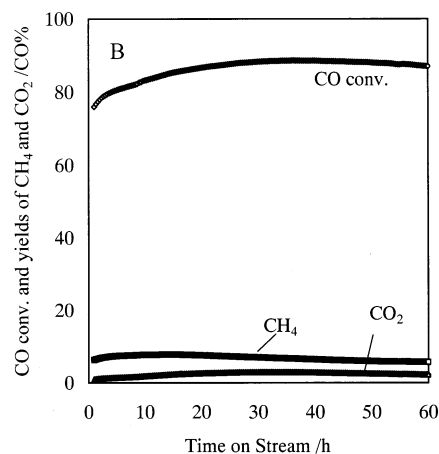
reduced at 400 °C are smaller than that of the Co(N)/SiO<sub>2</sub> catalyst reduced at 400 °C, although the activities of these catalysts were measured with similar CO conversions. These results may be due to the fact that the metallic cobalt particles formed on the Co(A+N)/SiO<sub>2</sub> catalysts reduced at 300 °C and on the Co(A)/SiO<sub>2</sub> catalyst reduced at 400 °C show weak interactions with the SiO<sub>2</sub> support and are significantly smaller than those on the Co(N)/SiO<sub>2</sub> catalysts, so that they become aggregated more significantly during FT synthesis. The decrease in CO conversion was not observed during the reaction, which may suggest that the metallic cobalt particles become aggregated at the initial 10 h of the reaction, before the reaction becomes stable.

The metallic cobalt particles on the Co(A+N)/SiO<sub>2</sub> catalysts reduced at 500 °C and on the Co(A)/SiO<sub>2</sub> catalyst reduced at 600 °C are small as well. However, these particles insignificantly aggregate during the reductions and during performing high-pressure FT synthesis. Therefore, high cobalt dispersions are kept and the turnover rates of the catalysts calculated based on the amounts of active sites on the freshly reduced catalysts are relatively higher, which may be due to the strong interactions between the cobalt particles and the SiO<sub>2</sub> support. These results indicate that the Co(A+N)/SiO<sub>2</sub> and Co(A)/SiO<sub>2</sub> catalysts reduced at 500–600 °C have the advantage of good stability during performance of FT synthesis.

FT synthesis over the Co/SiO<sub>2</sub> catalysts may be structure-insensitive. However, those small cobalt particles showing weak interactions with the SiO<sub>2</sub> support may become aggregated during the performance of FT synthesis; it may give significant deviations when the turnover rates are calculated on the basis of the activity data at steady state and on the H<sub>2</sub> uptakes for the freshly reduced catalysts.

The cobalt catalysts in this work show very good stability for FT synthesis. To further investigate the catalytic stability of these catalysts for FT synthesis, those catalysts reduced at their optimum reduction temperatures, respectively, were tested for FT synthesis at an increased temperature (240 °C). Figure 3 shows the activity data of the Co(A+N)/SiO<sub>2</sub> catalyst reduced at 500 °C for FT synthesis, indicating the changes of CO conversion and yields of CH<sub>4</sub> and CO<sub>2</sub> with time on stream. Similar results are obtained for the Co(N)/SiO<sub>2</sub> catalyst reduced at 400 °C and for the Co(A)/SiO<sub>2</sub> catalyst reduced at 600 °C (not shown here).

From Figure 3, it is seen that CO conversions increase gradually at the initial 10 h of reaction and then become stable. In the whole process of 60 h reaction, CO conversions do not show significant decrease. Small changes in CO conversion after reaction for 30 h are due to the changes in the reaction temperature. But after FT synthesis for 20 h, yield of methane significantly decreases and suggests that during the reaction, distribution of the products slowly changes and the formation of long chain hydrocarbons becomes relatively



**Figure 3.** Changes in CO conversion and yields of CH<sub>4</sub> and CO<sub>2</sub> with time on stream on the Co(A+N)/SiO<sub>2</sub> catalyst reduced at 500 °C (B).  $P = 1.0$  MPa,  $T = 240$  °C,  $W/F = 5.0$  g h/mol.

favorable. Selectivities to CO<sub>2</sub> are very low for both the Co(N)/SiO<sub>2</sub> and the Co(A+N)/SiO<sub>2</sub> catalysts.

### Conclusions

For the freshly reduced Co(A+N)/SiO<sub>2</sub>, Co(N)/SiO<sub>2</sub>, and Co(A)/SiO<sub>2</sub> catalysts, H<sub>2</sub> chemisorptions are highest at the reduction temperatures of 500 °C, 300–400 °C, and 600 °C, respectively. For the Co(N)/SiO<sub>2</sub> catalyst reduced at 400 °C, Co(A+N)/SiO<sub>2</sub> catalyst reduced at 500 °C, and Co(A)/SiO<sub>2</sub> catalyst reduced at 600 °C, reduction degrees vary as Co(N)/SiO<sub>2</sub> > Co(A+N)/SiO<sub>2</sub> > Co(A)/SiO<sub>2</sub>; cobalt dispersions vary as Co(A)/SiO<sub>2</sub> > Co(A+N)/SiO<sub>2</sub> > Co(N)/SiO<sub>2</sub>. These results suggest that, when oxidized Co/SiO<sub>2</sub> catalysts with various interactions between Co precursor and SiO<sub>2</sub> support are reduced at their optimum reduction temperatures, respectively, the catalyst with stronger interactions between cobalt precursor and SiO<sub>2</sub> support shows higher cobalt dispersion but lower reduction degree. The activities for FT synthesis of the catalysts obtained by H<sub>2</sub> reducing the oxidized catalysts at their optimum temperatures, respectively, change as Co(A+N)/SiO<sub>2</sub> ≥ Co(A)/SiO<sub>2</sub> > Co(N)/SiO<sub>2</sub>. The activity results also indicate that well-dispersed cobalt species over the Co(A)/SiO<sub>2</sub> and Co(A+N)/SiO<sub>2</sub> catalysts favor the formation of short chain hydrocarbons to some extent. Turnover rates of the catalysts, which were calculated on the basis of the activity data at steady state and on the H<sub>2</sub> uptakes for the freshly reduced samples, are in a considerably wide range. This may be due to the fact that aggregation of those small cobalt particles by performing FT synthesis gives significant deviations in the turnover rate values.

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