Plasma-Assisted Catalyst Design

DOI: 10.1002/anie.200800657

# Glow-Discharge Plasma-Assisted Design of Cobalt Catalysts for Fischer–Tropsch Synthesis**

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In the last twenty years, remarkable advances in nanosciences and nanotechnology have given an impulse to the design of heterogeneous catalysts. Bell emphasized in 2003 the role of nanoparticle size in catalyst performance,[1] and Schlögl and Abd Hamid[2] proposed in 2004 that the synthesis of nanosized catalysts may require multidimensional structural control. Glow-discharge (luminous) plasma is obtained by applying a potential difference between two electrodes placed in a gas. The plasma provides energy for decomposition of metal precursors. Several active catalysts have been developed[3–6] by using glow discharge. The glow-discharge activation process is simple, quick, audio-visual, and easy to control. It does not require the high temperatures and significant amounts of compressed gases which are typically used in conventional catalyst pretreatments.

The increasing interest in Fischer–Tropsch (FT) synthesis has been due to the growing demand for clean fuels and utilization of abundant natural gas, coal, and biomass-derived synthesis gas.[7,8] Cobalt catalysts are preferred for FT synthesis due to their high productivity, high selectivity for heavy hydrocarbons, high stability, and low activity in the water-gas shift reaction.[7,8] The catalytic performance of cobalt catalysts in FT synthesis appears to be strongly affected by the size of the cobalt metal particles.[7–11] Conventional cobalt FT catalysts are prepared by aqueous impregnation of supports (silica, alumina, titania, etc.) with solutions of cobalt salts. After decomposition of the supported cobalt salts by calcination in an oxidizing atmosphere, the catalysts are reduced in hydrogen to generate cobalt metal sites.

The present work focuses on the effects of pretreatment with glow-discharge plasma on cobalt dispersion and reducibility in alumina-supported catalysts and their performance in FT synthesis. Details of catalyst preparation are given in the *Experimental Section*. Cobalt and platinum contents in catalysts were 15 wt% and 0.1 wt%, respectively. The conventionally calcined catalysts are denoted Co(Pt)-$Al_2O_3$-*T*, where *T* indicates the temperature of the calcination pretreatment and Pt indicates promotion with Pt. The monometallic and Pt-promoted catalysts that were prepared using glow-discharge plasma (shortened to: plasma-assisted catalysts) are designated Co-$Al_2O_3$-PNH and CoPt-$Al_2O_3$-PNH respectively (Table 1).

**Table 1:** Cobalt catalysts obtained conventionally or plasma-assisted.

| Catalyst | Size of $Co_3O_4$ from XRD [nm] | Cobalt metal particles<br>Superparamagnetic particles [%] | <br>*D* [nm] |
|---|---|---|---|
| Co-$Al_2O_3$-473 | 9.5 | 66 | – |
| Co-$Al_2O_3$-773 | 9.6 | 56 | – |
| Co-$Al_2O_3$-PNH | – | ca. 100 | 6.7 |
| CoPt-$Al_2O_3$-473 | 9.3 | 90 | – |
| CoPt-$Al_2O_3$-773 | 9.6 | 77 | – |
| CoPt-$Al_2O_3$-PNH | – | ca. 100 | 5.7 |

Monometallic and Pt-promoted cobalt catalysts prepared by calcination exhibited XRD patterns characteristic of $Co_3O_4$ spinel in addition to the patterns of $\gamma$-$Al_2O_3$. The sizes of the $Co_3O_4$ crystallites, calculated by using the Scherrer equation, are listed in Table 1. In the XRD patterns of plasma-assisted cobalt catalysts, no distinct peaks attributable to oxidized or reduced cobalt phases were detected. The absence of the diffraction peaks attributable to cobalt phases suggests either very small crystalline or amorphous cobalt oxide particles. The XANES spectra of the plasma-assisted catalysts (Figure 1a) indicate the presence of the $Co_3O_4$ phase. This suggestion is consistent with EXAFS data (Figure 1b). The Fourier transform moduli of these catalysts exhibit a broad peak at 1.3 Å, which is attributed to contributions from $Co^{2+}$–O and from $Co^{3+}$–O coordination, and a peak at 2.5 Å with a shoulder at 3.04 Å, which arise from different cobalt coordination shells in $Co_3O_4$. A lower intensity of the peaks attributed to Co–O and Co–Co coordination than in the reference $Co_3O_4$ is indicative of the presence of smaller particles.

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[**] W. Chu thanks the CNRS and USTL for providing financial support during his stay as invited scientist. Financial support by the NSFC of China (20590360) and by the Ministry of Sciences and Technologies of China (2005CB221406) is acknowledged. P.A.C. is grateful to the financial support of the Russian Foundation for Fundamental Research (grant no. 06-03-32500-a). The authors thank S. Nikitenko for help with X-ray absorption measurements. ESRF is acknowledged for use of beamtime.

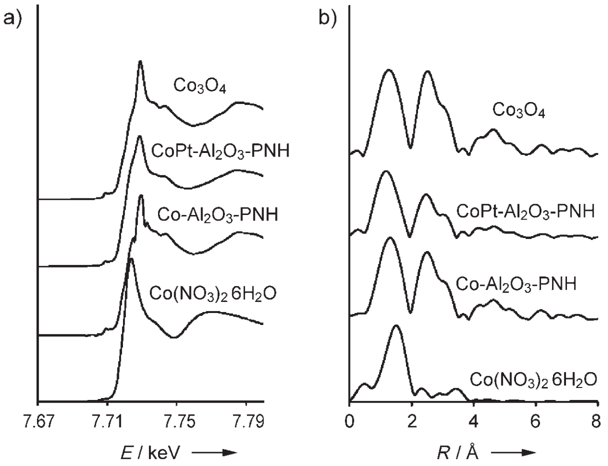

**Figure 1.** XANES spectra (a) and EXAFS $k^2$-weighed Fourier transform moduli (b) of plasma-assisted catalysts.

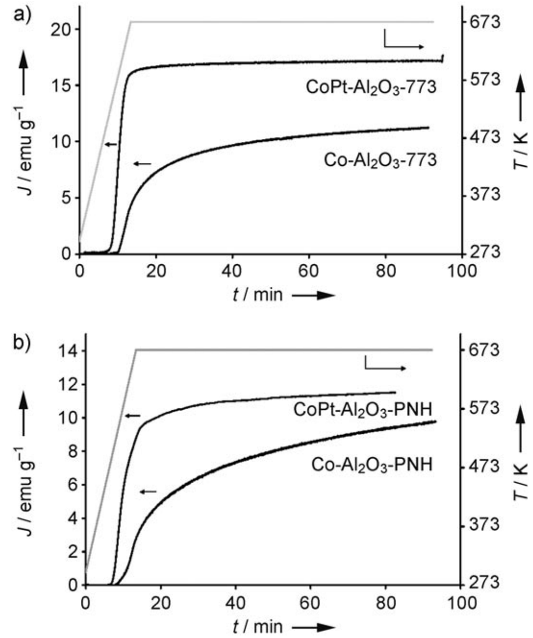

**Figure 2.** Variation of magnetization during temperature ramping and temperature dwelling in hydrogen at 673 K: a) calcined catalysts; b) plasma-assisted catalysts.

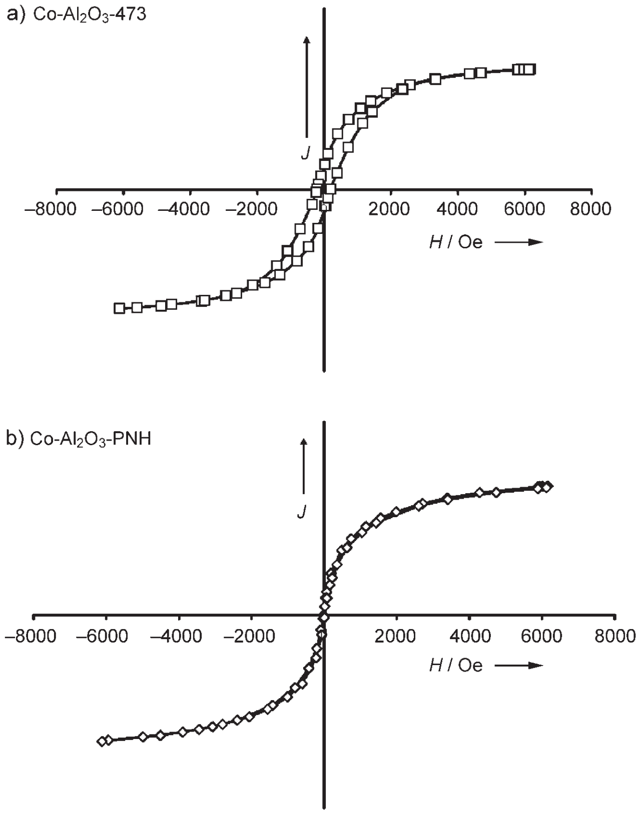

**Figure 3.** Field dependence measured for conventional and plasma-assisted monometallic catalysts reduced at 673 K.

Both XANES and EXAFS data suggest almost complete decomposition of cobalt nitrate in monometallic and Pt-promoted cobalt catalysts under glow discharge. Almost identical X-ray absorption data characteristic of $Co_3O_4$ were previously reported[12] for monometallic and Pt-promoted cobalt catalysts that were calcined in air at temperatures above the decomposition temperature of cobalt nitrate (ca. 423 K).[13]

The reducibility of cobalt catalysts was investigated by the in situ magnetic method. Cobalt oxides are paramagnetic at room and higher temperatures, while metallic cobalt has ferromagnetic properties below the Curie temperature (1388 K[14]). This suggests that the magnetization in strong magnetic fields (saturation magnetization) is proportional to the concentration of the metallic cobalt phase. The magnetizations measured for plasma-assisted and conventional catalysts during temperature ramping and temperature dwelling at 673 K in a flow of hydrogen are shown in Figure 2. Promotion with Pt of both conventional and plasma-assisted cobalt catalysts significantly enhances cobalt reducibility. This is consistent with previous reports[7,12,15] on the effect of Pt on cobalt reducibility in supported catalysts. Figure 2 also indicates that the plasma pretreatment of monometallic Co-$Al_2O_3$ catalysts slightly retards cobalt reduction. Indeed, cobalt in Co-$Al_2O_3$-PNH is reduced much more slowly than cobalt in Co-$Al_2O_3$-773.

Figure 3 displays the dependence of magnetization on the magnetic field (field dependence) for both conventional and plasma-assisted monometallic catalysts that were reduced at 673 K in hydrogen. The Co-$Al_2O_3$-473 catalyst exhibits a field dependence curve with hysteresis (Figure 3 a). This is indicative of the presence of single-domain ($d < 20$ nm) or multidomain ($d > 20$ nm) ferromagnetic cobalt metal particles. The particle size analysis[16] based on the variation of coercive force during mild oxidation yielded average sizes of cobalt metal particles in both monometallic and Pt-promoted conventional cobalt catalysts of less than 20 nm. This finding is consistent with the results of the XRD analysis (Table 1). Thus, it can be suggested that the conventional catalysts do not contain multidomain ferromagnetic particles ($d > 20$ nm). In this case, the particle size distribution in the catalysts can be evaluated from Equation (1)[7,16,17] where $\gamma$ is the fraction

$$\gamma = 1 - \frac{2J_\mathrm{r}}{J_\mathrm{S}} \qquad (1)$$

of superparamagnetic particles with diameters smaller than 7 nm at room temperature, $J_\mathrm{r}$ the residual magnetization (at zero magnetic field), and $J_\mathrm{s}$ the saturation magnetization. The fractions of superparamagnetic particles in cobalt catalysts reduced at 673 K are presented in Table 1.

Interestingly, the field-dependence curve of the plasma-assisted monometallic catalyst is very different from that of the calcined sample (Figure 3b). The absence of hysteresis is characteristic of superparamagnetic cobalt metal particles smaller than 7 nm.[7,16] A similar shape of the field-dependence curve (without hysteresis) was also observed for reduced CoPt-$Al_2O_3$-PNH. The particle size (Table 1) was calculated under the assumption of spherical particle morphology from field-dependence curves by using the Langevin equation.[7,16] Thus, plasma pretreatment results in a remarkable increase in cobalt dispersion in both monometallic and Pt-promoted cobalt catalysts.

Previous reports suggest that cobalt dispersion in FT catalysts is strongly affected by the mechanism and kinetics of decomposition of cobalt nitrate. Van de Loosdrecht et al. observed the beneficial effect of higher space velocity during calcination on cobalt dispersion.[10] De Jong et al. used NO/He mixtures to decompose the metal nitrate in cobalt- and nickel-supported catalysts.[11] Higher metal dispersion was attributed to a more moderate rate of metal nitrate decomposition in the presence of NO. Thus, a more gentle decomposition of cobalt nitrate in the glow discharge, which proceeds at temperatures much lower than conventional calcination, could possibly result in enhanced cobalt dispersion.

The results of catalytic evaluation of monometallic and Pt-promoted catalysts are listed in Table 2. Both conventional and plasma-assisted monometallic cobalt catalysts are much less active in FT synthesis than their Pt-promoted counterparts. Note that pretreatment with plasma produces catalysts which have similar or higher activity than their conventional counterparts. Carbon monoxide conversion increased from about 3 % over conventional Co/$Al_2O_3$ to 5.6 % over the plasma-enhanced Co-$Al_2O_3$-PNH catalyst. The plasma-assisted CoPt catalyst exhibited a carbon monoxide conversion of 26.3 %, which is higher than that obtained with conventional Pt-promoted catalysts (19–24 %). The selectivity to $C_{5+}$ hydrocarbons of about 73 % is similar to the values previously observed at atmospheric pressure for conventional cobalt FT catalysts.[12,13] The results of catalytic evaluation are consistent with the characterization data, which are indicative of much higher cobalt dispersion when decomposition of cobalt nitrate is conducted in plasma instead of by conventional calcination. Higher cobalt dispersion was observed in both monometallic and Pt-promoted plasma-assisted catalysts. Higher cobalt dispersion accompanied by a relatively small loss in cobalt reducibility leads to high catalytic activity of the plasma-assisted catalysts in FT synthesis.

***Table 2:*** Catalytic performance of conventional and plasma-assisted cobalt catalysts in FT synthesis.[a]

| Catalyst | CO conversion [%] | $CH_4$ selectivity [%] | $C_{5+}$ selectivity [%] |
|---|---|---|---|
| Co-$Al_2O_3$-473 | 3.3 | 8.3 | 84.2 |
| Co-$Al_2O_3$-773 | 2.7 | 6.5 | 79.8 |
| Co-$Al_2O_3$-PNH | 5.6 | 8.5 | 73.4 |
| CoPt-$Al_2O_3$-473 | 23.5 | 11.7 | 67.8 |
| CoPt-$Al_2O_3$-773 | 19.3 | 9.6 | 72.1 |
| CoPt-$Al_2O_3$-PNH | 26.3 | 9.6 | 72.7 |

[a] Conditions: $p = 1$ bar, $T = 463$ K, gas hourly space velocity (GHSV) = 1800 $\mathrm{mL\,g^{-1}\,h^{-1}}$, $H_2$/CO = 2.

## *Experimental Section*

All cobalt catalysts were prepared by impregnation of Puralox SCCA-5/170 γ-alumina ($S_\mathrm{BET} = 165\ \mathrm{m^2\,g^{-1}}$, pore diameter of 8.3 nm, and total pore volume of 0.477 $\mathrm{cm^3\,g^{-1}}$, Sasol) with aqueous solutions of cobalt nitrate. For preparation of the catalysts promoted with Pt, the impregnating solution also contained dihydrogen hexachloroplatinate. After impregnation the catalysts were dried at 373 K in an oven. To obtain conventional cobalt/alumina catalysts, the impregnated and dried samples were calcined in a flow of air at 473 or 773 K for 5 h with a temperature ramping of 1 $\mathrm{K\,min^{-1}}$.[12] To obtain plasma-assisted cobalt catalysts, the dried samples were exposed at ambient temperature to glow-discharge nitrogen plasma for 45 min and then to hydrogen plasma for another 45 min ($V = 100$ V, frequency 13.56 MHz, initial gas pressure 50 Pa). The cobalt catalysts were then reduced in a flow of hydrogen at 673 K for 5 h at a rate of temperature increase of 3 $\mathrm{K\,min^{-1}}$.

X-ray powder diffraction patterns were recorded with $\mathrm{Cu_{K\alpha}}$ radiation. The average $Co_3O_4$ crystallite size was calculated for both 422 ($2\theta = 56.0°$) and 511 ($2\theta = 59.5°$) diffraction lines by using the Scherrer equation. The X-ray absorption spectra at the Co K-edge were measured in transmission mode at the European Synchrotron Radiation Facility (DUBBLE-CRG, Grenoble, France). The XANES spectra after background correction were normalized by the edge height. After subtracting the metal atomic absorption, the $k^2$-weighted EXAFS signal was transformed without phase correction from $k$ space to $r$ space.

The in situ magnetic measurements were performed with a Foner vibrating-sample magnetometer.[16] The catalysts were reduced at 673 K in pure hydrogen with a temperature ramping of 28.2 $\mathrm{K\,min^{-1}}$. The field dependences were measured at 280 K by scanning the intensity of the magnetic field up and down to 6.2 kOe. The FT catalytic measurements were carried out in a fixed-bed stainless-steel microreactor for at least 24 h at each of the specified experimental conditions. Carbon monoxide contained 5 % $N_2$, which was used as an internal standard. Analysis of $H_2$, CO, $CO_2$, and $CH_4$ was performed with a 13X molecular-sieve column, while hydrocarbons ($C_1$–$C_{20}$) were separated in 10 % CP-Sil5 on a Chromosorb WHP packed column. The hydrocarbon selectivities were calculated on carbon basis.

Received: February 10, 2008
Published online: May 28, 2008

**Keywords:** Fischer–Tropsch synthesis · heterogeneous catalysis · magnetic properties · plasma chemistry · supported catalysts

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