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Synthesis and Characterization of Silica-Supported Cobalt Nanocatalysts Using Strong Electrostatic Adsorption

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Abstract: Strong Electrostatic Adsorption (SEA), a simple yet logical method, was employed to synthesize cobalt catalysts supported on silica. Mono-dispersed non-porous silica sphere was synthesized as a model support using modified Stöber method. Point of zero charge (PZC) of silica synthesized in-house was determined using equilibrium pH at high oxide loading (EpHL) method. Cobalt uptake versus pH was studied to determine the optimum pH. High cobalt uptake at basic pH and low cobalt uptake at acidic pH indicates electrostatic interaction between the cobalt complexes in the precursor solution and the hydroxyl group on the support's surface. Catalysts prepared at optimum pH were characterized using TPR, XPS and TEM. TPR shows reduction peak at high temperature (587°C) indicating strong interaction between cobalt and silica support. XPS shows presence of Co²⁺ species on the surface, but no cobalt-ammine complex was detected. TEM images show fairly well dispersed cobalt particles on the support. SEA was deemed a suitable method to prepare supported cobalt catalysts.

Key words: Cobalt catalysts, Strong Electrostatic Adsorption (SEA), FTS, TEM, XPS, TPR

INTRODUCTION

Fischer-Tropsch Synthesis (FTS) which synthesizes high quality clean fuel from syngas has received revived attention as a promising renewable energy resource. This process enables monetization of abundant natural gas and coal reserves compared to the dwindling crude oil reserve. It also produces environmentally friendly fuel which has low sulfur and aromatic ring content.

Supported cobalt has been found to be a good choice of catalyst for FTS. According to Borg *et al.* (2008), FTS activity is a function of number of cobalt metallic particle on the surface, which is exposed for syngas reaction. This factor in turns depends on the cobalt loading, dispersion of cobalt species and its reducibility. Hence, an ideal supported catalyst would have uniformly distributed cobalt species that undergoes complete reduction forming metallic cobalt particle with high dispersion that guarantees optimum use of cobalt.

Using carbon nanofibers, which is an inert model support, Bezemer *et al.* (2006) reported that structural sensitivity of cobalt FTS catalysis seems to have a threshold value of 6 nm. For cobalt metallic particle smaller than 6 nm, Turn over Frequency (TOF) decreased while methane selectivity increased as the particle size became smaller. For silica supported cobalt catalysts, average

cobalt particle size of 4.6±0.8 nm has showed impressive enhancement both in terms of activity and selectivity (Den Breejen *et al.*, 2009).

Most of the methods employed to prepare cobalt catalysts yielded non-uniformly distributed cobalt metallic particles. Strong electrostatic adsorption (SEA) provides a simple and yet logical explanation of mechanism of cobalt precursor deposition on the oxide support (Regalbuto, 2007). Empirical wise, results also shown that this method will yield higher dispersion with narrower distribution compared to conventional impregnation (Jiao and Regalbuto, 2008a; D'Souza *et al.*, 2007). Mechanism of electrostatic adsorption is shown in Fig. 1.

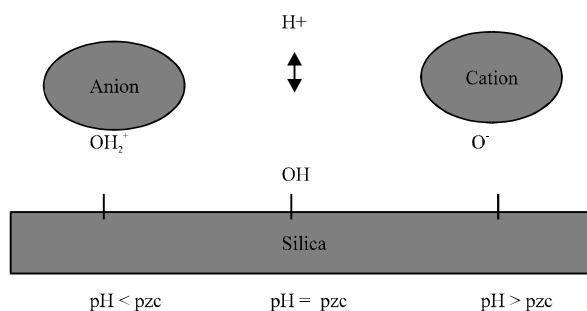


Fig. 1: Mechanism of electrostatic adsorption

SEA is a catalyst preparation method which is based on concept of electrostatic attraction of oppositely charged particle. Silica and other metal oxides contain hydroxyl groups on its surface. Point of zero charge (PZC) is the pH value of a medium where the hydroxyl groups on the surface of the support remain neutral. In a pH < PZC medium, the hydroxyl groups will protonate and become positively charged and thus attracting anions. When pH > PZC, the hydroxyl groups will deprotonate and become negatively charged and attracting cations. In other words, pH value plays an important role in the deposition of metal precursor.

Jiao and Regalbuto (2008b) have conducted a series of studies to prepare noble metals supported on silica and SBA-15 (mesoporous silica with periodic pore structure). By using cationic hexaamines complexes of the noble metal, it was found that metal uptake increase significantly at pH > PZC. All samples prepared via SEA at respective optimum pH showed smaller particle size and higher dispersion compared to those prepared via dry impregnation method. The absence of metal particles in the residue solution after several washing and higher reduction temperature suggested a stronger interaction of metal species with the support.

Compared to other metal complexes, cobalt(III) hexaamines (CoHA) prepared via the SEA method was found to be reducible at very high temperature (800°C), thus, the larger cobalt particle was formed due to sintering (but still smaller than those prepared via dry impregnation).

An in depth study found that cobalt hexaamines was molecularly adsorbed on the support and transformed into cobalt tetraamines (CoTA) after drying. The CoTA formed have very high stability (Park and Regalbuto, 1995). It remained robust through calcination at 450°C and is reducible only at 1000°C. In other words, although SEA has been proven as a feasible and logical method to yield high metal dispersion, but cobalt hexaamines complex is still an inadequate precursor.

Objective of the research was to prepare cobalt catalysts supported on non-porous silica (a model support) using SEA method. Non-porous silica with smooth surface and regular spherical shape will facilitate imaging using TEM to enable the study of morphology of cobalt particles. Cobalt nitrate that can be oxidized easily during calcination will be used as a precursor.

MATERIALS AND METHODS

Non-porous silica support was synthesized by hydrolysis of TEOS following modified Stöber method (Zabidi *et al.*, 2008). Silica synthesized was then calcined

at 500°C for 3 h to remove residue of reactants. Its surface area and pore volume were determined by nitrogen adsorption at low temperature using Micromeritics ASAP 2000.

Equilibrium pH at high oxide loading (EpHL) method (Park and Regalbuto, 1995) was employed to determine PZC of the support. Solutions at pH values in the range of 2-13 were prepared by adding nitric acid or ammonium hydroxide into distilled water. Silica was weighed for specific surface loading. Surface loading (SL) was calculated using following formula:

$$SL(m^2 L^{-1}) = \frac{\text{Specific surface area (m}^2 \text{ g}^{-1}) \text{ mass (g)}}{\text{Volume of solution (L)}}$$

Then 50 mL of each solution was added into weighed silica in a conical flask. Mixture was shaken for 1 hour on a rotary shaker before measurement of final pH value. The plateau in the final pH versus initial pH plot indicates the PZC of silica support.

To conduct the cobalt uptake versus pH survey, pH of precursor solution was adjusted to range of 2-13. Weighed silica was added into the solutions and shaken for 1 h. After that, final pH was measured. 5 milliliter of filtered solution of each sample was tested for content of cobalt via atomic absorption spectroscopy (Shimadzu model AA 6200) and UV-VIS spectrophotometer (Shimadzu model 1240).

After these two preliminary steps, an optimum pH range was determined. At the selected pH, cobalt precursor was adsorbed on support from an excess solution (to prevent pH shift) at 5% metal loading. Sample was filtered and dried in air for 24 h. Dried sample was then calcined in tubular furnace at 500°C for 1 h under N₂ flow to remove residue of reactants.

The calcined sample was analyzed using a Philips Tecnai Transmission Electron Microscope (TEM) operating at 200 keV. X-ray Photoelectron Spectroscopy (XPS, Thermo-Fisher K-Alpha) was used to determine the chemical state of the samples at 50 keV pass energy. X-ray photoelectron spectra obtained were analyzed using the Avantage software for peak fitting and chemical state identification. The reducibility of the catalyst was investigated using H₂ temperature-programmed reduction (TPR, Thermo-Finnigan TPDR0 1100). Sample was pretreated in nitrogen flow at 20 mL min⁻¹ up to 110°C then analyzed using 5% H₂/N₂ at 20 mL min⁻¹ and ramp to 900°C at 5°C min⁻¹.

RESULTS AND DISCUSSION

Synthesis of non-porous silica: Figure 2 shows the mono-dispersed, non-porous silica spheres synthesized

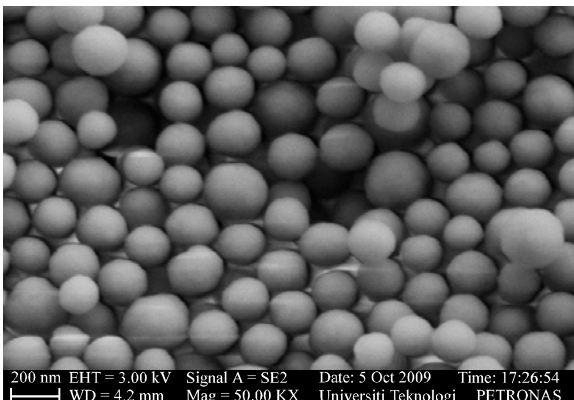


Fig. 2: FESEM of silica support

in-house. Average diameter of silica sphere was found to be 180 nm with a low variance of 12%. Its spherical shape and uniformly distributed particle size facilitates microscopy imaging via TEM and FESEM. This in turn will facilitate the study of morphology of cobalt particles on the silica support at each preparation steps.

Figure 3 shows Type II Isotherm plot of silica obtained when nitrogen adsorption at 77 K was used to determine its surface area. Type II isotherm indicates non-porous structure of the silica support. The BET surface area was found to be $17.8287 \text{ m}^2 \text{ g}^{-1}$.

Determination of PZC: Figure 4 displays the pH shift of silica at surface loading of $2000 \text{ m}^2 \text{ L}^{-1}$. The wide plateau indicates the PZC of the silica support was found to be 4.25 ± 0.25 , which is in agreement with value reported in previous studies (Park and Regalbuto, 1995).

Silica used in the studies has shown a maximum shift of 3.61 pH unit (from pH 7.76 to 4.15), which indicates strong buffering effects. Changes in acidity will change the charges of the surface hydroxyl group from positively charged to negatively charge. This in turn, will affect its interaction with the cobalt complexes in the solution.

Co-uptake versus pH: Figure 5 displays cobalt uptake versus final pH of precursor solutions at a range of 2 to 11. The pH higher than 12 was not studied because it has been reported that such pH will lead to significant silica dissolution. It was found that in acidic medium, there was very little cobalt uptake. This may be due to the repulsive interaction between the protonated hydroxyl groups on the surface and the cobalt hexaaqua complex $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ which were both positively charged.

When the pH was increased to be basic, there was a drastic increment in the cobalt uptake. This may be due to

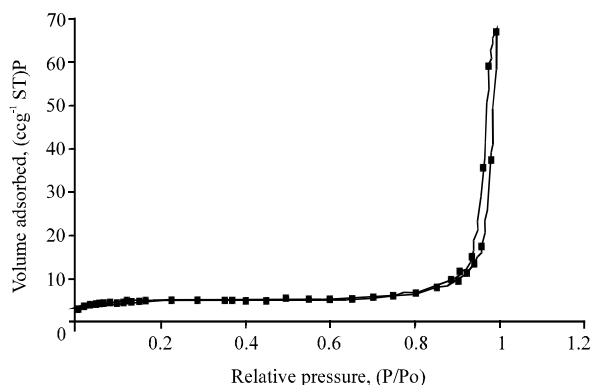


Fig. 3: Type II isotherm plot of silica support

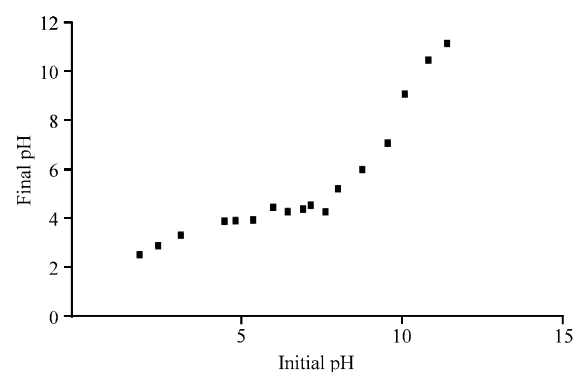


Fig. 4: pH shift of silica support

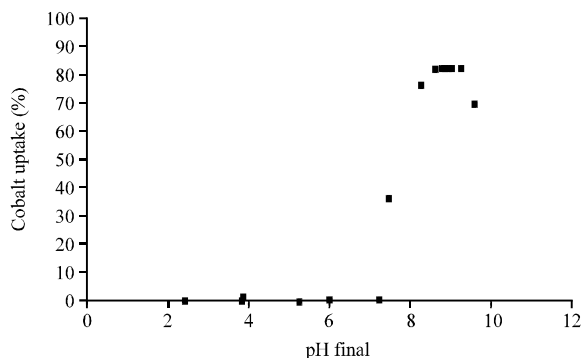


Fig. 5: Cobalt uptake versus pH_{final} for 5%Co/Silica

deprotonation of surface hydroxyl groups, which became negatively charged and hence exerting strong electrostatic attraction to the cobalt complexes.

For 5% loading precursor solution, 100% cobalt uptake was achieved in pH range of 8.768 to 9.937. Extended studies show 100% cobalt uptake was achieved using loading as high as 20% at optimum pH. However, when pH was increased to more than 10, there was a decrement in Co uptake. According to Regalbuto (2007); this might be due to ionic strength effect which suppress

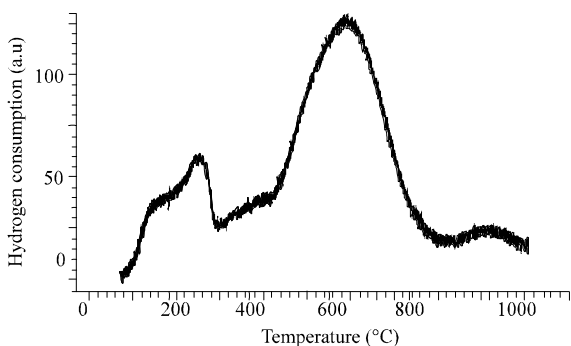


Fig. 6: TPR of sample L5

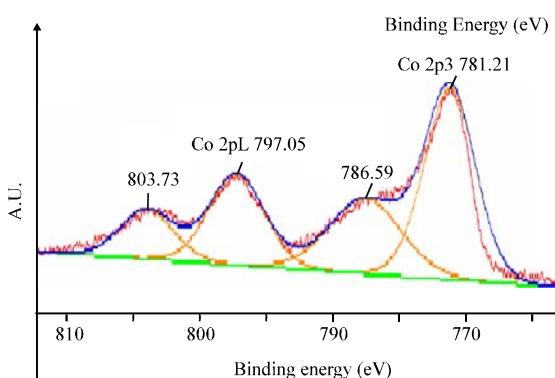


Fig. 7: Co2p3 spectra of sample L5

the cobalt adsorption on the support surface. No significant silica dissolution was observed in all the studies.

It was also found that at natural pH (without any adjustment using nitric acid and ammonia solution), the precursor has initial pH of 6.735 and final pH of 5.732. Cobalt uptake at this pH was found to be very low (3.40%). Hence, adjustment of pH of precursor solution is an important measure to generate maximum cobalt uptake.

The optimum pH was found to be in the range of 8.768 to 9.937 which generate 100% cobalt uptake without significant silica dissolution. Subsequent studies conducted in this range of pH showed consistent 100% cobalt uptake at 5% loading.

Characterization of catalysts prepared at optimum pH range:

Figure 6 displays TPR for sample L5 which is a 5%Co/Silica catalysts prepared using the SEA method at optimum pH. The first two reduction peaks at lower temperature of 178°C and 268°C were normally attributed to reduction of cobalt oxide to metallic cobalt (Khodakov *et al.*, 1997a,b). At much higher temperature, a broad peak with shoulder was observed at 587°C.

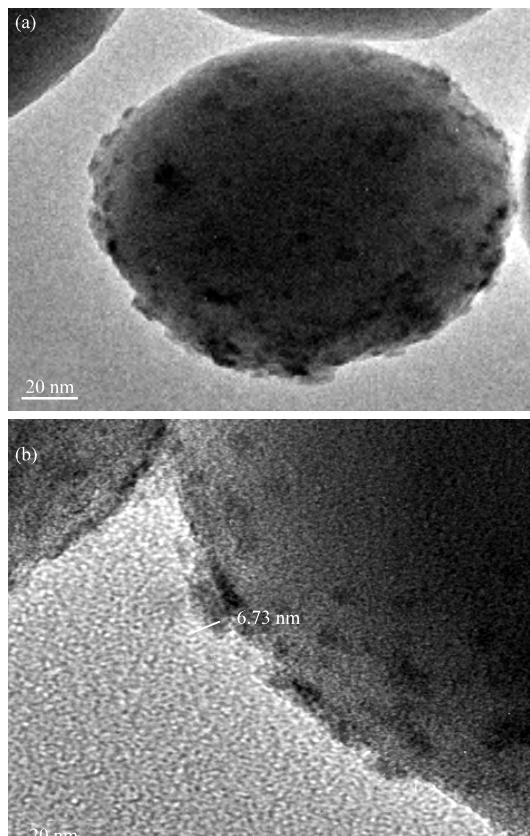


Fig. 8: TEM images of sample L5

Reduction peak at such high temperature is normally attributed to the presence of cobalt-silicate or cobalt ammines which are hard to reduce. However, it might also indicate a strong interaction between the adsorbed cobalt complex and the deprotonated silanol group on the silica surface. Besides, it was also reported that smaller cobalt particles to have lower reducibility.

Figure 7 displays XPS spectra of sample L5 obtained using K-Alpha XPS and analyzed using Avantage software. From the spectra, it was observed that Co2p_{3/2} peak of sample shifted to higher binding energy (781.18eV) compared to metallic Co (778eV) due to interaction with Si and O. Large spin-orbital split (16eV) indicates presence of Co²⁺ species (Sun *et al.*, 2003). A strong satellite peak at +5.38 eV from Co2p₃ indicates presence of cobalt (II) oxide or cobalt silicates. According to Girardon *et al.* (2005), it is difficult to distinguish between cobalt (II) oxide and cobalt silicates species.

N_{1s} peak was not observed in the XPS spectra. This may suggest complete decomposition of Co-nitrate precursor and also no residue of cobalt ammines complex (D'Souza *et al.*, 2007) after calcination.

Figure 8a and b display TEM images of sample L5. Figure 8a shows that cobalt particle was distributed on a silica sphere surface with no significant agglomeration. Figure 8b shows that the cobalt particle size is narrowly distributed and have an average value of 5.2 nm with a standard deviation of 1.2 nm. Narrowly distributed cobalt particle size suggest that SEA was deemed a suitable and yet simple method to prepare supported cobalt catalysts. The small particle size might contribute to the low reducibility of cobalt oxide at temperature lower than 500°C.

CONCLUSION

Point of zero charge of silica synthesized in-house were found to be the same as those reported in literature. 100% cobalt uptake was achieved in a basic precursor solution which suggests electrostatic interaction between cobalt complex in the precursor solution and deprotonated hydroxyl groups on the silica support surface according to the SEA model.

Sample L5 has been subjected to TEM characterization show acceptable cobalt dispersion. No cobalt ammine complex which has high resistance to reduction was found on the support surface. Both TPR and XPS suggest formation of cobalt (II) oxide which is reducible at lower temperature. SEA was deemed a feasible method to prepare silica supported cobalt nanocatalysts.

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