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Co/CNF Catalysts Tailored by Controlling the Deposition of Metal Colloids onto CNFs: Preparation and Catalytic Properties

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Abstract: Carbon nanofiber-supported Co nanocomposites were prepared by means of a modified ethylene glycol (EG) process, in which the Co salts are reduced in EG and are subsequently deposited onto carbon nanofibers (CNFs). It has been found that the deposition of cobalt colloids onto CNFs can be tailored by simply adjusting the pH of the EG and by heating the mixture of CNFs and colloidal solution at 100 °C for some time. The pH value (<7) and the temperature (at least 100 °C) for heating the mixture of CNFs and colloidal solution are found to be the key factors for depositing Co particles onto CNFs. The obtained Co/CNFs have a high and homogeneous dispersion of spherical Co metal particles with a narrow size distribution of 10–15 nm with a peak around 13.5 nm; this result is consistent, to a certain degree, with the value of 12.8 nm obtained from the XRD study. The different states of the stabilizer including carboxylates (pH >7) and carboxylic acids (pH <7) as well as the decomposition of carboxylic acids during heat treatment were monitored by using FTIR and UV-visible spectroscopy. On the basis of experimental results, the mechanism of depositing cobalt colloids onto CNFs is also addressed. The as-synthesized Co/CNF catalysts show excellent activity and regioselectivity for the 1-octene hydroformylation.

Keywords: carbon nanofibers · cobalt · colloids · hydroformylation · nanostructures · supported catalysts

Introduction

Nano-sized metallic colloids have attracted great interest in the surface chemistry and catalysis communities, because of their large surface area and high ratio of atoms at the surface.[1–11] Up to now, it has been demonstrated that the use of nano-sized metallic colloids as catalysts can improve activity and selectivity in hydrogenation,[12–13] hydroformylation,[14] and electrocatalysis.[15–17] In these cases, the colloids need to be stabilized by making use of organic stabilizers, such as thiolates, amines, phosphonates, and carboxylates; these stabilizers are essential to keep the finely dispersed state of colloids during the metal colloids synthesis.[1–2] Recently, a novel method for synthesis of metal colloids in ethylene glycol (EG) without adding traditional protective agents was reported, in which the colloids were stabilized by carboxylates (COO^-) coming from EG.[11,13,15–17]

It is known that the catalyst utilization can be improved by supporting metallic colloids onto a support. The supported metallic colloids catalysts are commonly prepared by the synthesis of metallic colloidal solutions, followed by the deposition of the nano-sized metal onto a suitable support.[13,16–19] However, it is difficult to obtain highly dispersed metal particles due to the effects of the organic stabilizers. Oxidation treatment has been proved to be effective for making highly dispersed metal catalysts in a controllable and reproducible way.[1] For example, Bock and co-workers[16] prepared Pt–Ru colloids in EG and deposited them onto high surface area carbons. It was also reported that Pt could be deposited onto carbon nanotubes by EG reduction, resulting in highly dispersed Pt nanoparticles.[15] However, to the best of our knowledge, the effects of the stabilizer (carboxylates), that is, how they regulate the deposition of metal colloids onto support materials, have not been addressed thoroughly.

In this paper, we report on the synthesis of nano-sized cobalt particles in a range of 10–15 nm and the homogeneous deposition onto CNFs by controlling the decomposition of the stabilizer (carboxylates) using a modified EG process. Compared with other methods for the synthesis of support-

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ed catalysts, our approach is simply to adjust the pH value of the colloidal solution and to heat the mixture of CNFs and colloidal solution under controlled conditions. These conditions are found to be critical for obtaining highly dispersed Co nanoparticles that are homogeneously deposited onto CNFs, which were found to exhibit excellent activity and regioselectivity for the 1-octene hydroformylation. The mechanism involved in the process of depositing cobalt colloids onto CNFs is also discussed.

Results and Discussion

The details for the synthesis of Co/CNF catalysts are shown in Table 1. The Co loading amount is found to depend on the pH value and the temperature for heat treatment of the mixture of CNFs and colloidal solution (termed as CS hereafter). The heat treatment temperature (at least 100 °C) is essential to obtain supported cobalt nanoparticles with high catalytic performance. TEM studies did not reveal the presence of any Co particles in the CS samples that did not undergo heat treatment (Figure 1a, CNF2 catalyst). Instead, the Co nanoparticles were observed in the filtrate solution of the mixture due to the protection effect of the stabilizers in the EG. It is also found that the pH value below 7 of the Co3 (the mixture of CNFs and cobalt colloids in EG, pH 4, and heat treated at 100 °C for 24 h) samples is important for making supported Co nanoparticles catalysts. The Co loading varied, depending on the preparation conditions. Because of this, the Co loading on CNF1, CNF3, and CNF4 catalysts is 7.4, 5.4, and 0.9 wt %, respectively, which corresponds to the pH of 4, 6, and 8, respectively, in EG; however, in all cases the theoretical loading amount should be 10.0 wt % according to the precursor $Co(OH)_2$ to be loaded. These results show clearly that the Co loading amount can be tailored by simply adjusting the pH value.

Table 1. The details for the preparation Co/CNF catalysts.

Samples	pH	Heat treatment temperature [°C]	Loading of cobalt (wt %)
CNF1	4	100	7.4
CNF2	8	25	0
CNF3	6	100	5.1
CNF4	8	100	0.9

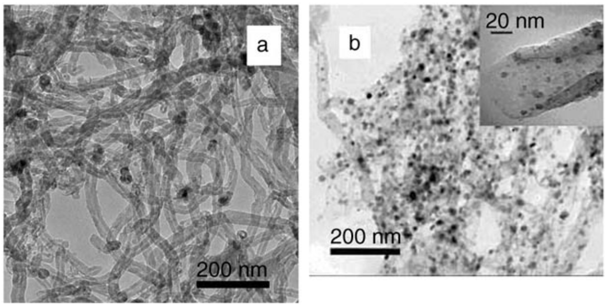


Figure 1. TEM images of CNF1 samples: a) untreated and b) treated by heating the mixture of CNFs and colloidal solution at pH 4 and 100 °C.

Figure 1b shows the typical TEM image of the CNF1 sample, from which it can be seen that the spherical cobalt particles on CNFs are quite uniform and distributed homogeneously. Based on the TEM measurement of about 300 particles in random regions, the average size of cobalt particles is estimated to be around 13.5 nm. The size distribution of CNF-supported cobalt particles is rather narrow and features in a lognormal distribution. Figure 2 shows the XRD patterns of Co/CNFs, from which it can be seen that the (111) diffraction peak of the face centered cubic (fcc) cobalt phase is weak and shadowed by the carbon (100) peak, implying that the size of cobalt particles on the CNFs is quite small and highly dispersed. The average diameter of the Co^0 crystallites calculated by the Scherrer equation is 12.8 nm, which is in good agreement with the TEM result of 13.5 nm discussed above.

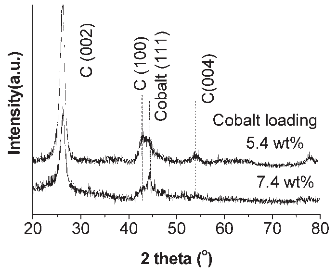


Figure 2. XRD patterns of Co/CNF catalysts.

An attempt has been made to understand the deposition mechanism of Co colloids into CNFs, for this purpose the colloidal solution was monitored by FTIR and UV-visible spectroscopy. Figure 3 shows the FTIR spectra of Co1 (cobalt colloids in EG, pH > 7), Co2 (cobalt colloids in EG, pH 4), and Co3 (the mixture of CNFs and cobalt colloids in EG, pH 4, and heat treated at 100 °C for 24 h) samples. For comparison, the FTIR spectrum of EG is also shown. As ex-

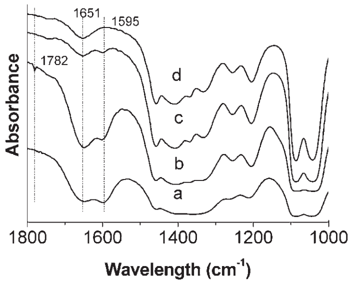


Figure 3. FTIR spectra of cobalt colloids in ethylene glycol: a) Co1 (pH > 7); b) Co2 (pH 4); c) Co3 (pH 4, and heat treated at 100 °C for 24 h); d) EG.

pected, for the Co1 sample, the FTIR spectrum shows a peak at 1600 cm^{-1} that corresponds to carboxylates (COO$^-$). In the case of the Co2 sample, the peak at 1600 cm^{-1} diminishes and a new peak at 1780 cm^{-1} corresponding to carboxylic acid (COOH) appears; this behavior is consistent with previous reports.[20–21] FTIR spectroscopy was further used to verify the decomposition of carboxylic acid during the heat treatment step. Compared to the Co2 sample, the peak of the Co3 sample at 1780 cm^{-1} disappears. This indicates that when the pH of the colloidal solution decreases to a certain value, ionizing conditions (COO$^-$) would be transformed to un-ionized conditions (COOH) and the subsequent heat treatment would result in the decomposition of carboxylic acid.

Figure 4 shows the changes in the UV-visible spectra of Co1, Co2, Co3, and EG samples. Three new peaks around 267, 288, and 317 nm are evident after the Co salts are reduced in EG, indicating that the peaks are due to the interaction between carboxylates (COO$^-$) and cobalt colloid; this also determines the stability of the colloid solution. With respect to the Co1 sample, the absorption peaks of the Co2 sample at approximately 320 nm disappear. This implies that when the pH of Co1 sample decreases to a certain value, the ligands are protonated and become detached from the cobalt colloids, which would destroy the stability of Co colloid solution.[1] In the case of Co3 sample, notable peaks around 250 and 280 nm corresponding to the carboxylic acid (COOH) in stable cobalt colloids in the solution disappear. Because of the above-mentioned changes, cobalt colloids are capable of being homogeneously deposited onto CNFs.

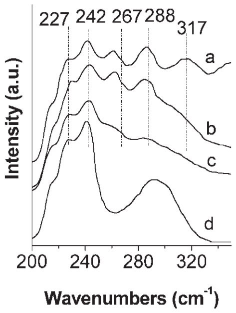


Figure 4. UV-visible spectra of the synthesis cobalt colloids in ethylene glycol: a) Co1 (pH > 7); b) Co2 (pH 4); c) Co3 (pH 4, and being treated at 100 °C for 24 h); d) EG.

On the basis of the results presented above, a mechanism for depositing metallic colloids onto CNFs is proposed and schematically illustrated in Figure 5. For the synthesis of metallic colloids in alkaline EG (pH > 12), EG acts as a reducing agent for metal precursor salts and can be oxidized to carboxylic acid (glycolic and oxalic acid), as shown in Scheme 1.[16]

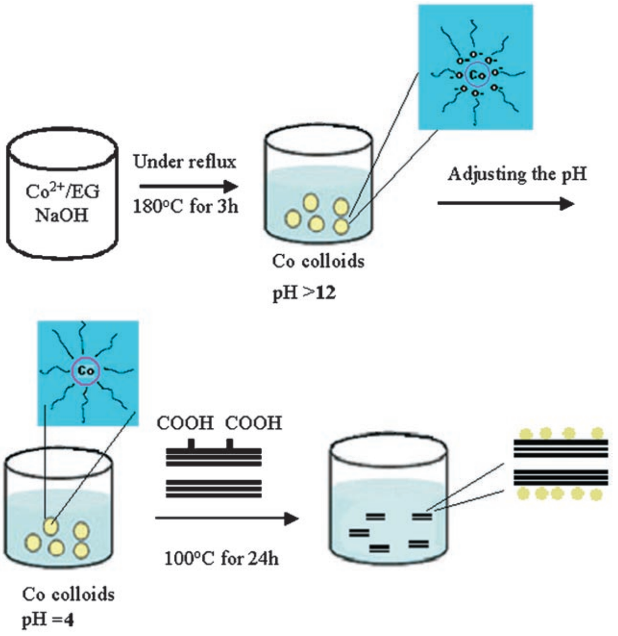
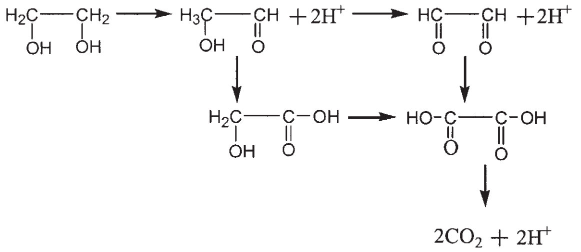


Figure 5. Schematic diagram illustrating the experimental procedure to make Co/CNF catalyst.



$$\underset{\text{OH}}{\text{H}_2\text{C}}-\underset{\text{OH}}{\text{CH}_2} \longrightarrow \underset{\text{OH}}{\text{H}_3\text{C}}-\underset{\text{O}}{\overset{}{\underset{\|}{\text{CH}}}} + 2\text{H}^+ \longrightarrow \underset{\text{O}}{\underset{\|}{\text{HC}}}-\underset{\text{O}}{\underset{\|}{\text{CH}}} + 2\text{H}^+$$

$$\underset{\text{OH}}{\text{H}_2\text{C}}-\underset{\text{O}}{\underset{\|}{\text{C}}}-\text{OH} \longrightarrow \text{HO-}\underset{\text{O}}{\underset{\|}{\text{C}}}-\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-OH} \longrightarrow 2\text{CO}_2 + 2\text{H}^+$$

Scheme 1.

Carboxylic acid adsorbs readily on cobalt surfaces, and as noted before, the adsorbed carboxylic acid resembles a kind of surface metal–carboxylates (FTIR evidence).[22] In the case of the alkaline EG (pH > 12), ions (COO$^-$) are predominant for the carboxylic acids that adsorbs more easily on cobalt surfaces and functions to stabilize the cobalt colloids. In principle, when the pH of the colloidal solution decreases to a certain value, ions (COO$^-$) would be protonated to be un-ionized (COOH). Though the interaction between carboxylic acids and the cobalt colloid surface is weak in comparison to carboxylates (COO$^-$), it should be strong enough to stabilize the cobalt colloids. In our case, after adjusting the pH of the mixture of CNFs and colloidal solution to below 7, no Co particles are found to be present on CNFs (Figure 1). The carboxylic acid in nature favors the stabilization of metal colloids in EG, but does not favor the deposition of metal colloids onto CNFs. The measures adopted in the present study, that is, adjusting the pH of the mixture of CNFs and colloidal solution to below 7, and then heating the mixture at 100 °C to make the carboxylic acids decompose gradually, help to destroy the stability of cobalt colloids, which leads to the homogeneous dispersion of cobalt particles onto CNFs.

The catalytic performance of CNF-supported Co nanoparticles with 7.4 wt % loading in the hydroformylation of 1-octene is shown in Figure 6. The results show that at 130 °C and 5.0 MPa of syngas pressure, the main products of the 1-octene hydrogenation are C^9-aldehyde with other products being isomers of 1-octene that can be circulated for further hydroformylation after being separated from the product. Under the conditions adopted in this study, the Co/CNF catalyst with a loading of 7.4 wt % is found to be highly active and stable, which is better than the Co catalyst with a loading of 8.7 wt % that was prepared by the traditional impregnation method.[23] It is assumed that the higher catalytic performance of Co/CNF catalysts for 1-octene hydroformylation are due to the high dispersion of cobalt particles on CNFs, implying that the homogeneous distribution of cobalt metal particles on CNFs is the key to the better performance of Co/CNF catalysts. The excellent catalytic activities might be also attributed to the unique structure, electrical properties, and the high external surface of CNFs.[9,15,23–24]

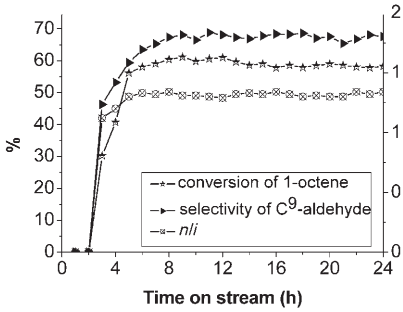


Figure 6. Hydroformylation of 1-octene over Co/CNF catalyst with cobalt loading of 7.4 wt %

Conclusion

In summary, a modified EG process has been used to synthesize a highly dispersed Co/CNF catalyst under mild conditions. It has been found that adjusting pH and heating the mixture of CNFs and colloidal solution are necessary steps to control the deposition and distribution of cobalt colloids on CNFs. A possible mechanism of cobalt colloids deposition onto carbon nanofiber (CNFs) is discussed. The as-synthesized Co/CNF catalysts show excellent activity and regioselectivity for the 1-octene hydroformylation. It can be expected that this work will lead to a new approach for making carbon-nanofiber-supported metals that are of potential use as catalysts for the hydroformylation of olefins.

Experimental Section

Materials: CNFs used in this study were purchased from Shenzhen Nanotech Port (NTP; China). The CNFs had an outer diameter of 40–60 nm with a length of 20–100 μm, and the N_2 BET surface area was 50–60 m^2g^{-1}. Before loading catalyst, the CNFs were treated in 4.0 N HNO_3 under reflux at 120 °C for 4 h.

Preparation of CNF-supported Co catalysts: The CNF1 catalyst was prepared according to the procedure shown in Figure 5. To get a colloidal solution of cobalt, the pH of cobalt nitrate (20 %) in EG was adjusted to 13 by using NaOH (2.5 M in EG). The solution was refluxed at 180 °C for 3 h to ensure the complete reduction of Co (the obtained sample was termed as Co1 hereafter). After cooling the Co1 sample to room temperature, its pH value was adjusted to 4 (the obtained sample was termed as Co2 hereafter) by adding HCl (2.5 M in EG). Then, the CNFs was suspended in EG and mixed with the Co2 sample under ultrasonic stirring for 30 min. The mixture was refluxed at 100 °C for 24 h to ensure the complete deposition of Co colloids onto the CNFs (the obtained sample was termed as Co3 hereafter). The CNF-supported Co catalysts were filtered and washed with deionized water and absolute ethanol in sequence, and then dried at 70 °C in air for 8 h. In comparison to other synthesis methods,[15–16] in our case the pH value of the colloidal solution was adjusted to <7 and the mixture of CNFs and colloidal solution was heated under controlled conditions, which were found to be critical for depositing Co colloids onto the CNFs, and for controlling the Co particle size distribution.

Following the same procedure described above, three more catalysts (CNF2, CNF3, and CNF4) were synthesized under identical conditions as for the CNF1 catalyst; the only differences were as follows: for CNF2, no heat treatment was adopted; for CNF3 and CNF4, the pH value was adjusted to 6 and 8, respectively.

Characterization: UV-visible spectroscopy (V-550, Japan) was used to monitor the deposition process of cobalt colloids in EG. FTIR spectra of samples were recorded on a Thermo FTIR spectrometer (Nicolet NEXUS 470, USA). All catalyst samples were examined by using transmission electron microscopy (TEM, Philips Tecnai G^2 20, operated at 200 kV) and XRD (D/max-2400, operated at 40 kV and 100 mA, $Cu_{K\alpha}$ radiation).

1-Octene hydroformylation: The hydroformylation of 1-octene was conducted at 130 °C and 5 MPa in a fixed-bed reactor in flowing gas of H_2/CO (50:50 v/v) with a space velocity of 0.1716 h^{-1}. 1-Octene mixed with cyclohexane in a volume ratio of 5:95 was continuously injected into the reactor by using a high-pressure liquid pump. Before the reaction, the catalyst was reduced in flowing hydrogen, during which the reactor was first ramped at 2 °C min^{-1} to 350 °C, and then was kept at 350 °C for 2 h. After the reduction, the catalyst bed was cooled to reaction temperature. For each run, 500 mg of catalyst was used. The reactants and products were analyzed by using GC-MS (Agilent 6890N GC/5973 MSD, equipped with a HP-INNOWAX capillary column and FID detector). The loading amount of Co metal in catalysts was measured by using inductively coupled plasma emission spectrometry (ICP-OES).

Acknowledgements

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