Final Report: "Novel Reforming Catalysts"
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Objectives

1. Investigate the stabilization of Co and Ni by MCM-41 incorporation for the reverse reforming reactions such as methanation of CO and CO_2. Compare these results with the same reactions on Co supported on single-walled carbon nanotubes (SWNT).
2. Develop carbon nanotubes as a support for aqueous phase reforming reactions on Co, Pt and bimetallic catalysts.
3. Do a feasibility study of nanotube-based catalysts for photocatalytic generation of hydrogen for methanol/water.

Technical Barriers

The technical barriers to aqueous phase reforming have been related to catalyst stability: silica in the form of structured MCM-41 is thermally a more stable support for Co and Ni than conventional high surface area amorphous silica but hydrothermal stability is not demonstrated. Carbon nanotube supports, in contrast, are highly stable under hydrothermal reaction conditions. A technical barrier to the use of SWNT as supports is the possible need to functionalize them to counter bundling in the aqueous environment and to graft the catalyst to the carbon tube to maintain a high dispersion.

Abstract

Our goal is development of novel reforming catalysts, e.g., stable low temperature aqueous reforming catalysts for oxygenated reactants. This reaction currently requires difficult reactors and analyses. Our strategy has been to screen carbon supported catalysts for reactivity by a reverse reaction, CO methanation, which is simpler (in number of mechanistic steps, reactor design, product analyses, etc.), and then to perform stability tests under actual aqueous reforming conditions. This is the order in which the results are presented.

CO and CO_2 Methanation on MCM-41 and SWNT supported Catalysts:

Carbon monoxide methanation was chosen as the probe catalytic reaction to compare the carbon nanotube supported Co catalyst with well defined Co incorporated MCM-41

and Co impregnated MCM-41. The cobalt was dispersed on both single walled carbon nanotubes (SWNT) and multiwalled carbon nanotubes (MWNT) using two different techniques, 1) retaining the Co used for the SWNT synthesis and 2) decorating functionalized SWNT with Co using solution phase sonication. In the first method SWNT is produced by our normal techniques (e.g. refs. 1-2) and then the MCM-41 used for SWNT synthesis is removed by dissolution of the silica matrix in dilute NaOH. After silica removal, the SWNT sample contains as much as 23.5 wt% cobalt and 0.2 wt% residues. The problem with this method, however, is that much of the Co is inaccessible for reaction and is covered by carbon. In Table #1 the characterization of selected catalysts is shown. The SWNT-supported Co catalyst after methanation (to remove the carbon from the particles) shows considerably higher CO chemisorption as expected for more accessible particles.

Co supported on the SWNT catalyst system has a higher turnover frequency then supported on MCM-41. This is not just a particle size effect although the SWNT-based catalyst provided greater dispersion. The SWNT-based catalyst performed better than both a 1% Co incorporated MCM-41 catalyst (very small Co particles on the order of 1-3nm) and better than a 10% Co impregnated catalyst with much larger sized (10-60nm) cobalt particles (characterization shown in Table#1). The SWNT with Co retained from reaction has both large and small Co particles present. This catalyst showed superior specific activity when compared to both of the Co-MCM-41 catalysts. The SWNT catalyst with only small Co particles added back after cleaning did not perform as well, however, as the one with the Co from the synthesis. It is theorized that hydrogen is effectively dissociated on the large particles and spills over onto the SWNT. This was checked by carrying out hydrogen uptake experiments on SWNT with small Co particles (large particles covered with carbon) and with SWNT covered with small and large cleaned particles. The small particles are 0.8-3nm and larger ones are 10-60nm. The catalyst with only small Co particles was not as effective for hydrogen storage as the one with both large and small Co particles formed in SWNT synthesis.
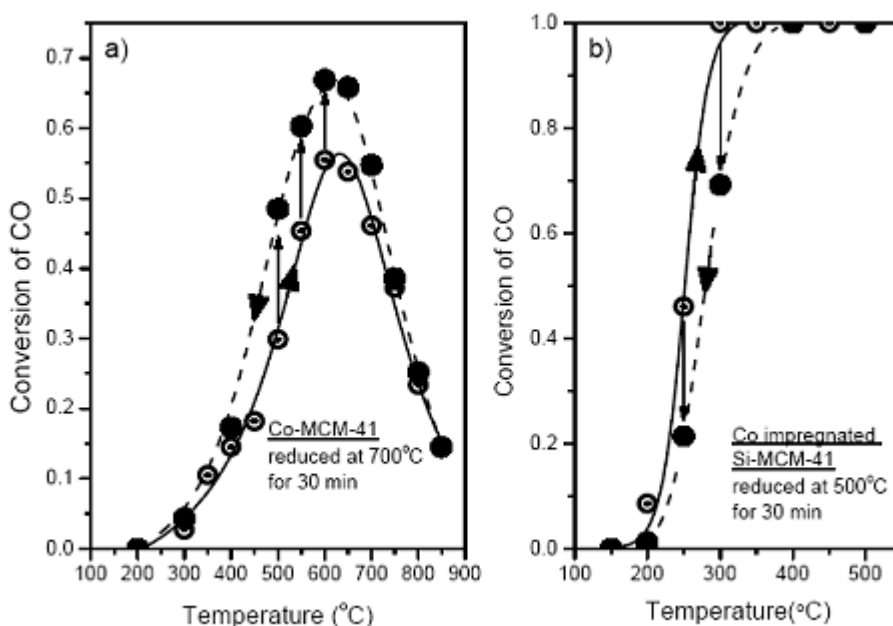
Table#1 Catalyst Characterization

Sample	Total Co, (wt %)	Hydrogen treatment	CO uptake amount (μmol/g solid)
Before methanation (Silica removed SWNT)	13	none	0.31
After methanation (Silica removed SWNT)	13	Methanized at 400°C for 30 min	24.5
1 wt% Co-MCM-41(incorp)	1	Reduced at 500°C for 30 min	0.48
10 wt% Co/MCM-41 (impreg)	10	Reduced at 500°C for 30 min	6.82
Sonicated SWNT in the Co nitrate solution	6	Reduced at 400°C for 30 min	0.6

CO methanation also provided a probe reaction to provide complementary evidence for anchoring and occlusion on Co- and Ni-MCM-41 catalysts. Figure 1 shows a temperature programmed CO methanation results on the impregnated and incorporated Co catalysts. The incorporated catalyst, Fig. 1 (a), shows gradual improvement of the CO conversion as the reduction temperature increases from 700°C to 900°C without degradation of the activity. As previously reported, all of the Co ions will be completely reduced at 900°C, and presumably large metallic particles are formed by vigorous migration on the surface, resulting in the deactivation of catalyst [1]. However, Co-MCM-41 reduced at 900°C shows the highest activity without any deactivation, which suggests that there is another factor making metallic clusters stable other than the anchoring effect (because all Co has been reduced leaving no ions as anchors). Partial occlusion of small metallic clusters by amorphous silica, as observed earlier, can constrain the migration of clusters on the surface, resulting in a stabilization of catalytic activity. On the other hand, the impregnated Co catalysts show different patterns of CO methanation, Fig. 1 (b), depending on the reduction temperature. The impregnated Co catalysts reduced at 500°C for 30 min and 900°C for 30 min show opposite CO methanation results under and over 400°C. In order to explain this phenomenon, hydrogen TPR was carried out for the Co impregnated catalyst and details are given in Publication 4.

Two major species are detected on the surface of the Co impregnated catalyst; cobalt oxide, Co_3O_4 and CoO under 500°C and cobalt silicate like material over 500°C.[2] Therefore, if the catalyst is reduced at 500°C for 30 min, only approximately half of the Co can be reduced to metallic clusters, resulting in the lower CO methanation activity compared to the sample reduced at 900°C for 30 min in which all Co species are completely reduced. There will not be a serious migration at the moderate temperature, 400°C. However, the vigorous migration of the reduced metallic clusters on the surface will start as the reaction temperature increases beyond 400°C, resulting in lower activity of the sample reduced at 900°C. When the Co impregnated sample is reduced at 500°C, a significant amount of irreducible cobalt silicate like material exists on the surface, as proved by running TPR. This material can act as anchoring sites for the metallic clusters to a certain extent [3], therefore, the higher catalytic activity was observed in this sample compared to the catalyst reduced at 900°C.

From these results, it can be suggested that the Co ions directly incorporated into MCM-41 catalysts are a superior system compared to the impregnated catalysts as far as the stability is concerned. The catalytic stability is an important factor for a reaction requiring a long life time and high reaction temperature under a harsh condition.

Fig1.

Aqueous Phase Reforming:

    We have demonstrated carbon nanotubes decorated with Co or Pt are superior as catalysts for the aqueous phase reforming of ethylene glycol as compared to traditional oxide supported catalysts. Characterization of the SWNT supports showed that they provide extremely high surface area supports. Nitrogen adsorption showed up to $1600m^2/gm$.

    SWNT characteristics depend on the chemical and physical nature of the template. In the "old" C10 Co-MCM-41 made using 11.5 pH and 1% Co incorporation with 650°C pre-reduction in H_2 and 750°C reaction using CO disproportionation to SWNT the (6,5) tube corresponding to 0.7nm SWNT was produced. For the "new" C10 Co-MCM-41 the Co loading is 3 wt%, but more importantly the synthesis pH for the template was 10.5 (making the Co more reducible) and both higher pre-reduction and reaction temperatures were used (750°C pre-reduction and 850°C reaction temperature). The higher temperatures lead to nearly complete reduction of Co to the metal which increases the carbon nanotube yield to >30% but increases the tube diameter to a mean of 0.84nm. These measurements by N_2 adsorption are consistent with those obtained by Raman, fluorescence and NIR absorption spectroscopies. The new C10 SWNT was chosen as the

initial support for the aqueous phase reforming reaction due to the high surface area measured. The diameter of the SWNT is important because the heat of asorption of hydrogen on a SWNT increases strongly as tube size decreases below 0.8nm.
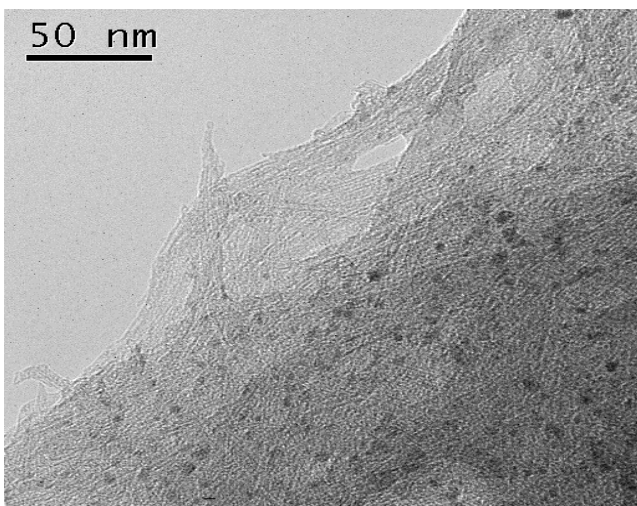

Figure #2 Co on SWNT approximately 3nm by EXAFS

An advantage of using SWNT as a support with the very high surface area and carbonyl defects is that high metal loadings can be achieved while maintaining reasonably high dispersions. Hydrogen production has been found to scale with loading in the regime from 3-5%. The initial SWNT catalysts tested contained 10%Pt or 10% Co with particle sizes in the 3-5nm range. Initial screening tests showed similar product profiles to a 5%Pt alumina catalyst with a similar dispersion. 50mg catalyst (5% Pt in alumina, 10% Pt in SWNT and 10% Co in SWNT) was put in a stainless steel reactor and reduced in hydrogen at 450^0C for 2h at atmospheric pressure, and after the system cooled down, nitrogen was introduced and the pressure is increased to 400 psi. Ethylene glycol (10% aqueous solution) was fed into the reactor at a rate of 0.06ml/min via an HPLC pump. The temperature was then increased to 225^0C for the reaction. Gas phase products were measured by GC at continuous intervals. Steady state was approached more quickly with the SWNT based catalysts compared to alumina supported catalysts. Details are given in publication #4. MWNT supports are discussed in publications #5 and #6.

Bimetallic Catalysts

We have performed a study of Pt-Co bimetallic catalysts supported on SWNT and MWNT for aqueous phase reforming (APR) using the probe molecule ethylene glycol. Previous work using alumina support had suggested that the Pt-Co bimetallic was superior to Pt alone [4]. The first objective was to develop a catalyst on a support that is stable in aqueous media at reaction temperatures above 200°C, i.e., a carbon support. Using SWNT as our carbon support, we demonstrated that both Pt/SWNT and Pt-Co/SWNT are superior to the alumina counterparts, based on Pt mass time yield, and both have modestly better hydrogen selectivity. This is discussed in detail in publication #4.

The bimetallic catalysts were prepared by sequential impregnation and resulted in a core-shell structure with Co as the core and a Pt-Co alloy phase as the shell, in which Pt was atomically dispersed, as determined by X-ray absorption spectroscopy. The high APR activity and selectivity indicates that the Pt species is on the outer surface of the catalytic particles. It is likely that Co is not fully covered by Pt, and may also contribute to the activity. However, Co is not active on its own so this must be viewed as either Co modifying Pt activity or, more likely, Pt modifying the oxidation of Co under reaction conditions. In subsequent work (publication #6) we have demonstrated that separate Pt and Co particles can behave synergistically, presumably by hydrogen spillover from Pt particles to Co particles to keep them in an active reduced state which cannot be maintained in the absence of Pt. A comparison of a Yale synthesized SWNT with a commercial SWNT and with activated carbon indicates that the Yale synthesized carbon nanotubes provide a better support primarily for physical reasons, because of a combination of high surface area (1790 m^2/g) and mesopore volume (2.77 cm^3/g) while the commercial SWNT has comparable mesoporosity (but low surface area) and activated carbon has comparable surface area but low mesoporosity (mostly microporosity).

While SWNT provide a stable support, some attributes of these carbon supports are positive for the APR reaction but there is further engineering required. Oxygen functionalization is beneficial to anchor precursors and the resulting metal particles, resulting in improved Pt (or Co) dispersion. The oxygen functional groups (OCG) also effect the APR activity, mainly through the competitive adsorption of ethylene glycol and water on the catalyst surface. The introduction of OCG increases the hydrophilicity of the SWNT support and therefore, the local concentration of water around the support. The decrease in local concentration of ethylene glycol leads to lower activity in terms of TOF. The increase of active sites and the decrease of TOF affect activity in opposite directions, leading to similar catalyst mass time yields. Understanding these opposing effects of OCG provides a background for improved design, i.e., tuning the degree of OCG such that most are "consumed" by interaction of the metal particles but with little residual to affect the hydrophilicity sensed by the reactants.

References

1. Y. Chen, D. Ciuparu, S. Lim, G.L. Haller and L. Pfefferle, "Synthesis of Uniform-Diameter Single-Walled Carbon Nanotubes in Co-MCM-41: Effects of the Catalyst Prereduction and Nanotube Growth Temperatures", *J. Catalysis*, 225(2), 2004, 453.
2 D. Ciuparu, Y. Chen, S. Lim, G.L. Haller and L. Pfefferle, "Uniform-Diameter Single-Walled Carbon Nanotubes Catalytically Grown in Cobalt-Incorporated MCM-41", *J. Phys. Chem B*, 108(2) (2004) 503.
3. Aqueous-phase reforming of oxygenated hydrocarbons over Sn-modified Ni catalysts," J. W. Shabaker, G. W. Huber, and J. A. Dumesic, J. Catal. 222 (2004).
4. G. W. Huber, Appl. Catal. B Environ. 62 **(**2006**),** 226.

Publications (including patents) acknowledging the grant or contract

1. Luo, ZT; Pfefferle,LD; Haller,GL; Papadimitrakopoulos,F. (*n.m*) abundance evaluation of single-walled carbon nanotubes by fluorescence and absorption

spectroscopy. *Journal of the American Chemical Society*, 128 (48): 15511-15516 Dec 6 2006.

2. G. Du, S. Lim, Y. Yang, C. Wang, L. Pfefferle, G. Haller "Methanation of carbon dioxide on Ni incorporated MCM-41 catalysts" J. Catalysis, vol 249 (2), 370-379, 2007.

3. S. Lim, C. Wang, Y. Yang, D. Ciuparu L. Pfefferle, G. Haller "Evidence for anchoring and partial occlusion of metallic clusters on the pore walls of MCM-41 and affect on the stability of the metal clusters" Catalysis Today, vol. 123(1-4), 122-132, 2007.

4. Wang, X., Li, N., Pfefferle, L., Haller G, Pt-Co bimetallic catalyst supported on single walled carbon nanotube: XAS and aqueous phase reforming activity studies Source: Catalysis today [0920-5861] Wang, Xiaoming yr:2009 vol:146 iss:1-2 pg:160 - 165

5. Wang, X., Li, N., Webb, J, Pfefferle, L., Haller G., Effect of surface oxygen containing groups on the catalytic activity of multi-walled carbon nanotube supported Pt catalyst Source: Applied catalysis. B, Environmental, 2010 vol:101 iss:1-2 pg:21 -30

6. Wang, X., Li, N., Pfefferle, L., Haller, G., Pt-Co Bimetallic Catalyst Supported on Single-Walled Carbon Nanotubes: Effect of Alloy Formation and Oxygen Containing Groups Source: The journal of physical chemistry. C [1932-7447] Wang, Xiaoming, 2010 vol:114 iss:40 pg:16996 -17002