

## V.D.19 Novel Reforming Catalysts

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### Objectives

1. To investigate the stabilization of Co and Ni by MCM-41 incorporation for the reverse reforming reactions, CO and CO<sub>2</sub> methanation. To compare these results with the same reactions on Co supported on single-walled carbon nanotubes (SWNT).
2. To develop carbon nanotubes as a support for aqueous phase reforming reactions on Co, Pt and bimetallic catalysts.
3. To perform a feasibility analysis synthesizing and testing GaN nanotubes/wires as supports for photocatalytic reforming of alcohols.

### 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. The carbon nanotube supports 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. On the feasibility of GaN nanotubes/wires as supports for photocatalytic reforming of alcohols, the barrier is the synthesis of sufficient quantities of the material to test and provide an economic scalable synthesis.

### Abstract, Progress Report and Future Directions

Our goal is development of novel reforming catalysts, e.g., stable low temperature aqueous reforming catalysts for oxygenated reactants. The novelty is the design of high dispersion metals e.g. Co, Pt and Co-Pt bimetallics, on SWNT supports. Our strategy has been to screen catalysts for reactivity by the 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<sub>2</sub> Methanation on MCM-41 and SWNT Supported Catalysts

Carbon monoxide methanation was chosen as the probe catalytic reaction to compare the SWNT supported Co catalyst with well defined Co incorporated MCM-41 and Co impregnated MCM-41. The cobalt was dispersed on the SWNT using two different techniques, 1) retaining the Co used for the SWNT synthesis and 2) decorating cleaned 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 C10 templated MCM-41 used as catalyst. After silica removal, the SWNT sample (1-1.7 nm diameter) 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 Co particles.

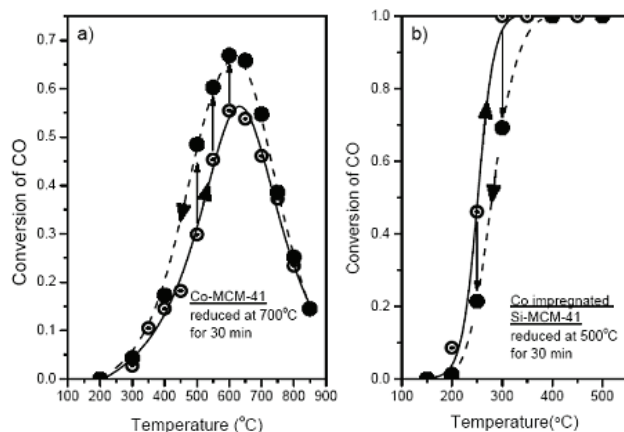
TABLE 1. Catalyst Characterization

Sample	Total Co, (wt %)	Hydrogen treatment	CO uptake amount ( $\mu\text{mol/g solid}$ )
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

The Co supported on the SWNT catalyst system has a higher turnover frequency than either of the Cobalt MCM-41 catalysts. 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 1-3 nm) and better than a 10% Co impregnated catalyst with much larger sized (10-60 nm) 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 cobalt 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 0.8-3 nm and larger ones are 10-60 nm. The catalyst with only small Co particles was not as effective for hydrogen uptake as the one with both large and small Co particles formed in SWNT synthesis.

CO methanation also provided a probe reaction to provide complementary evidence for anchoring and occlusion on Co- and Ni-MCM-41 catalysts. Temperature programmed CO methanation (TPM) results for the incorporated (1% Co-MCM-41) and impregnated (1% Co/MCM-41) catalysts show that *incorporating* the metal into the MCM-41 provides particle stabilization even after significant reduction. The Co-MCM-41 (metals present during MCM-41 synthesis) exhibits gradual improvement of the CO conversion as the reduction temperature increases from 700°C to 900°C without degradation of the activity (see Figure 1a where catalyst activity increases after cycling to 900°C). As previously reported, all of the Co ions will be completely reduced at 900° [3]. The Co-MCM-41 reduced at 900°C, shows the highest activity without deactivation, which suggests that there is another factor stabilizing metallic clusters besides the anchoring effect



**FIGURE 1.** TPM for the Co incorporated catalyst (1a, left) and Co impregnated catalyst (1b right). Solid line is the heating cycle, dashed line is the cooling cycle.

(all of the 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. Consistent with this idea, the impregnated Co catalysts with little or no occlusion show different patterns of CO methanation activity as a function of the reduction temperature (Figure 1b). The impregnated Co catalysts reduced at 500°C for 30 min deactivate after cycling to high temperatures.

In order to explain this phenomenon, hydrogen temperature programmed reduction (TPR) was carried out for the Co impregnated catalyst. Cobalt oxides,  $\text{Co}_3\text{O}_4$  and CoO were observed under 500°C and a cobalt silicate like material over 500°C [4]. When this catalyst is reduced at 500°C for 30 min, only approximately half of the Co can be reduced to metallic clusters. There will not be a serious migration at the moderate reaction temperatures, 400°C, however vigorous migration of the reduced metallic clusters on the surface will start as temperature increases beyond 400°C, resulting in lower activity of the sample reduced at 900°C.

These results demonstrate 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 harsh conditions. X-ray absorption fine structure results confirmed the stability of both Ni-MCM-41 and Co-MCM-41 (metal incorporation) catalysts showing that the catalyst particle size does not change much over the range of conditions run.

**Future Work:** The results for the Co-MCM-41 and Ni-MCM-41 are drafted for a paper submission. Further work will be carried out for the SWNT supported catalysts especially investigating the dual particle size advantages. We will also repeat experiments using different SWNT diameters to explore hydrogen uptake effects.

### Aqueous Phase Reforming

We have demonstrated SWNT decorated with Co or Pt as catalysts for the aqueous phase reforming of ethylene glycol. Characterization of the SWNT supports showed that they can provide extremely high surface area supports. Nitrogen adsorption showed up to 1600  $\text{m}^2/\text{gm}$ . SWNT characteristics depend on the chemical and physical nature of the template. In the "old" C10 Co-MCM-41 made using 11.5pH and 1% Co incorporation with 650°C pre-reduction in  $\text{H}_2$  and 750°C reaction using CO disproportionation to SWNT, the (6,5) tube, corresponding to 0.7 nm SWNT was

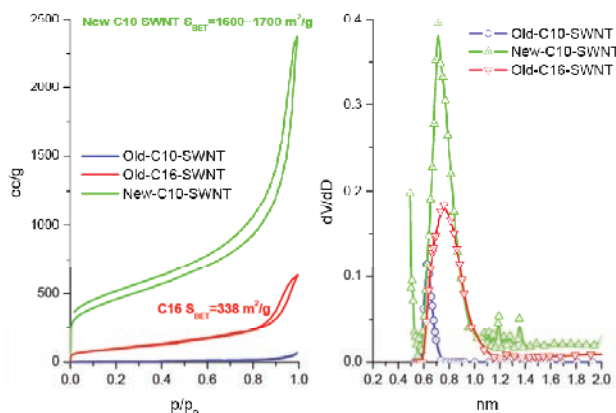


FIGURE 2.  $N_2$  Adsorption Data for SWNT

predominantly produced. This is seen in Figure 2 where  $N_2$  adsorption isotherms are depicted.

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 (700°C pre-reduction and 850°C reaction temperature). The higher temperatures lead to nearly complete reduction of Co to the metal which increases the SWNT diameter produced. The shift observed by these measurements by  $N_2$  adsorption is 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.

We have demonstrated that an important advantage of using SWNT as a support with the very high surface area and carbonyl defects is that high metal loadings (>10%) can be achieved while maintaining 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 3-5 nm range. Initial screening tests showed similar product profiles to a 5%Pt alumina catalyst with a similar dispersion. 50 mg of catalyst (5% Pt in alumina, 10% Pt on SWNT and 10% Co on SWNT) was placed in a stainless steel reactor and reduced in hydrogen at 450°C for 2 h 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 0.06 ml/min via an HPLC pump. The temperature was then increased to 225°C for the reaction. Gas phase products were measured periodically by GC. Steady state was approached more quickly with the SWNT based catalysts and product distributions were similar between Pt/alumina and Pt/SWNT but enough runs were not performed for true parametric studies and mass

balances on products and reactants need to be closed. Still these results are promising for this application in terms of stability and the ability to disperse large amounts of metals to achieve higher rates.

**Planned work:** Bimetallic catalysts are being prepared and characterized. Initially Pt:Co in ratios from 1:1 to 1:6 will be tested. Partitioning of the metals between pure and bimetallic phases will be evaluated using EXAFS with quenched samples after reaction. The diameter of the SWNT will also be addressed and we will use the 0.7 nm SWNT and MWNT (3-10 nm) to understand whether the differences in hydrogen spillover affect the activity and selectivity of the reforming reaction.

### GaN Nanotubes for Photocatalysis Supports

One goal of this project is to examine the possibility of using GaN nanotubes for the photocatalytic conversion of methanol to hydrogen. In order to do this we need to develop a synthesis methodology to provide a reasonable amount of GaN nanotubes without extraneous materials. At the start of this grant period we had synthesized GaN nanotubes using a high temperature CVD method but they were in the presence of many GaN nanowires.

We have now developed a method for the selective synthesis of GaN nanotubes using solution phase sonication followed by annealing in ammonia. X-ray absorption fine structure (EXAFS) spectroscopy showed that these tubes were GaN (see Figure 3). Calculations by Sohrab Ismail-Beigi confirm that these materials should be good photocatalytic supports.

**Future Work:** We now have a method to produce 100mg quantities of the GaN nanostructures. This will allow us to test its utility as a support for photocatalytic conversion of methanol to hydrogen.

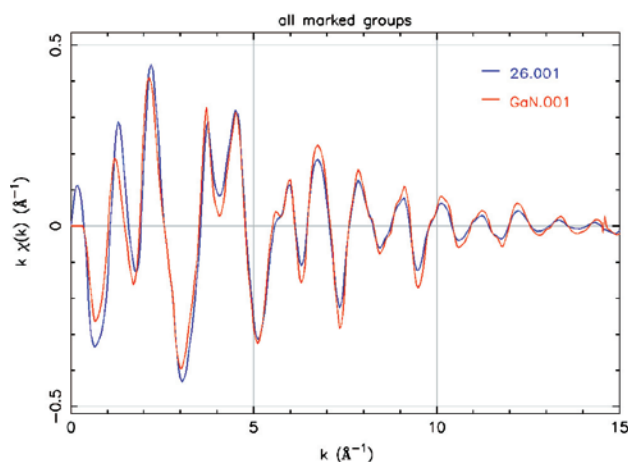


FIGURE 3. EXAFS on Sample #J7 750 Compared to GaN Reference

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**Publications (Including Patents) Acknowledging the Grant or Contract**

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