

## **Effects of Carbonyl Bond and Metal Cluster Dissociation and Evaporation Rates on Predictions of Nanotube Production in HiPco**

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### **ABSTRACT**

The high-pressure carbon monoxide (HiPco) process for producing single-wall carbon nanotubes (SWNT) uses iron pentacarbonyl as the source of iron for catalyzing the Boudouard reaction. Attempts using nickel tetracarbonyl led to no production of SWNTs. This paper discusses simulations at a constant condition of 1300 K and 30 atm in which the chemical rate equations are solved for different reaction schemes. A lumped cluster model is developed to limit the number of species in the models, yet it includes fairly large clusters. Reaction rate coefficients in these schemes are based on bond energies of iron and nickel species and on estimates of chemical rates for formation of SWNTs. SWNT growth is measured by the co-formation of  $\text{CO}_2$ . It is shown that the production of  $\text{CO}_2$  is significantly greater for  $\text{FeCO}$  due to its lower bond energy as compared with that of  $\text{NiCO}$ . It is also shown that the dissociation and evaporation rates of atoms from small metal clusters have a significant effect on  $\text{CO}_2$  production. A high rate of evaporation leads to a smaller number of metal clusters available to catalyze the Boudouard reaction. This suggests that if  $\text{CO}$  reacts with metal clusters and removes atoms from them by forming  $\text{MeCO}$ , this has the effect of enhancing the evaporation rate and reducing SWNT production. The study also investigates some other reactions in the model that have a less dramatic influence.

## INTRODUCTION

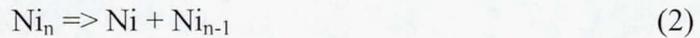
In the high-pressure carbon monoxide (HiPco) process the Boudouard reaction, catalyzed by iron, produces single-wall carbon nanotubes (SWNT).<sup>1,2</sup> Whereas using iron carbonyl as a catalyst yields significant amounts of SWNTs, attempts to use nickel as a catalyst have not led to SWNT production. At first, differences in the nucleation rates of iron and nickel were thought to have a significant effect on production. However, parametric studies of nucleation did not show a significant influence on production since there are other pathways to produce dimers and larger clusters without direct Fe + Fe nucleation. It was noted that one difference between iron and nickel is their different affinities for bonding with CO. Sunderlin, et al.<sup>3</sup> report the bond energy for NiCO is about 170 kJ/mol (20468 K) and that of FeCO of about 35 kJ/mol (4214 K). The higher binding energy of NiCO will result in slowing down of its dissociation and possibly speed up its formation compared with FeCO. In the models we have included cluster growth by the exchange reaction



where the reaction rate is taken to be the gas kinetic rate (Me=metal). These reactions are less likely for nickel because the binding energy of NiCO (170 kJ/mol) is only slightly smaller than that of Ni<sub>n-1</sub>Ni ( $E_a = 203$  kJ/mol,  $n=2$ ). This is not the case for Fe<sub>n-1</sub>Fe where FeCO bond energy  $E_a$  is 35 kJ/mol, whereas that of Fe-Fe is about two times greater, 75 kJ/mol. The reverse of these reactions is the "CO enhanced evaporation" reactions in which CO abstracts Me from the cluster. Since the binding energy of NiCO is much stronger than FeCO we might expect greater loss of nickel clusters compared with iron

clusters. Unfortunately, we do not have any reliable rate coefficients for these reactions for  $n > 0$ .

Another factor to be considered is the direct or normal evaporation of small metal clusters, such as



If they evaporate too fast, clusters may not be able to form, hence reducing the possibility of SWNT production. In the present models the smallest metal cluster that produces SWNTs is that of  $\text{Fe}_{10}$  or  $\text{Ni}_{10}$ . Therefore, clusters must grow to at least that size before SWNTs can be catalyzed. Several sets of rate coefficients are investigated for these evaporation reactions.

These possibilities were studied parametrically using estimates of reaction rate coefficients based on limited knowledge of bond energies from the literature. The following discussion addresses the source of rate coefficients for various reactions in the models. These reactions are categorized as metal carbonyl dissociation and recombination reactions, dimer dissociation, and cluster evaporation (2), dimer nucleation, to some extent the exchange reactions (1), and the reaction



Other reactions in the model, such as cluster growth and CO attachment reactions have been discussed in Ref. 4.

Cluster evaporation data for iron and nickel can be estimated using the formula of Rao, et al.<sup>5</sup> (denoted "Girshick" in this article).

The expressions for cluster growth  $\beta_{ij}$  and evaporation  $E_i$  are, respectively,

$$\beta_{ij} = \left( \frac{3v_1}{4\pi} \right)^{1/6} \sqrt{\frac{6kT}{\rho_p} \left( \frac{1}{i} + \frac{1}{j} \right)} (i^{1/3} + j^{1/3})^2 \quad (4)$$

$$E_i = \beta_{1,j-1} n_s \exp\left(\Theta \left[ j^{2/3} - (j-1)^{2/3} \right]\right) \quad (5)$$

where  $\Theta = \frac{\sigma s_1}{kT}$  is the dimensionless surface energy, and  $v_1$  is the hard-sphere collision frequency of monomers,  $\rho_p$  is the density of bulk iron,  $i$  and  $j$  are the number of atoms in the colliding clusters,  $\sigma$  is the surface tension of the bulk metal,  $s_1$  is the surface area of the monomer (atom),  $k$  is the Boltzmann constant, and  $T$  is the temperature. The saturation number density  $n_s$  is a function of temperature determined from a Clausius-Claperon type relation,  $p_s = p_{\text{vref}} \exp(-E_v/kT)$ , where  $p_{\text{vref}}$  is a reference pressure and  $E_v$  is the energy required to remove an atom from the surface of the bulk substance. In the present study the saturation vapor pressure was determined by curve fits to the data of Ref. 6. Table 1 gives the parameters that were used in (4) and (5).

## RESULTS

There are two sets of comparisons that were considered in comparing the influence of various reactions on the predicted growth of nanotubes. One is for iron and the other for a “cooked-up” model of nickel. The basic rate coefficients for the model are those of the Ames 2001 version<sup>7</sup> which were based on Krestinin, et al.<sup>8</sup> and calculations of rate coefficients for  $\text{Fe}(\text{CO})_x$  decomposition from Sunderlin, et al.<sup>1</sup> bond energies. The basic differences in these iron and nickel models are the rate coefficients for carbonyl reactions and the metal cluster growth and evaporation reactions. The basic model is a

variation of that described in Ref. 7, in which the iron clusters  $Fe_n$  and their corresponding  $Fe_nCO$  and  $CNT_n$  clusters are lumped into groups having 8, 16, 32, 64, ..., 2048 iron atoms. Thus that model accounts for the agglomeration of clusters. Variations in the reaction rates that were assessed are those mentioned in the previous section. Definitions of these reactions and rate coefficient sources are given in the following paragraph.

Carbonyl rates are defined by those reactions of the form



For iron, these rates were determined by Ames Research Center using the bond energies of Sunderlin, et al.<sup>3</sup> For nickel, the rates were determined by simple substitution of the bond energy into the Arrhenius expressions for iron. No attempt was made to adjust the pre-exponential factors.

For both the iron and nickel models the reaction  $MeCO + MeCO \Rightarrow Me_2 + 2 CO$  was taken from Krestinin<sup>8</sup> original set of reactions with its rate coefficient for iron. This reaction is usually negligible. It only has an influence on the results when there is no other mechanism to form  $Me_2$ .

The  $MeCO$  bond energy exhibits its greatest influence when considering its dissociation. Two estimates were compared, one taken for the value of iron and the other for the value of nickel, 23.9 kJ/mole (2875 K Ames) and 170 kJ/mole (20433 K) based on Sunderlin's data, respectively.

Dissociation of metal dimers has a small influence on the results. The Krestinin<sup>8</sup> value of the rate coefficient was used. These results and those using an estimate based on Girshick's evaporation expression (5) were compared for iron. The surface tension in that

expression was adjusted until the activation energy matched that of the bond energy for the iron dimer 75 kJ/mol (or 9047 K)<sup>9</sup>. For nickel, the rate coefficient for iron was used, except the dissociation energy for Ni<sub>2</sub> was substituted in the Arrhenius energy term. The other method used expression (5) with the values for nickel substituted, 203 kJ/mol (or 24476 K).

Three models of evaporation of iron atoms from clusters were used. The first was the original set from Krestinin, et al. for iron. The second was based on (5) using the rates determined from the surface energy of Ref. 4, and the third was based on adjusting the surface energy until the activation energy for the dimer equals the bond energy of 75 kJ/mole (9047 K). For nickel, three variations were studied: Krestinin<sup>8</sup> values corresponding to iron, the Ref. 4 Girshick values, and the Girshick value calculated from (5) for nickel property data of 203 kJ/mole (24476 K) bond energy and its vapor pressure. Fig. 1 gives the evaporation rate coefficients for each model, evaluated at 1300 K. There are three basic sources of rates: Krestinin, et al.<sup>8</sup>, Rao/Girshick<sup>4</sup> equation (5) evaluated using nominal properties of Fe, and equation (5) with the surface tension adjusted so that the activation energy in the Arrhenius expression for dimer dissociation equals the value given in Ref. 9.

The conditions of this study are for a constant temperature of 1300 K and 30 atmospheres pressure, arbitrarily run for 0.1 seconds. The amount (mole fraction) of carbon dioxide produced at the end of this time was a measure of the effectiveness of the model. The starting amount of iron pentacarbonyl is 17 ppm in carbon monoxide. The basic cluster model is that called the Binary 2048 model. Metal clusters have 1-8, 16, 32, 64, 128, 256, 512, 1024, and 2048 atoms. In this model there is a smaller number of

species so that the cases run very fast. The chemical rate equations were solved using program SENKIN of the CHEMKIN 3.61 package. The results of a set of calculations are presented in Tables 2 and 3 for iron and nickel, respectively.

### **Iron**

The nominal iron case is denoted AD in Table 2. All the rates are based on the Ames model except that evaporation of the large iron clusters was determined from (5), Girshick. This model produced a CO<sub>2</sub> mole fraction of 0.001 in 0.1 s. Variations on this model using other values of Fe<sub>2</sub> dissociation and Girshick evaporation rates for small Fe-clusters only slightly affected the results. Reducing the Fe-Fe nucleation rate to zero reduced production by almost two orders of magnitude for the nominal case, but slightly increased CO<sub>2</sub> in the other cases where Girshick evaporation rates were used along with a smaller bond energy of 75 kJ/mole. When the smaller bond energy is used along with Krestinin,<sup>8</sup> evaporation rates for small clusters, the amount of CO<sub>2</sub> is significantly reduced. It appears that evaporation takes its toll on cluster formation, hence their ability to catalyze the Boudouard reaction. The situation is exacerbated when the evaporation of clusters is based on calculations of the rate coefficients using (5) and the 75-kJ/mole bond energy, especially when the dimer dissociation rate coefficient uses this bond energy in its Arrhenius coefficient.

To test the influence of the exchange of Fe from reactions with FeCO they we deleted in the last case in Table 2. There was a negligible effect on the results, indicating that these reactions are not important.

## Nickel

The models for nickel as a catalyst are based on more approximate estimates of the rate coefficients than the basic iron model. Probably, the most representative nickel models are cases no. 3 and 6 of Table 3. In those cases the rate coefficients have been modified to account for the bond energies associated with nickel. At 0.1 seconds the amount of CO<sub>2</sub> produced in those two cases is  $5.37 \times 10^{-15}$  and  $9.92 \times 10^{-25}$ , respectively. This is negligible production, and reflects the nature of the strong NiCO bond 170 kJ/mole (20422 K). This strong bond prevents the formation of Ni clusters, thus inhibiting SWNT growth. The influence of the bond energy is demonstrated in cases 1, 2, 4, and 7, where the NiCO dissociation rate was made the same as for iron. In those cases the production of CO<sub>2</sub> is similar to that for the iron model. Behavior similar to that of iron is seen in the influence of Ni-Ni dimer formation. When NiCO bond energy of 170 kJ/mole is used there is some influence of the NiCO + NiCO reaction and the NiCO + Ni<sub>n</sub> exchange reactions, as seen in cases 6, 8, 9, and 10. These reactions are neglected in the models of Dateo, et al. (Ref. 5).

## CONCLUSIONS

Simulations of reactions in the HiPco process for SWNT production were carried out to investigate the influence of various possible reactions in the scheme and the effect of bond energy differences between iron and nickel. Time dependent calculations were made for a constant temperature of 1300 K and pressure of 30 atmospheres using a premixed reactor solution to the chemical rate equations. The principle metric for evaluating the models was the mole fraction of CO<sub>2</sub> produced by the Boudouard reaction, which is a measure of the total production of SWNTs.

It was found that the metal-CO bond energy has a major influence on the production of CO<sub>2</sub>. The higher NiCO bond energy almost eliminates production of CO<sub>2</sub>, whereas, the smaller bond energy of FeCO leads to significant production. Also, the rate of dimer dissociation and small cluster evaporation affects the production of CO<sub>2</sub> by limiting the rate of cluster growth, and thus the number of clusters available to catalyze SWNT growth. This suggests that if CO reacts with metal clusters and removes atoms from them by forming MeCO, and then this has the effect of enhancing the evaporation rate and reducing SWNT production.

Because of the possibility of producing dimers via FeCO reactions, the rate of direct Fe + Fe => Fe<sub>2</sub> dimer formation did not have a big influence on CO<sub>2</sub> production. The same was observed for nickel if the bond energy of Ni-CO was assumed to be equal to that of iron, a nonrealistic circumstance.

### ACKNOWLEDGEMENTS

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**Table 1 Parameters used in Equation (5) for cluster evaporation rates**

Model	Surface Tension, $\sigma$ N/m	Ref. Vapor Pressure, $P_{vref}$ Pa	$E_v$ Vapor K	Atom Radius, $r_1$ M	Atom Surface Area, $s_1$ $m^2$
Girshick Iron	1.7	$6.83 \times 10^{11}$	47400	$1.40 \times 10^{-10}$	2.46E-19
Girshick Fit to Ni Dimer bond	2.53*	$9.64 \times 10^{11}$	49170	$1.35 \times 10^{-10}$	2.29E-19
Girshick fit to Fe dimer bond	3.65*	$6.83 \times 10^{11}$	47400	$1.40 \times 10^{-10}$	2.46E-19

\*Inferred by adjusting it in Eqn. (5) to make  $E_a$  equal to dimer bond energy

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Table 2 Production of SWNTs with iron catalyst as indicated by CO<sub>2</sub> mole fraction for ten combinations of rate coefficients and dimer nucleation

Fe Cluster Model			T=1300 K		P=30 atm		
Desig.	Carbonyl Rates	FeCO + Fen	Fe <sub>2</sub> Dissoc.	Fen Evap. $\delta > n > 2$	Fen Evap. $n \geq 8$	CO <sub>2</sub> Produced at 0.1 s No Fe-Fe Nucleation	CO <sub>2</sub> Produced at 0.1 s Fe-Fe Nucleation 4E15
AGd	Ames	yes	Krestinin Ea=134 kJ/mole	Girshick	Girshick	1.05E-03	4.84E-04
AG	Ames	yes	Girshick	Girshick	Girshick	1.05E-03	4.88E-04
AGdw	Ames	yes	Ames Ea=75.2 kJ/mole	Girshick	Girshick	1.87E-05	1.02E-03
AD	Ames	yes	Krestinin Ea=134 kJ/mole	Krestinin	Girshick	2.37E-05	1.00E-03
AB	Ames	yes	Ames Ea=75.2 kJ/mole	Krestinin	Girshick	8.97E-08	5.33E-06
AW	Ames	yes	Krestinin Ea=134 kJ/mole	Eqn. (5) w/Ea=75.2 kJ/mole bond	Eqn. (5) w/Ea=75.2 kJ/mole bond	1.56E-18	9.19E-15
AWd	Ames	yes	Eqn. (5) w/Ea=75.2 kJ/mole bond	Eqn. (5) w/Ea=75.2 kJ/mole bond	Eqn. (5) w/Ea=75.2 kJ/mole bond	9.19E-27	2.75E-25
AGw	Ames	yes	Eqn. (5) w/Ea=75.2 kJ/mole bond	Girshick	Girshick	n/a	4.09E-07
ANoX	Ames	No	Krestinin Ea=134 kJ/mole	Krestinin	Girshick	n/a	1.00E-03

Table 3 Nickel catalyst production of SWNTs as indicated by CO<sub>2</sub> mole fraction for ten combinations of rate coefficients and dimer nucleation

Ni Cluster Model			T=1300 K				P=30 atm			
Case	Designation	Carbonyl Rates Ni(CO) <sub>x</sub> x=2,4	NiCO + Ni <sub>n</sub>	NiCO+NiCO	NiCO Dissociation	Ni <sub>2</sub> Dissociation	Ni <sub>n</sub> Evaporation 8>n>2	Ni <sub>n</sub> Evaporation n>8	CO <sub>2</sub> Produced at 0.1 s No Ni+Ni Nucleation	CO <sub>2</sub> Produced at 0.1 s Ni+Ni Nucleation 4E15
1	AWNiWOIdFeCO	Sunderlin	yes	0	Ames Fe Ea=24 kJ/mole	Ames from 203 kJ/mole bond	Girshick from 203 kJ/mole bond	Girshick from 203 kJ/mole bond	1.23E-03	4.80E-04
2	AWNiOldFeCONiCONiCO	Sunderlin	yes	Krestinin Fe-rate	Ames Fe Ea=24 kJ/mole	Ames from 203 kJ/mole bond	Girshick from 203 kJ/mole bond	Girshick from 203 kJ/mole bond	1.23E-03	4.80E-04
3	AWNiS	Sunderlin	yes	0	Sunderlin Ea=170 kJ/mole	Ames from 203 kJ/mole bond	Girshick from 203 kJ/mole bond	Girshick from 203 kJ/mole bond	n/a	5.37E-15
4	AGNiOldFe2	Sunderlin	yes	0	Ames Fe Ea=24 kJ/mole	Girshick from 203 kJ/mole bond	Girshick from 203 kJ/mole bond	Girshick from 203 kJ/mole bond	1.47E-06	4.12E-04
5	AGNoXNiNoNuNoNiCONiCONiCO	Sunderlin	No	0	Ames Fe Ea=24 kJ/mole	Ames Fe Ea=134 kJ/mole	Girshick from 203 kJ/mole bond	Girshick from 203 kJ/mole bond	7.72E-25	n/a
6	AWNi	Sunderlin	yes	0	Sunderlin Ea=170 kJ/mole	Girshick from 203 kJ/mole bond	Girshick from 203 kJ/mole bond	Girshick from 203 kJ/mole bond	n/a	9.92E-25
7	ADNiOldFe2	Sunderlin	yes	0	Ames Fe Ea=24 kJ/mole	Ames Fe Ea=134 kJ/mole	Girshick Fe	Girshick Fe	3.89E-06	9.72E-04
8	ADNi	Sunderlin	yes	0	Sunderlin Ea=170 kJ/mole	Ames Fe Ea=134 kJ/mole	Ames Fe	Girshick Fe	1.19E-19	1.19E-19
9	ADNiCONiCONiCO	Sunderlin	yes	Ames Fe-rate	Sunderlin Ea=170 kJ/mole	Ames Fe Ea=134 kJ/mole	Ames Fe	Girshick Fe	3.27E-17	3.27E-17
10	ADNoNuNoNiCONiCONiCOx	Sunderlin	no	0	Sunderlin Ea=170 kJ/mole	Ames Fe Ea=134 kJ/mole	Ames Fe	Girshick Fe	3.72E-25	n/a

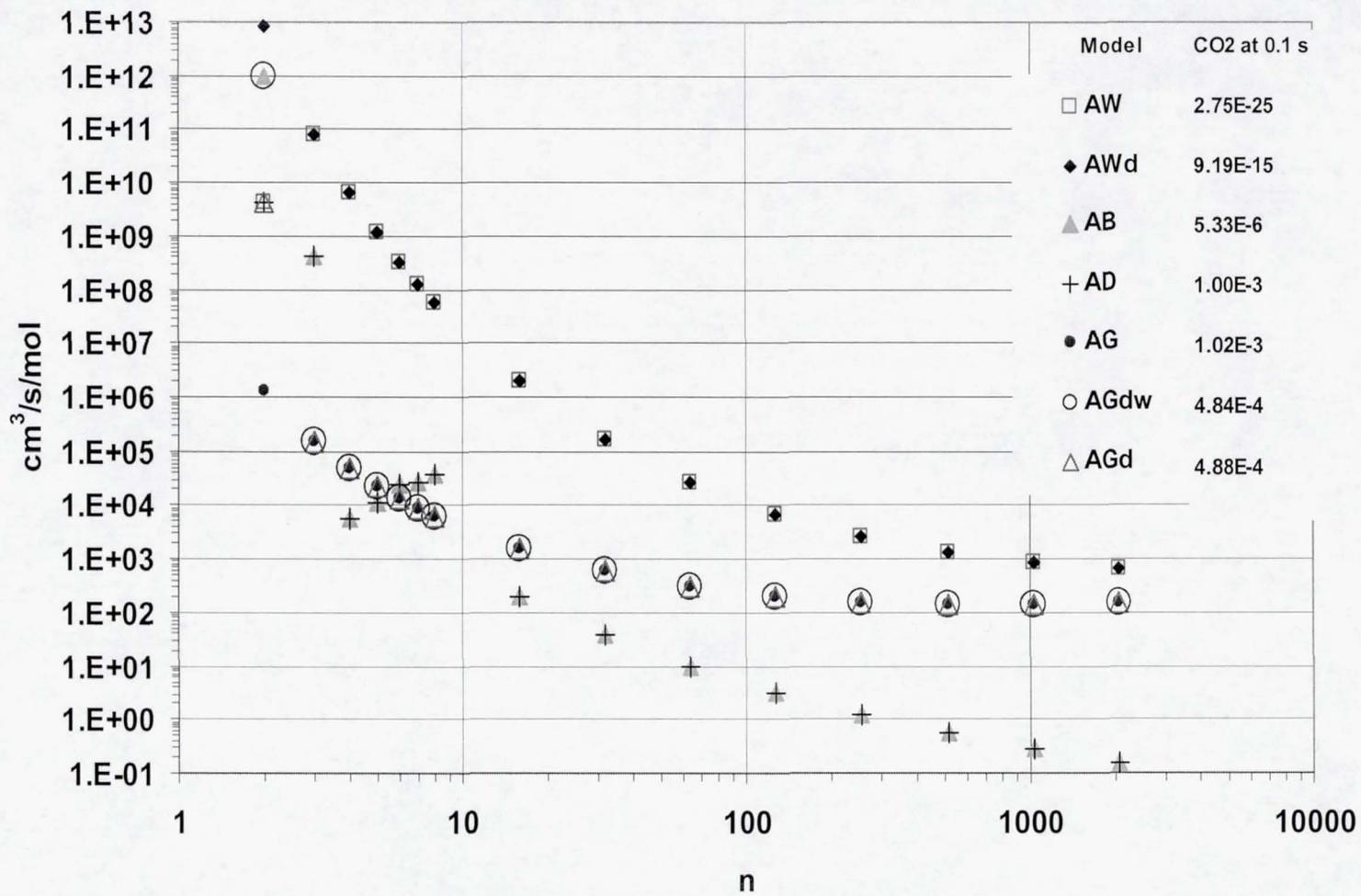


Fig. 1 Reaction rate coefficients at 1300 K for iron clusters used in various reaction schemes. Also shown in the legend is the amount of CO<sub>2</sub> produced after 0.1 seconds in the various models at 30 atm.