CNT Production through the Catalytic Decomposition of Methane on $Ni-Cu/\gamma-Al_2O_3$ at Varying $Ni-Cu$ Ratios: An *Ab Initio* and Empirical Investigation

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Abstract: The decomposition of a single CH_4 molecule on $Ni-Cu/\gamma-Al_2O_3$ catalyst surface with varying $Ni-Cu$ ratios for CNT production was determined through *ab initio* calculations with experimental verification. The structural model was based on empirical XRD characterization data from experimentally-prepared catalysts. Structural relaxation and *ab initio* molecular dynamics simulations were performed using Materials Studio 2016 DMol [1] with the Local Density Approximation – Vosko-Wilk-Nusair (LDA-VWN) exchange correlation functional, Gaussian double zeta plus polarization function basis set (DNP) at $2 \times 2 \times 1$ k-point calculation and orbital cut-off of 3.5 Å, with simulation parameters: $T = 1,148$ K, time step = 1.9 fs (78.5 a.u.), simulation time of 0.38 ps, with the canonical NVT (constant amount (N), volume (V) and temperature (T)) thermodynamic ensemble and Generalized Gaussian Moment (GGM) thermostat. *Ab initio* simulation data predicted a decrease in C deposition time with 1:1 $Ni-Cu/\gamma-Al_2O_3$. Empirical data from TGA and SEM analyses confirmed higher CNT yield on 1:1 $Ni-Cu/\gamma-Al_2O_3$. *Ab initio* calculations indicated an increase in binding energy magnitude with the formation of a $Ni-Cu$ alloy. This increase in energy is attributed to the calculated decrease in crystal size, and was verified by the decrease in average CNT diameter produced on 1:1 $Ni-Cu/\gamma-Al_2O_3$. These findings demonstrate the viability of CTDM as a technology for CNT production, as well as its adaptability to simpler catalytic systems for industrial or commercial applications.

Key words: *Ab initio*, alumina, carbon nanotubes, methane decomposition, molecular dynamics, nickel-copper.

1. Introduction

The production of carbon materials, such as CNTs (Carbon nanotubes), has been done through CCVD (Catalytic chemical vapor deposition) [2, 3] using Ni -based catalysts. However, carbon deposition on Ni reduces available active sites and decreases catalytic activity [5]. As such, various modifications have been done on Ni -based catalysts to improve their catalytic performance and efficiency [6, 7].

One of the most common CCVD technologies is the CTDM (Catalytic thermal decomposition of methane) [7] on $Ni-Cu/\gamma-Al_2O_3$ catalysts due to the susceptibility of Ni and $\gamma-Al_2O_3$ to carbon deposition and the

catalytic-promoting property of Cu [8, 9].

In addition, *ab initio* calculations have been conducted on the mechanisms involving the dissociation and reaction of CH_4 on various catalytic surfaces [10-14], but so far only few have conducted simultaneous theoretical and experimental investigation on them.

The decomposition of CH_4 on unsupported amorphous Ni and $Ni-Cu$ purely through AIMD (*Ab initio* molecular dynamics) simulation was investigated in a previous study [14, 15]. In this study, in comparison, similar AIMD investigations were conducted with the following key differences: the layering of $\gamma-Al_2O_3$ support material underneath the $Ni-Cu$ metal layers with varying $Ni-Cu$ ratios, the construction of the catalyst model based on and compared with experimental data, the improvement on

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AIMD simulation parameters and the consideration of theoretical factors in the structure of the $Ni-Cu$ crystal lattice and their correlation to both theoretical and empirical CNT production.

2. Methodology

2.1 Model Parameters

Simulation models of $Ni-Cu/\gamma-Al_2O_3$ with 1:0, 1:1, and 0:1 $Ni-Cu$ molar ratios were prepared based on empirical XRD (X-ray diffractograms) characterization data, preserving the metal (1 1 1) lattice configuration.

The 1:0 $Ni-Cu$ layer was prepared from a single unit crystal of FCC (Face-centered cubic) Ni , cleaved to (1 1 1) – associated with CH_4 dehydrogenation [16] – followed by structural relaxation.

The 1:1 $Ni-Cu$ layer was prepared by replacing symmetrically located Ni atoms into Cu atoms until the desired 1:1 $Ni-Cu$ molar ratio was achieved, followed by structural relaxation.

The 0:1 $Ni-Cu$ layer was prepared from a single unit crystal of face-centered cubic (FCC) Cu , cleaved to (1 1 1), followed by structural relaxation.

The support material layer was prepared from Hermann-Mauguin Fd-3m, Schoenflies group number 227 O7h or “213 P4132” Al_2O_3 corresponding to the lattice structure of $\gamma-Al_2O_3$ [17, 18], followed by

structural relaxation.

The resulting metal layer was then mounted onto the $\gamma-Al_2O_3$ layer, preserving the lattice configuration of $\gamma-Al_2O_3$, followed by the final phase of structural relaxation for each $Ni-Cu$ ratio.

A single CH_4 molecule was added into the system, capped with a vacuum to eliminate lateral interaction. There were no physical constraints imposed on the system for system stability and to allow thermal expansion. The resulting initial state structures are shown in Fig. 1.

The MD atomic legend for the molecular models is shown in Fig. 2.

2.2 Computational Parameters

AIMD calculations were conducted through DMol [1, 19] with the LDA (Local density approximation) [19-22] VWN (Vosko-wilk-nussair) [23] specific local exchange correlation functional – sufficient for metal oxide structures – and Gaussian double zeta plus polarization function (DNP) basis set [24]. The $(2 \times 2 \times 1)$ k-point was used for Brillouin zone (reciprocal lattice unit cell) sampling with an orbital cut-off of 3.5 Å.

Dynamics simulations were conducted with a time step of 1.9 fs (78.5 a.u.) – sufficient to satisfy the constant energy simulation criterion – for a total simulation time

Fig. 1 Initial State Structures:(a) CH_4 on 1:0 $Ni-Cu/\gamma-Al_2O_3$: 32 Ni atoms, 85 total atoms; (b) CH_4 on 1:1 $Ni-Cu/\gamma-Al_2O_3$: 16 Ni atoms, 16 Cu atoms, 85 total atoms, and (c) CH_4 on 0:1 $Ni-Cu/\gamma-Al_2O_3$: 32 Cu atoms, 85 total atoms.

Fig. 2 Molecular dynamics atomic legend.

of 0.38 ps (200 steps). The canonical NVT (constant amount (N), volume (V) and temperature (T)) thermodynamic ensemble [25] with the Generalized Gaussian Moment thermostat [26] were used for temperature control at 1,148 K. The software environment and interface were contained in BIOVIA Materials Studio 2016.

3. Results and Discussion

3.1 Crystal Size and Structure

The calculated lattice parameters (lattice angles: α , β , γ and cell volume) of the catalyst models are shown in Table 1.

Calculations predicted a 4.8% decrease in primitive (crystal) cell volume from 1:0 $Ni-Cu/\gamma-Al_2O_3$ to 1:1 $Ni-Cu/\gamma-Al_2O_3$. This is counter-intuitive since Cu has a slightly larger atomic radius (128 pm) than Ni (124 pm). In the absence of Ni , calculations predicted a 3.9% increase in cell volume.

The decrease in cell volume in the presence of both Ni and Cu is indicative of the formation of a $Ni-Cu$ alloy and suggests an increase in inter-atomic

interaction.

The data in Table 2 and their relationship in Fig. 3 indicate a strong positive correlation between cell volume and *ab initio* binding energy magnitude. This confirms the increase in inter-atomic energy with the formation of a $Ni-Cu$ alloy that resulted in the decrease in crystal size.

Calculated XRD for 1:0 $Ni-Cu/\gamma-Al_2O_3$, 1:1 $Ni-Cu/\gamma-Al_2O_3$, and 0:1 $Ni-Cu/\gamma-Al_2O_3$ are shown in Figs. 4 a, 4b and 4c, respectively. The migration of the highest peak ($\blacktriangledown$) from $2\theta = 46^\circ$ (1:0 $Ni-Cu/\gamma-Al_2O_3$) to $2\theta = 43.5^\circ$ (1:1 $Ni-Cu/\gamma-Al_2O_3$) and to $2\theta = 41.8^\circ$ (0:1 $Ni-Cu/\gamma-Al_2O_3$) can be observed. This is in agreement with empirical characterization results shown in Fig. 5.

This peak migration is attributed to the formation of a homogeneous $Ni-Cu(1\ 1\ 1)$ alloy – a determining factor in CNT production – while the difference between the empirical ($2\theta = 44^\circ$) and calculated ($2\theta = 46^\circ$) XRD angles can be attributed to the presence of more than one Ni crystal type ($Ni(1\ 1\ 1)$, $Ni(2\ 0\ 0)$ and $Ni(2\ 2\ 0)$).

3.2 *Ab Initio* Molecular Dynamics

Key findings from AIMD simulations are shown in Table 3. The *C-metal* initial bonding time was measured from the initial state to the moment the C atom formed a bond with the catalyst surface. The CH_4 annihilation time was measured from the initial

Table 1 Crystal size and structure data.

Catalyst	Crystal lattice parameter			
	α	β	γ	Cell volume ($\text{\AA}^3$)
1:0 $Ni-Cu/\gamma-Al_2O_3$	90.1876°	89.4195°	89.5064°	1042.95
1:1 $Ni-Cu/\gamma-Al_2O_3$	89.9874°	90.0077°	89.89.16°	992.792
0:1 $Ni-Cu/\gamma-Al_2O_3$	89.7762°	87.8577°	90.6147°	1085.92

Table 2 Cell volumes and binding energies.

Catalyst	Cell volume ($\text{\AA}^3$)	Binding energy (Ha)
1:0 $Ni-Cu/\gamma-Al_2O_3$	1,042.95	-26.6185
1:1 $Ni-Cu/\gamma-Al_2O_3$	992.792	-28.2080
0:1 $Ni-Cu/\gamma-Al_2O_3$	1,085.92	-25.9290

Fig. 3 Correlation between cell volume and binding energy.

Fig. 4 Calculated diffractogram for (a) 1:0 $Ni-Cu/\gamma-Al_2O_3$, (b) 1:1 $Ni-Cu/\gamma-Al_2O_3$ and (c) 0:1 $Ni-Cu/\gamma-Al_2O_3$.

Fig. 5 Empirical XRD analysis on $Ni-Cu/\gamma-Al_2O_3$ at varying $Ni-Cu$ ratios.

state to the moment more than half of the $C-H$ bonds have been broken. The C -deposition time was measured from the initial state to the moment the C atom formed more than one bond with the catalyst surface.

While it was not possible to plot the C -deposition time as a function of $Ni-Cu$ ratio due to the uncertainty in the magnitude at 0:1 $Ni-Cu/\gamma-Al_2O_3$, these data indicate an initial decrease in deposition time from 1:0 to 1:1 $Ni-Cu/\gamma-Al_2O_3$ followed by a marked increase with 0:1 $Ni-Cu/\gamma-Al_2O_3$. This suggests a higher C deposition rate on 1:1 $Ni-Cu/\gamma-Al_2O_3$, than on 1:0 $Ni-Cu/\gamma-Al_2O_3$, with the lowest being on 0:1 $Ni-Cu/\gamma-Al_2O_3$.

This is concurrent with empirical findings on CNT yield from TGA, as shown in Fig. 6, where there was an initial increase in CNT Yield with the addition of Cu from 1:0 to 1:1 $Ni-Cu/\gamma-Al_2O_3$ and a marked decrease in CNT yield in the absence of Ni .

SEM Analysis on the catalyst after CTDM yielded concurrent results with both AIMD and TGA data, with the highest amount of observable CNTs on 1:1 $Ni-Cu/\gamma-Al_2O_3$ and the lowest on 0:1 $Ni-Cu/\gamma-Al_2O_3$.

The average CNT diameters were also acquired from SEM analysis, and are shown and correlated with the $Ni-Cu$ ratio in Fig. 8.

The trend in empirical CNT diameter are concurrent with the differences in cell volume at varying $Ni-Cu$ ratios, with both the minimum CNT diameter and the minimum cell volume with 1:1 $Ni-Cu/\gamma-Al_2O_3$. Since the CNT diameter is dependent on the crystal size of

Table 3 AIMD simulation data.

$Ni-Cu$ ratio	$C-metal$ initial bonding time (fs)	CH_4 annihilation time (fs)	C deposition time (fs)
1:0	72.2	58.9	91.2
1:1	19.0	49.4	76.0
0:1	176.7	24.7	> 380

Fig. 6 TGA on CNT Yield $Ni-Cu/\gamma-Al_2O_3$ at varying $Ni-Cu$ ratios. **Fig. 7** SEM Analyses (20,000x magnification) on CNT grown on (a) 1:0 $Ni-Cu/\gamma-Al_2O_3$, (b) 1:1 $Ni-Cu/\gamma-Al_2O_3$ and (c) 0:1 $Ni-Cu/\gamma-Al_2O_3$. **Fig. 8** SEM analysis on average CNT diameter on $Ni-Cu/\gamma-Al_2O_3$ at varying $Ni-Cu$ ratios.

the catalyst [27], the decrease in CNT diameter on 1:1 $Ni-Cu/\gamma-Al_2O_3$ confirms the dependence of the lattice crystal size on the magnitude of the binding energy, or inter-cellular interaction.

4. Conclusions

Results indicated the significance of the formation

of the $Ni-Cu$ alloy both from an empirical and a theoretical perspective. The formation of the $Ni-Cu$ -alloy resulted in an increase in inter-cellular interaction, which caused a decrease in crystal size in the catalyst. This further resulted in the decrease in average CNT diameter produced. The increase in CNT yield is also attributed to the formation of the $Ni-Cu$

alloy by decreasing the C deposition time determined from *ab initio* calculations and supported by empirical TGA and SEM analysis.

An optimum Ni-Cu ratio (between 1:0 and 1:1 Ni-Cu) is implied based on regression analysis on CNT yield, the determination of which can be subject to further studies. Furthermore, the concurrence exhibited between simulation data and empirical data is significant to the production of CNTs from CTDM in the field of AIMD simulations, and will open more specific and directed avenues for future research.

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