Influence of Ni on Carbon Nanotube Production with Fe-Based Catalysts

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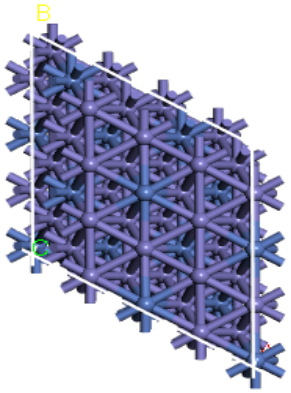
Supplementary Information (SI):

S1. Fig S1 The top and side views of the Fe_3Ni slabs with (111) planes provide a clear visualization of the atomic arrangement within the bimetallic alloy. In Fig. S1 (a), the top view of the Fe_3Ni alloy illustrates the arrangement of surface atoms, showcasing how Fe and Ni atoms are distributed across the surface, which plays a key role in adsorption properties and catalytic performance. In Fig. S1 (b), the side view of the Fe_3Ni slab along the (111) plane reveals the layered structure of the alloy, giving a more comprehensive understanding of how atoms are stacked within the lattice, influencing carbon adsorption and CNTs growth.

(a)



(b)

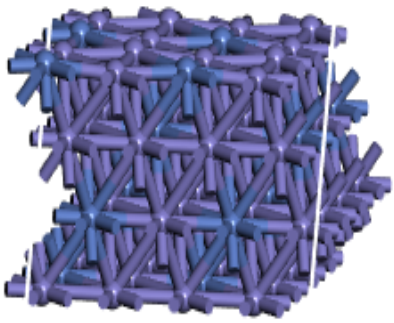


Fig. S1 Top views of Top views of the (a) Fe_3Ni alloy and (b) and side views of the Fe_3Ni alloy of the (111) planes, showing the atomic arrangements of the bimetallic.

S2. Binding Energy Calculation:

$$\Delta H_{surf\_ad} = E_{surf\_ad} - E_{surf} - E_{ad}$$

$$\Delta H_{surf\_ad} = Binding\ Energy$$

$$E_{surf\_ad} = Enengy\ of\ Suface\ with\ adsorbate$$

$$E_{surf} = Energy\ of\ surface$$

$$E_{ad} = Energy\ of\ adsorbate$$

S3. Bond Length

The bond length analysis reveals distinct interaction strengths between carbon and the different metal catalysts. The Ni–C bond displays the shortest bond length at 1.773 Å, suggesting a stronger interaction between carbon and nickel. This stronger bonding may enhance the adsorption of carbon species on Ni surfaces, which can influence catalytic activity. In contrast, the Fe–C bond exhibits the longest bond length of 1.921 Å, indicating a comparatively weaker interaction between carbon and iron. The Fe_3Ni–C bond, with an intermediate bond length of 1.792 Å, suggests a moderate interaction strength, reflecting a synergistic effect between Fe and Ni in the alloy. These differences in bond lengths are likely to play a critical role in determining the catalytic behaviour.

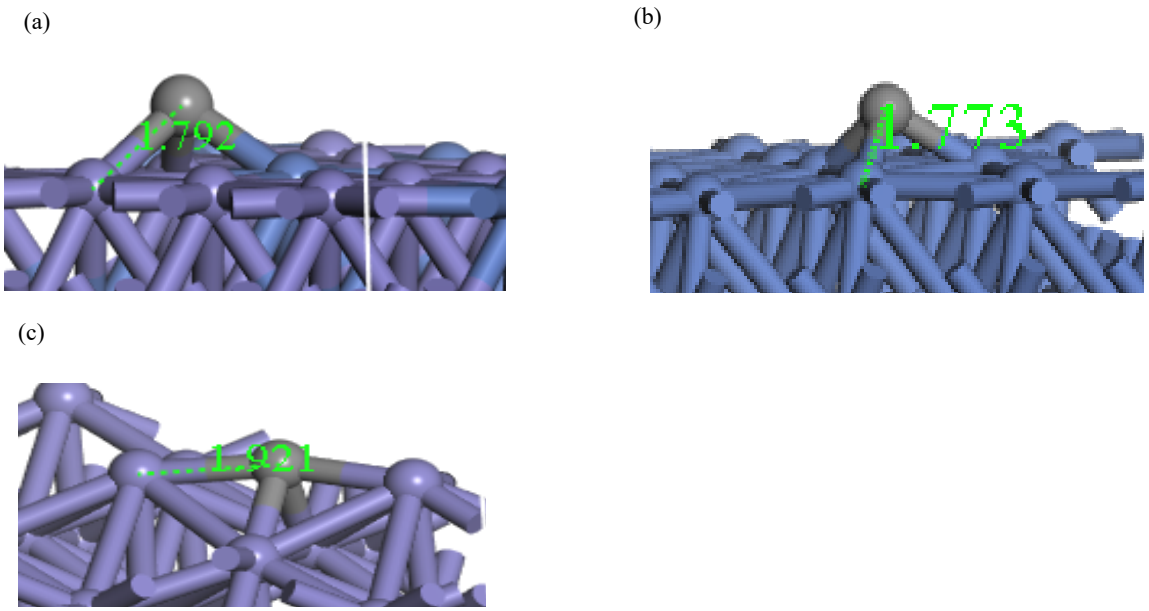


Fig. S2 Comparison of carbon bond lengths with (a)Fe_3Ni,(b) Ni, and (c)Fe catalysts, illustrating shorter bonds for Ni–C, longer bonds for Fe–C, and intermediate bond lengths for Fe_3Ni–C, reflecting varying interaction strengths and alloy effects.

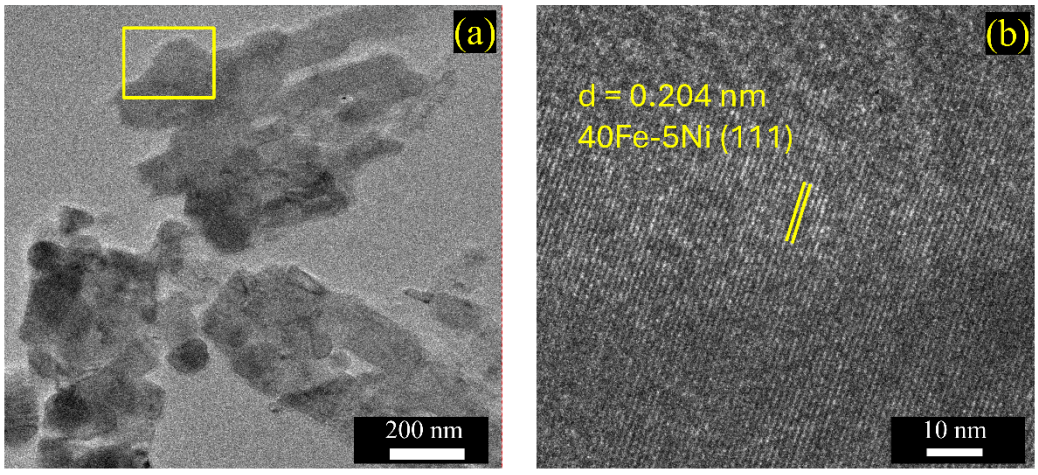
Table. 1 Bond length of different catalytic surfaces

Catalyst	Bond Length (Å)
Fe3Ni_C	1.792
Fe_C	1.921
Ni_C	1.773

S4. Raman Analysis[3-6]

Table. 2 I_D/I_G and I_{2D}/I_G ratios of CNTs formed by the different catalysts.

Catalyst	**I_D/I_G**	**I_{2D}/I_G**
40Fe-10Ni	0.517	0.69
40Fe-7Ni	0.514	0.75
40Fe-5Ni	0.378	0.67
40Fe-3Ni	0.475	0.73
40Fe-1Ni	0.521	0.72
40Fe-0Ni	0.543	0.73



S5. HR-TEM of catalyst which is used for the model in DFT calculation.

Fig. S3: The HR-TEM analysis showing the plane (1 1 1) for the fresh catalyst which is considered as model plane for the DFT calculation.

The (111) plane was selected for computational analysis based on its established use in modelling calculations for Fe-Ni systems, as highlighted in the literature.[1] Prior studies have underscored the significance of the (111) plane in Fe-Ni systems, particularly its role in facilitating the growth MWCNTs.[2] To further validate this choice and address the reviewer's concerns, HR-TEM analysis was performed, with the findings illustrated in the accompanying figure.

In Figure (a), the catalyst image is shown, while Figure (b) presents the lattice fringes with a measured d-spacing of 0.204 nm, confirming the presence of the (111) plane. This experimental evidence, derived from the 40Fe-5Ni catalyst, corroborates the computational model and emphasizes the relevance of the (111) plane in the catalyst's structural framework.[7-8]

References:

1 S. Takenaka, M. Serizawa and K. Otsuka, *J Catal*, 2004, **222**, 520–531.

2 U. P. M. Ashik and W. M. A. W. Daud, *J Taiwan Inst Chem Eng*, 2016, **61**, 247–260.

3 A. C. Ferrari, *Solid State Commun*, 2007, **143**, 47–57.

4 M. A. Gubanov, M. I. Ivantsov, M. V. Kulikova, V. A. Kryuchkov, N. V. Nikitchenko, M. I. Knyazeva, A. B. Kulikov, A. A. Pimenov and A. L. Maksimov, *Petroleum Chemistry*, 2020, **60**, 1043–1051.

5 M. S. Dresselhaus, G. Dresselhaus, R. Saito and A. Jorio, 2005, preprint, DOI: 10.1016/j.physrep.2004.10.006.

6 F. Cazaña, N. Latorre, P. Tarifa, J. Labarta, E. Romeo and A. Monzón, *Catal Today*, 2018, **299**, 67–79.

7 J. Li, E. Croiset and L. Ricardez-Sandoval, *Appl Surf Sci*, 2014, **317**, 923–928.

8 F. Zaera, A. J. Gellman and G. A. Somorjai, *Surface Science Studies of Catalysis: Classification of Reactions*, 1986, vol. 19.