DFT Studies of Small Ni Cluster on Graphene Surface: Effect of CO2 Activation

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The project was supported by National Basic Research Program of China (973 Program) (2011CB201202) & the National Natural Science Foundation of China (No. 21376154).

Figure and table Captions:

Figure S1. The optimized structures of (a) perfect-graphene sheet, (b) one Ni atom deposited on graphene with an elevation (h) of 1.498 Å.

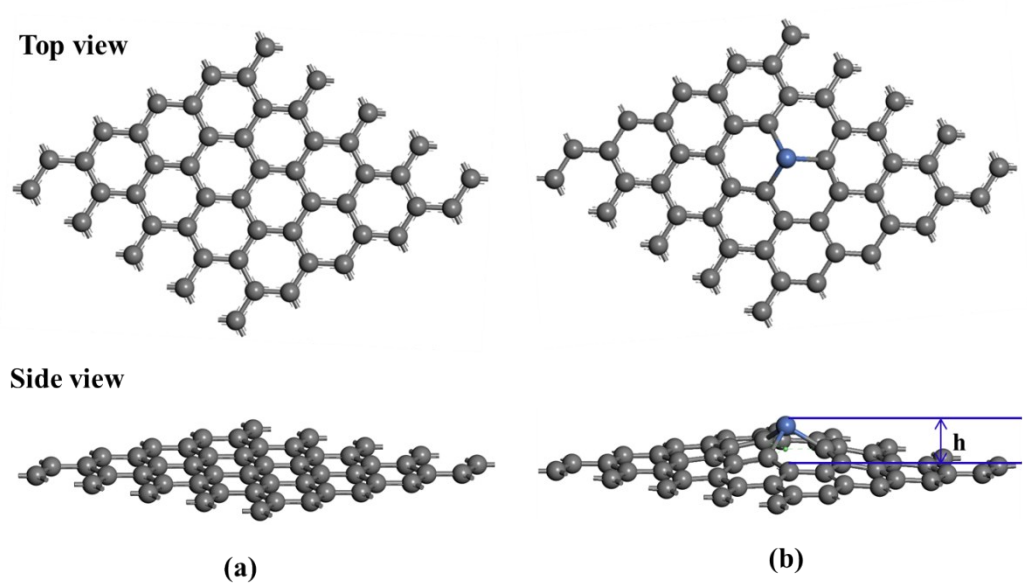
Figure S2. PDOS of Ni atom and C atom in a) three, b) five, c) seven and d) ten Ni atoms adsorbed on MGr. The PDOS is projected on the orbitals of C (red) and Ni (black) atoms.

Figure S3. Stable configurations ofCO_2 adsorbed on Ni_4, Ni_5, Ni_6 and Ni_{10}.

Figure S4. Stable configurations ofCO_2 adsorbed on MGr surface deposition of Ni_4, Ni_5, Ni_6 and Ni_{10}.

Figure S5. Sum of density of states projected on the atoms of the CO_2 molecule adsorbed on isolated Ni_4 (red), on MGr surface (blue) and on the Ni_4/MGr system (green). The zero energy is set to the highest occupied state of corresponding system.

Table S1 Binding energy E_B, C-O bond length $d_{C\text{-}O}$ and O-C-O angle$\alpha_{O\text{-}C\text{-}C}$ of CO_2 adsorbed on an isolated Ni_x cluster, on MGr and on a graphene doped Ni_x cluster.



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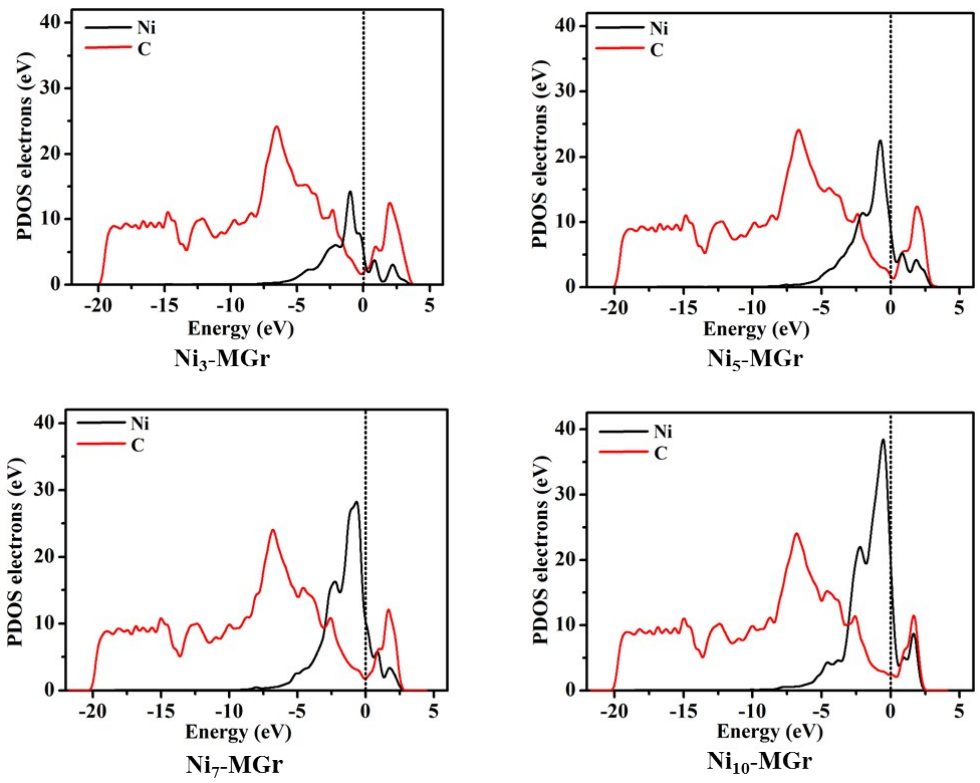

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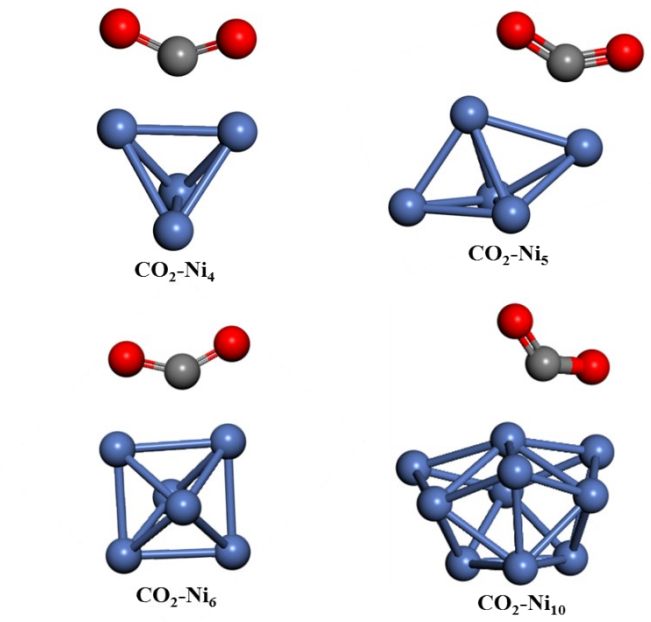
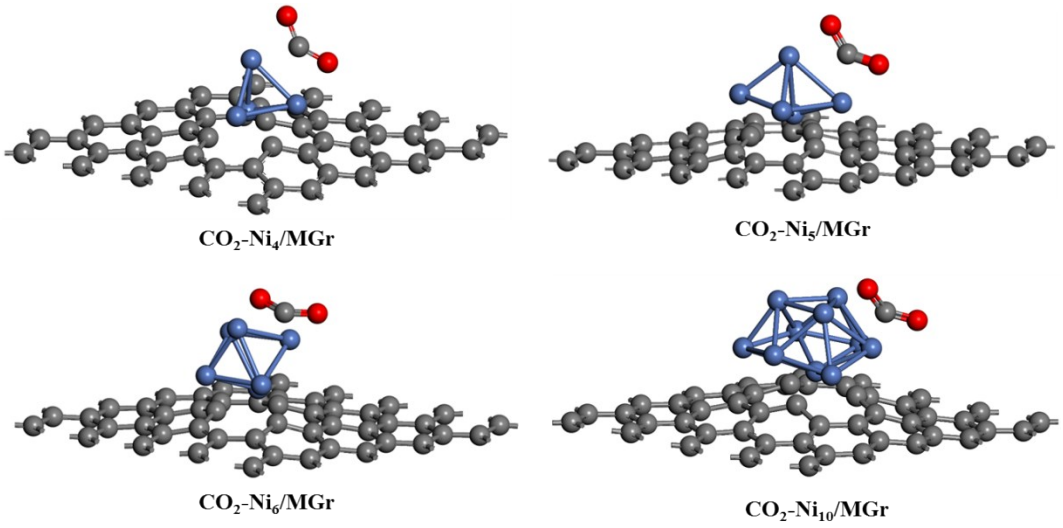


Figure S3. Stable configurations of CO_2 adsorbed on Ni_4, Ni_5, Ni_6 and Ni_{10} cluster.



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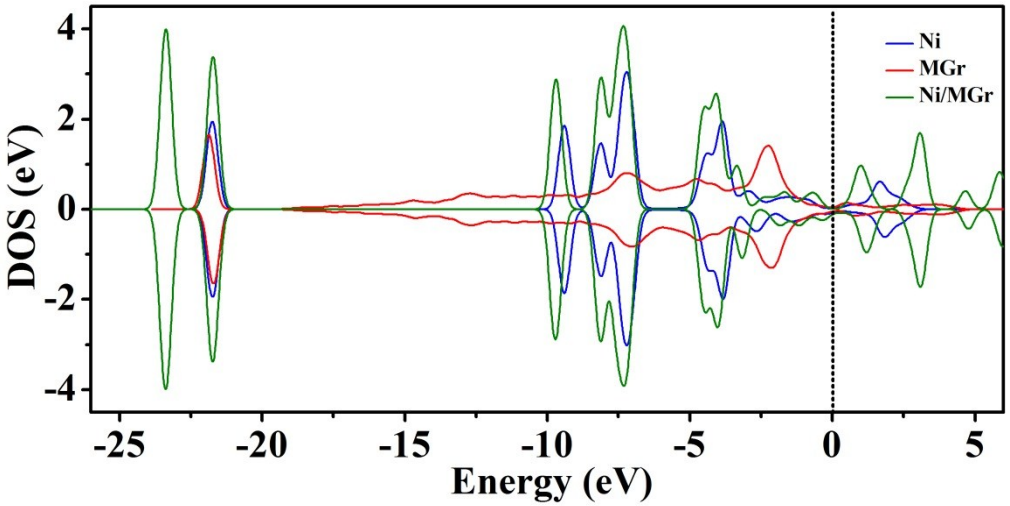

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Substrate	E_B,CO_2 **(eV)**	$d_{C\text{-}O(1)}$**(Å)**	$d_{C\text{-}O(2)}$**(Å)**	$\alpha_{O\text{-}C\text{-}O}$**(°)**
CO_2	-	1.175	1.175	180.00
MGr	-1.35	1.376	1.377	107.86
Ni_4 cluster	-1.80	1.263	1.262	136.26
Ni_4/MGr	-2.72	1.250	1.243	140.31
Ni_5 cluster	-1.55	1.250	1.260	138.00
Ni_5/MGr	-2.05	1.252	1.252	138.90
Ni_6 cluster	-1.43	1.263	1.248	138.23
Ni_6/MGr	-1.76	1.254	1.250	139.96
Ni_{10} cluster	-1.42	1.220	1.298	132.39
Ni_{10}/MGr	-4.03	1.239	1.265	138.29

It can be seen that, CO_2 molecule has the greatest transformation on MGr surface compared with the other adsorbing materials, which indicates that activation of CO_2 on MGr is the most obvious. For Ni_5 and Ni_6, the activation degree of CO_2 is similar, however, the E_B of CO_2 on Ni_x/MGr is lower than Ni_x, which can be expressed by two aspects: on one hand, Ni cluster, as a medium, can transfer electrons form CO_2 to MGr well, so the ability of combine with CO_2 and Ni_x/MGr enhanced significantly.

And the other hand is that, CO_2 molecule may change the electrons distribution of Ni_x/MGr, and leads to the system tend to be more stable when adsorbed on it.