Electronic Supplementary Material (ESI) for Green Chemistry.


# Supporting Information

## Ni-N synergy enhanced synthesis of formic acid via $CO_2$ hydrogenation under mild condition

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**Table S1:** The amount of $CO_2$ desorbed in the $CO_2$-TPD experiments.

| Sl. No. | Catalysts | $CO_2$ Desorbed ($cm^3/g$ STP) | | | | $CO_2$ uptake capacity (mmol/g) | Conversion (%) |
|---|---|---|---|---|---|---|---|
| | | Weak | Intermediate | High | Total | | |
| **1** | 2.5Ni/N-$TiO_2$ | 0.1367 | 0.0834 | - | 0.2201 | 0.3 | 9.6 |
| **2** | 1.0Ni/N-$TiO_2$ | 0.0927 | 0.1384 | - | 0.2311 | 0.39 | 11.29 |
| **3** | 0.5Ni/N-$TiO_2$ | 0.1535 | 0.0587 | - | 0.2122 | 0.24 | 7.79 |
| **4** | 1.0Ni/$TiO_2$ | 0.2062 | 0 | - | 0.2062 | 0.23 | 7.39 |

**Table S2:** Catalytic recylablity of 1Ni/N-$TiO_2$ catalyst

| Cycle | Conversion (%) | TON |
|---|---|---|
| Cycle 1 | 11.29 | 757 |
| Cycle 2 | 11.28 | 755 |
| Cycle 3 | 11.26 | 752 |
| Cycle 4 | 11.25 | 749 |

Reaction condition: Catalyst amount: 100 mg, Solvent: $H_2O$, Temperature: 353 K, Pressure: 60 bar, Time: 20 h

**Table S3:** The representation of deviation in $CO_2$ hydrogenation for 1Ni/N-$TiO_2$ catalyst

| Batch | Conversion (%) | TON |
|---|---|---|
| Batch 1 | 11.29 | 757 |
| Batch 2 | 11.28 | 755 |
| Batch 3 | 11.17 | 750 |
| Batch 4 | 11.27 | 754 |
| Average | 11.25 | 754 |
| Standard deviation | 0.06 | 2.94 |

Reaction condition: Catalyst amount: 100 mg, Solvent: $H_2O$, Temperature: 353 K, Pressure: 60 bar, Time: 20 h

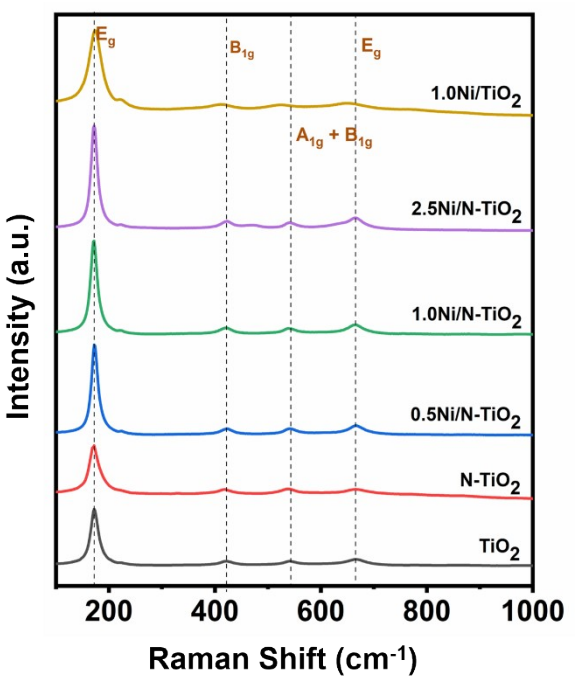


**Figure S1**: Raman Spectrum

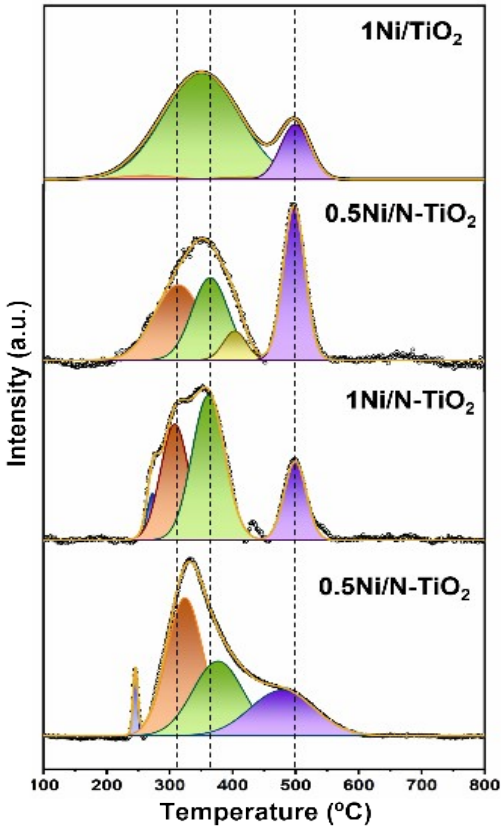


**Figure S2**: $H_2$-TPR profile

**$CO_2$ adsorption isotherm**

The $CO_2$ adsorption performance of as-prepared catalysts, including 2.5Ni/N-$TiO_2$, 1Ni/N-$TiO_2$, 0.5Ni/N-$TiO_2$, and 1Ni/$TiO_2$, were studied at 1 bar pressure and 298 K temperature, as shown in Fig. S3. Remarkably, the 1Ni/N-$TiO_2$ catalyst showed highest adsorption capacity of 0.39 mmol per g of catalyst, followed by 2.5 Ni/N-$TiO_2$ catalyst with adsorption capacity of 0.3 mmol/g. The lower adsorption capacity of 2.5 Ni/N-$TiO_2$ compared to 1Ni/N-$TiO_2$ is due to a lower surface area caused by higher metal loading. The 0.5 Ni/N-$TiO_2$ catalyst exhibits an adsorption capacity of 0.24 $cm^3/g$, whereas the N-undoped 1Ni/$TiO_2$ possesses an adsorption capacity of 0.23 $cm^3/g$ at standard temperature and pressure. It has been observed that $CO_2$ adsorbs strongly on 1Ni/N-$TiO_2$ as compared to 1Ni/$TiO_2$. These findings are in accordance with the DFT-predicted $CO_2$ adsorption behaviour as $CO_2$ adsorbs on $Ni_{13}$/N-$TiO_2$ (101) surface with a binding energy of -0.73 eV; whereas the binding energy of $CO_2$ on $Ni_{13}$/$TiO_2$ was calculated to be -0.50 eV.

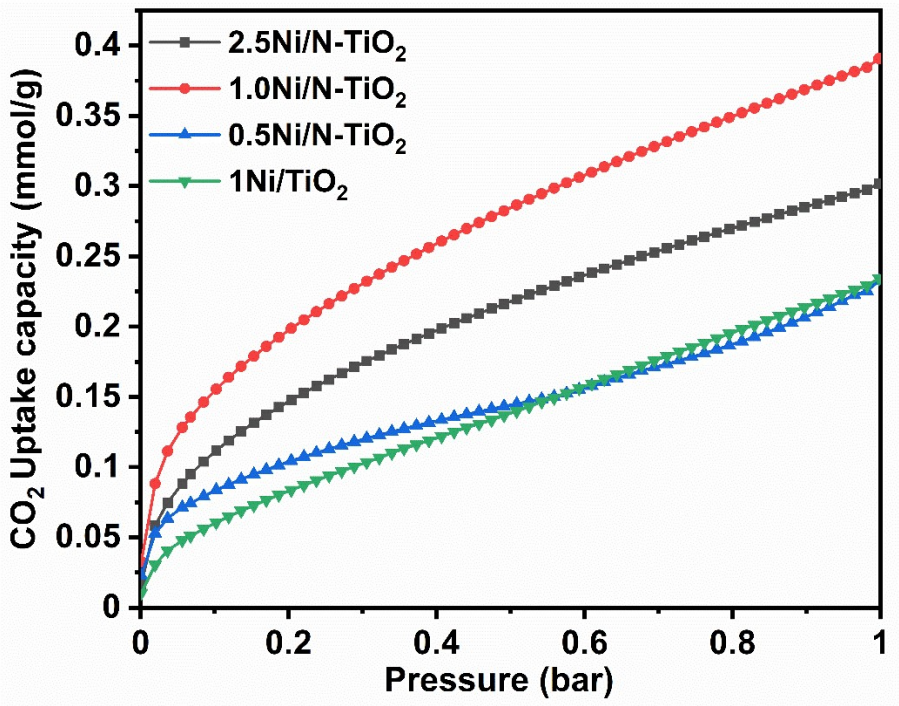


**Figure S3:** $CO_2$ adsorption isotherm at 1 bar and 298 K

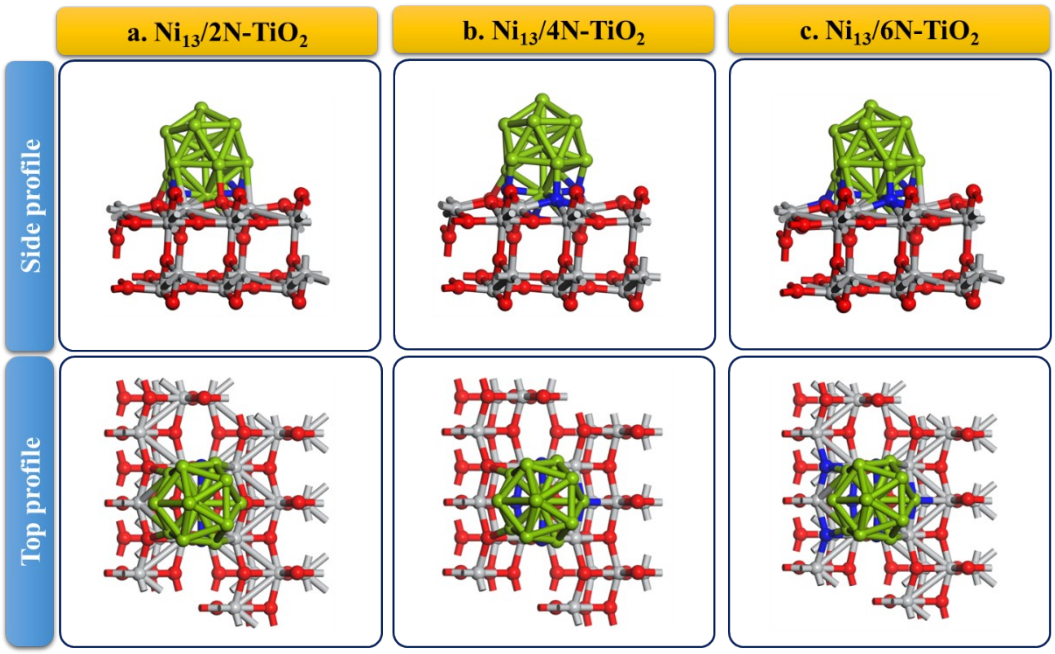


**Figure S4:** The DFT optimised structure of (a) $Ni_{13}$/2N-$TiO_2$ (101) surface (b) $Ni_{13}$/4N-$TiO_2$ (101) surface, and (c) $Ni_{13}$/6N-$TiO_2$ (101) surface Color code: Green: Nickel, Blue: Nitrogen, Gray: Titanium, and Red: Oxygen

**Effect of Nitrogen content on $CO_2$ adsorption**

The adsorption characteristics of $CO_2$ species on the $Ni_{13}$/2N-$TiO_2$ (101) surface and $Ni_{13}$/6N-$TiO_2$ (101) surface were investigated, employing the same calculation parameters set for the other calculations in the manuscript. Fig. S5 (a) shows that $CO_2$ was adsorbed on the $Ni_{13}$/2N-$TiO_2$ (101) surface in a bend configuration by forming three bonds, one of which the 'O' atom of $CO_2$ bonded to a Ni atom with a bond length of 2.09 Å and the rest of 'C' and 'O' atoms were together bonded to a neighbouring Ni atom possessing a bond length of 1.89 Å and 2.19 Å, respectively. The binding energy calculated for $CO_2$ on $Ni_{13}$/2N-$TiO_2$ was -0.55 eV, slightly higher exothermic than $Ni_{13}$/$TiO_2$ by 0.05 eV, which possesses binding energy of -0.50 eV. However, the stability of $CO_2$ on the $Ni_{13}$/2N-$TiO_2$ (101) surface was very close to the $Ni_{13}$/$TiO_2$ as compared to $Ni_{13}$/4N-$TiO_2$, which exhibits a binding energy of -0.73 eV. $CO_2$ was observed to be adsorbed on $Ni_{13}$/6N-$TiO_2$ (101) surface through the formation of three bonds in a similar manner in the case of $Ni_{13}$/2N-$TiO_2$, as can be seen in Fig. S5 (c). The bond length of the O-Ni bond was measured to be 2.06 Å, whereas the C-Ni bond and O-Ni bonds were calculated to be 1.88 Å and 2.23 Å, respectively. The binding energy of $CO_2$ on the $Ni_{13}$/6N-$TiO_2$ was computed to be -0.81 eV. It was observed that the binding energy of $CO_2$ was increased with the increase in the number of N atoms following the trend: $Ni_{13}$/$TiO_2$ (-0.5 eV) < $Ni_{13}$/2N-$TiO_2$ (-0.55 eV) < $Ni_{13}$/4N-$TiO_2$ (-0.73 eV) < $Ni_{13}$/6N-$TiO_2$ (-0.81 eV). This study reveals that the increasing number of N atoms enhances the basicity of the catalyst surface, due to which the acid-base interaction between the basic catalyst surface and the acidic $CO_2$ has increased, resulting in the stable adsorption of $CO_2$. However, if compared to $Ni_{13}$/$TiO_2$

surface, the adsorption of the $CO_2$ species was slightly exothermic by 0.05 eV on $Ni_{13}$/2N-$TiO_2$ surface, whereas it was significantly more exothermic on the $Ni_{13}$/4N-$TiO_2$ surface by 0.23 eV. Further increasing the number of N atoms on the $Ni_{13}$/4N-$TiO_2$ surface makes the $CO_2$ adsorption process higher exothermic. Nevertheless, the $CO_2$ adsorbs on $Ni_{13}$/6N-$TiO_2$ surface with a small increment of binding energy than $Ni_{13}$/4N-$TiO_2$ surface by 0.08 eV, relatively very close to $Ni_{13}$/4N-$TiO_2$ surface.

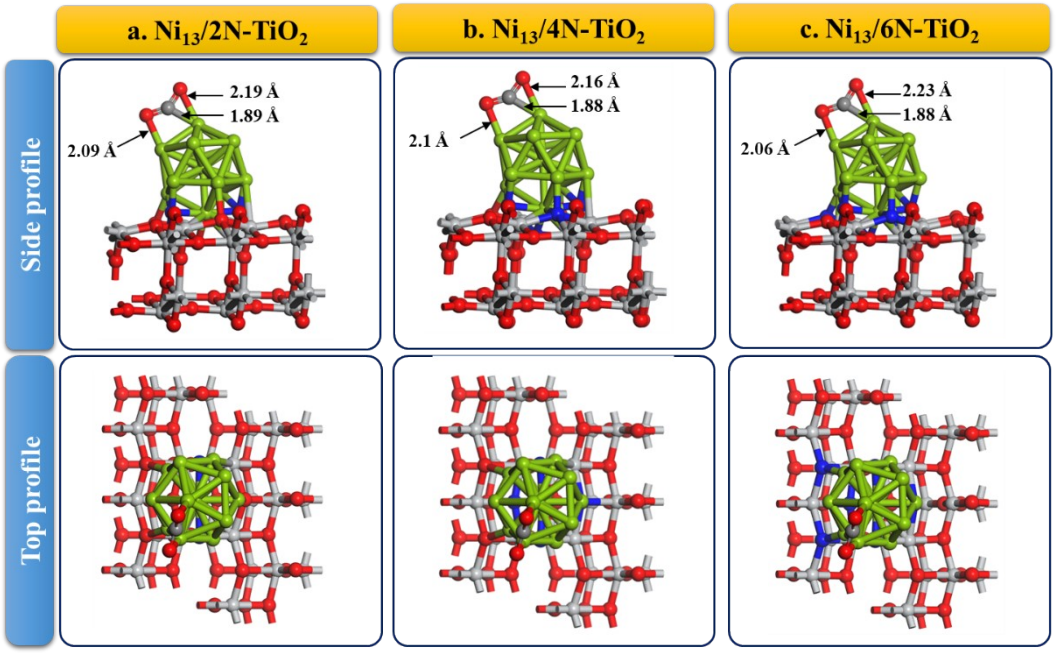


**Figure S5:** The DFT optimised geometry of the $CO_2$ adsorption at (a) $Ni_{13}$/2N-$TiO_2$ (101) surface (b) $Ni_{13}$/4N-$TiO_2$ (101) surface, and (c) $Ni_{13}$/6N-$TiO_2$ (101) surface Color code: Green: Nickel, Blue: Nitrogen, Gray: Titanium, Dark Gray: Carbon and Red: Oxygen

The stable configuration of the $Ni_{13}$/6N-$TiO_2$ model possesses no Ni-O bonding, as shown in Fig. 1 (c), which is not supported by catalyst characterization evidence, as discussed earlier. In contrast, $Ni_{13}$/4N-$TiO_2$ exhibited a significant enhancement in $CO_2$ bind energy than $Ni_{13}$/$TiO_2$, along with supporting the characterization data. Therefore, $Ni_{13}$/4N-$TiO_2$ was chosen to represent 1Ni/N-$TiO_2$ catalyst for further DFT calculations.