

Supplementary Materials

Combined Spectroscopic and Computational Study of Nitrobenzene Activation on Non-Noble Metals-Based Mono- and Bimetallic Catalysts

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Characterization of monometallic samples

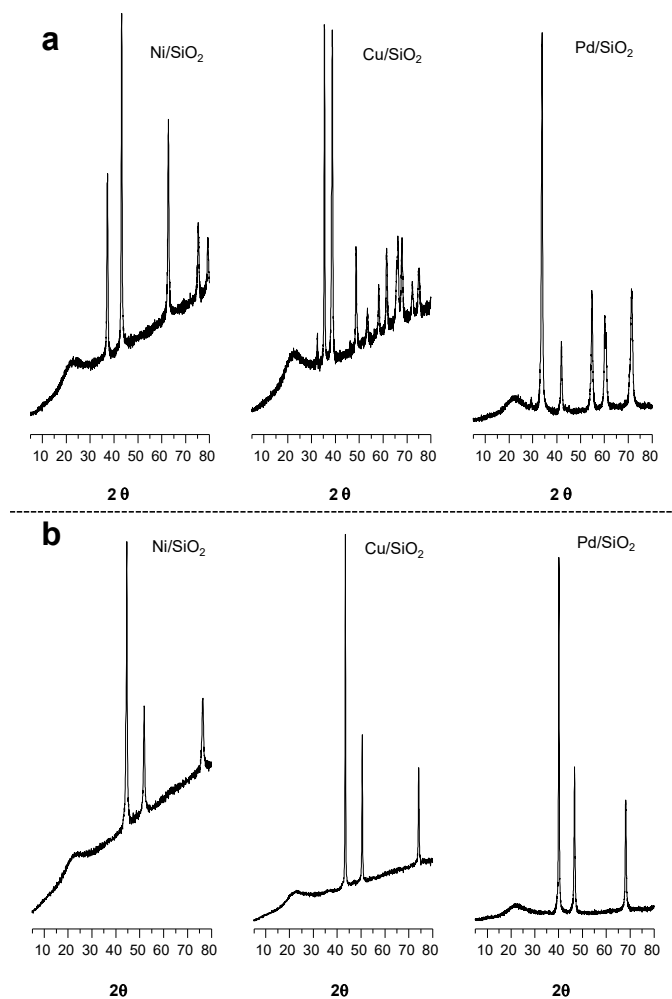


Figure S1. XRD pattern of the calcined (a) and (b) reduced monometallic Ni/SiO₂, Cu/SiO₂ and Pd/SiO₂ catalysts.

IR Study of nitrobenzene hydrogenation on monometallic samples

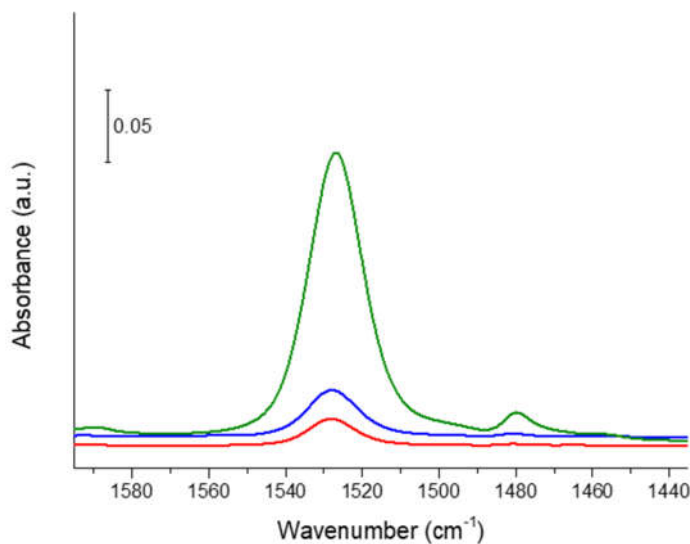


Figure S2. IR spectra of nitrobenzene adsorption at saturation coverage on Cu/SiO₂ (blue), Pd/SiO₂ (red), Ni/SiO₂ (green). Spectra normalized to sample weight. The lower intensity of the IR signal in the Cu/SiO₂ and Pd/SiO₂ samples agrees with the low interaction of nitrobenzene on both metals.

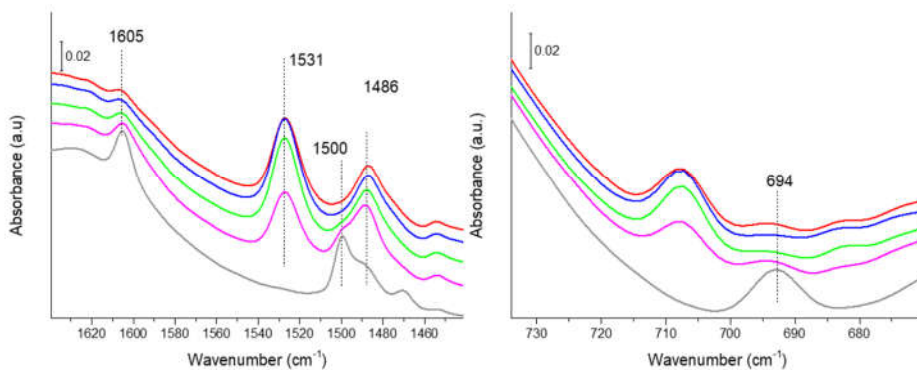


Figure S3. IR spectra of nitrosobenzene formed on the Ni/SiO₂ catalyst and after co-addition of H₂ at 25 °C (red line). Then, the temperature is increased to 90 °C (blue), 120 °C (green), 160 °C (magenta) and 200 °C (grey). Aniline formation (IR band at 1605, 1500 and 694 cm⁻¹) is detected at 200 °C.

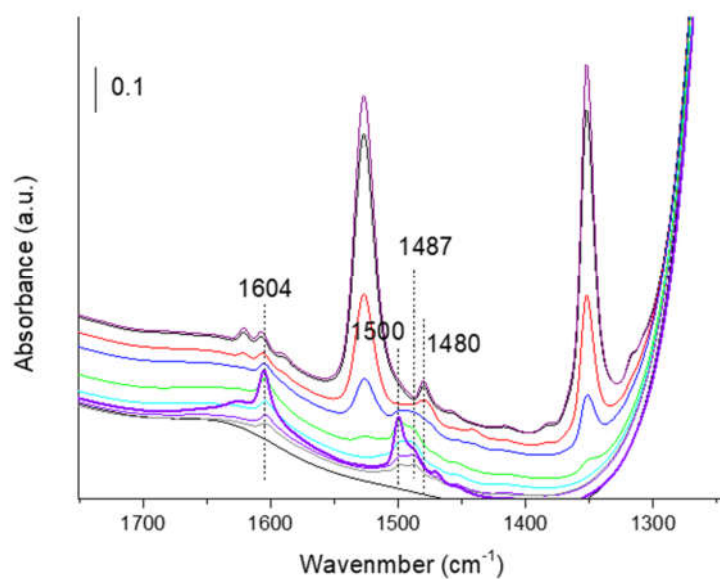


Figure S4. IR spectra of nitrobenzene and H₂ co-adsorbed on Ni/SiO₂, and their reactivity at increasing reaction temperature: 25 °C (black), 60 °C (red), 90 °C (blue), 120 °C (green), 140 °C (cyan), 180 °C (violet), 200 °C (grey). In violet bold after cooling down the sample from 180 °C to 25 °C allowing re-adsorption of the gas phase.

Characterization of bimetallic samples

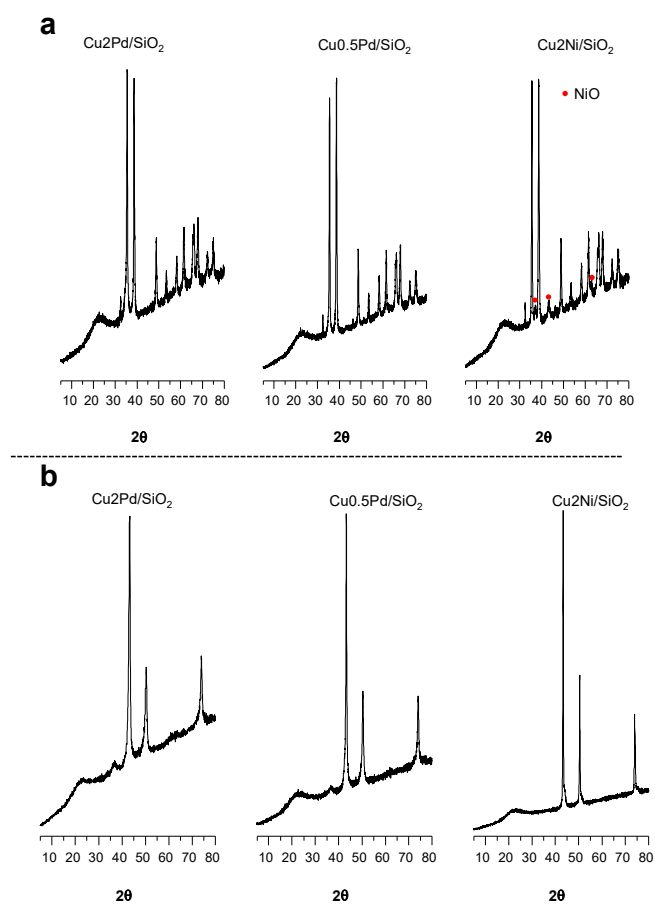


Figure S5. XRD pattern of the calcined (a) and (b) reduced bimetallic $\text{Cu}_2\text{Pd}/\text{SiO}_2$, $\text{Cu}_{0.5}\text{Pd}/\text{SiO}_2$ and $\text{Cu}_2\text{Ni}/\text{SiO}_2$ catalysts.

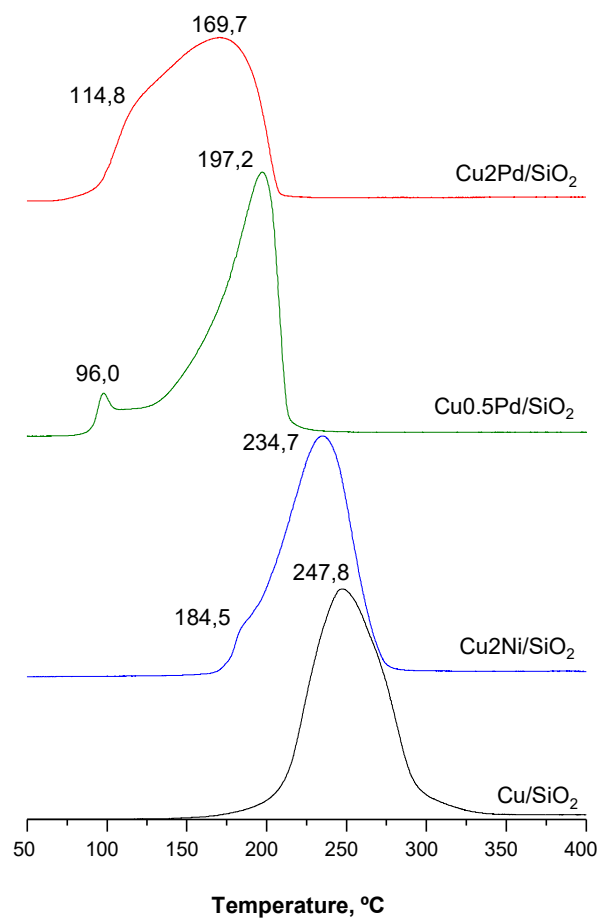


Figure S6. TPR-H₂ of monometallic Cu/SiO₂ and bimetallic Cu₂Pd/SiO₂, Cu_{0.5}Pd/SiO₂ and Cu₂Ni/SiO₂ catalysts . The addition of Pd or Ni to the Cu monometallic catalyst, favour H₂ activation (as determined from the H₂D₂ isotopic exchange experiments), resulting in a higher catalyst reducibility.

Table S1. Surface composition determined by XPS.

| sample | Si: Pd (Ni): Cu | Pd(Ni)/Cu |
|---------------------------------------|-----------------|-----------|
| Cu _{0.5} Pd/SiO ₂ | 97: 0.5: 2.5 | 0.2 |
| Cu ₂ Pd/SiO ₂ | 96: 0.7: 3.4 | 0.2 |
| Cu ₂ Ni/SiO ₂ | 98: 0.6: 0.7 | 0.9 |

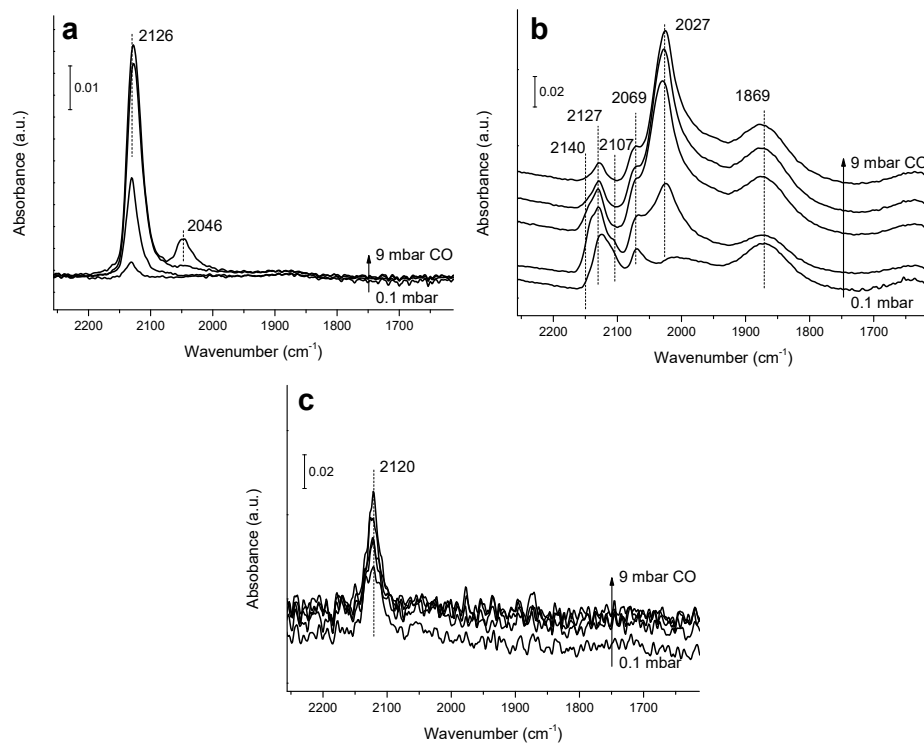


Figure S7. IR spectra of CO adsorption at $-170\text{ }^{\circ}\text{C}$ on (a) $\text{Cu}_{0.5}\text{Pd}/\text{SiO}_2$, (b) $\text{Cu}_2\text{Pd}/\text{SiO}_2$, (c) $\text{Cu}_2\text{Ni}/\text{SiO}_2$.