Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

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Supporting Information

Activated Interior of Clay Nanotubes for Agglomeration-tolerant Catalysis

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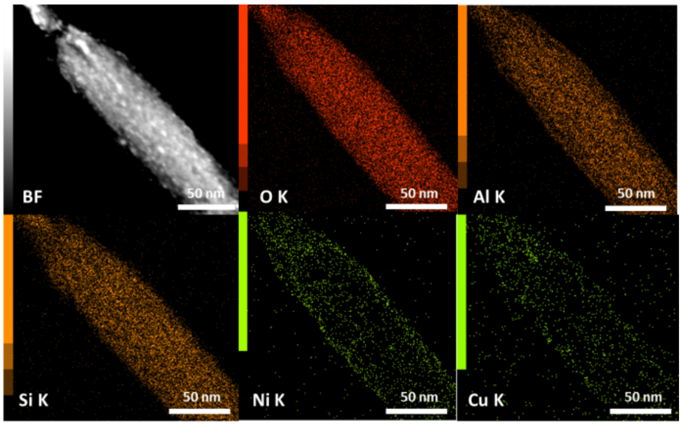


Figure S1. EDX mapping images for the Cu-Ni nanoparticles decorating the Halloysite nanotubes surface.

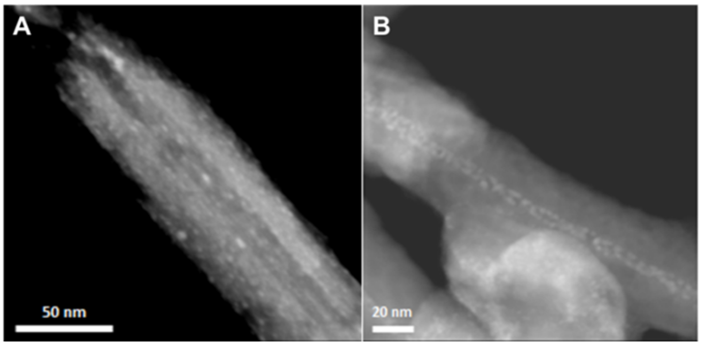


Figure S2. HAADF images of (A) Cu-Ni/Halloysite and (B) Cu-Ni@Halloysite materials.

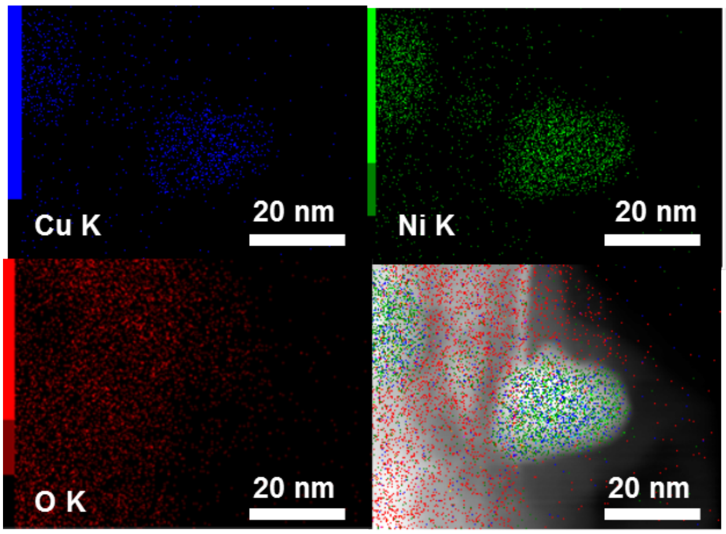


Figure S3. EDX mapping images of an individual Cu-Ni alloy nanoparticle.

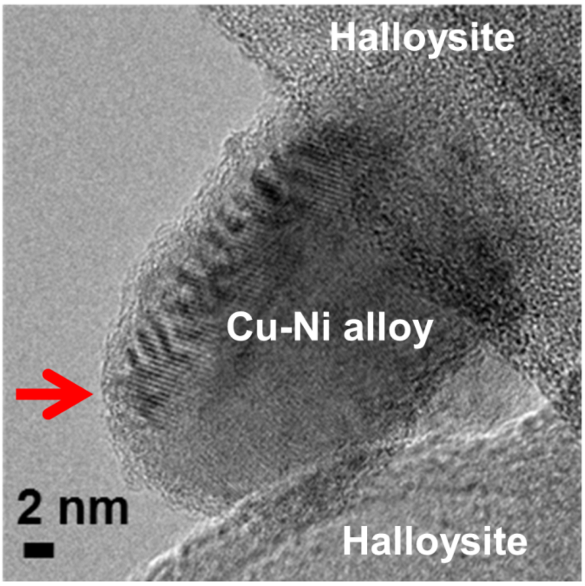


Figure S4. High-resolution TEM image of an individual Cu-Ni alloy nanoparticle. Cu-Ni alloy surface is exposed to the atmosphere at the point indicated by an red arrow.

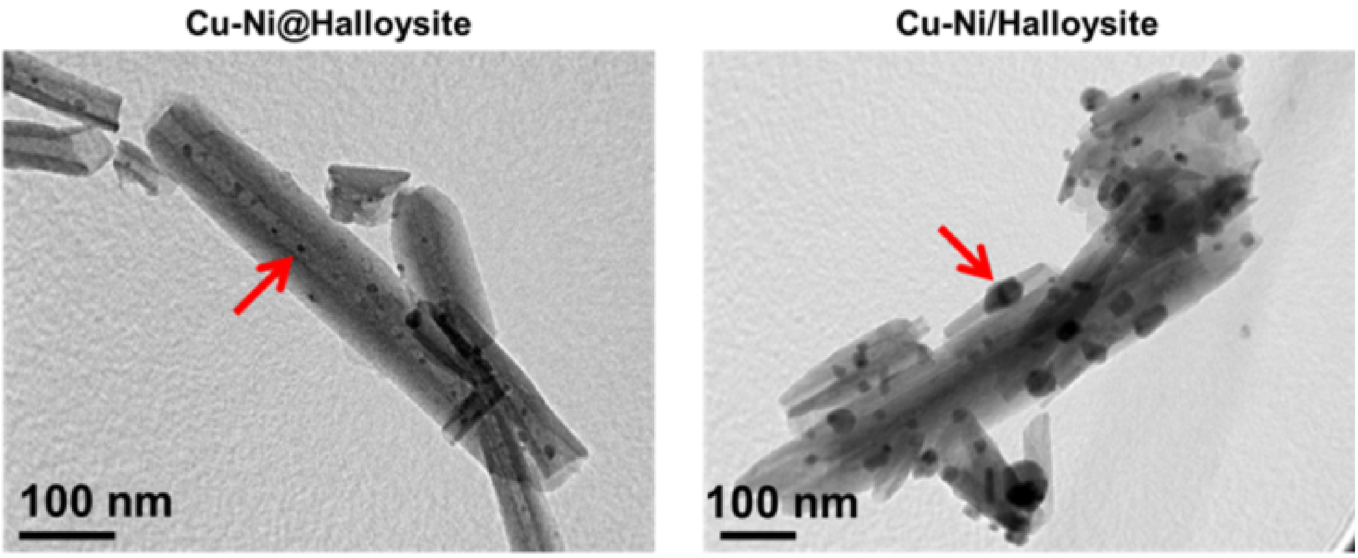


Figure S5. TEM images of the catalysts after the repeated NO remediation catalysis. Red arrows correspond to the Cu-Ni nanoparticles.

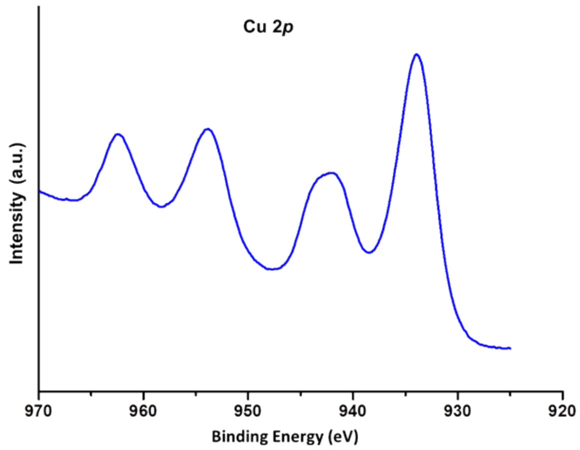


Figure S6. XPS profile of CuO reference nanoparticles.

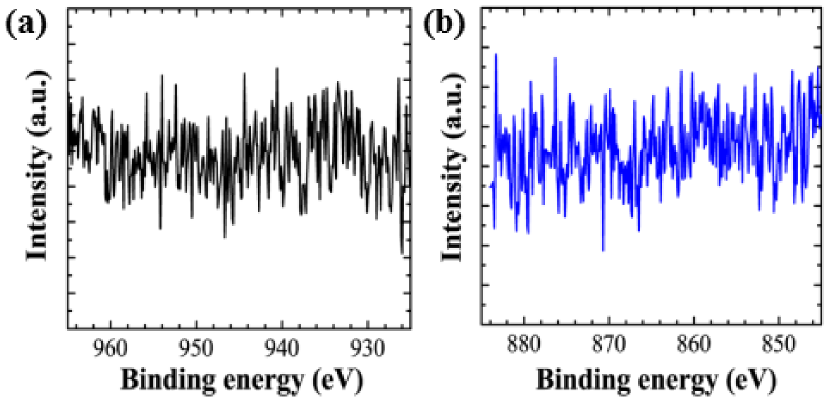


Figure S7. XPS spectra for the Cu-Ni@Halloysite in the Cu 2*p* region (a) and in the Ni 2*p* region (b).

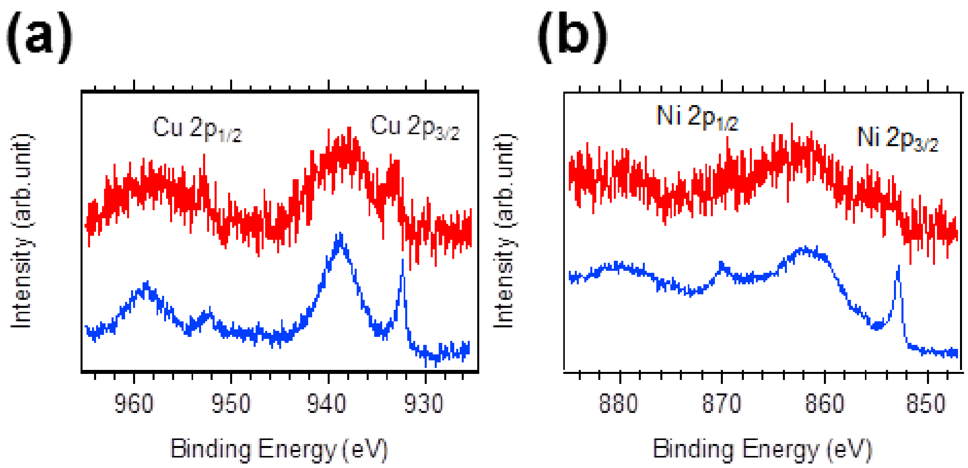


Figure S8. (a) HAXPES spectra in the Cu 2*p* region for the Cu-Ni@Halloysite (red) and the Cu-Ni/Halloysite (blue). (b) HAXPES spectra in the Ni 2*p* region for the Cu-Ni@Halloysite (red) and the Cu-Ni/Halloysite (blue).

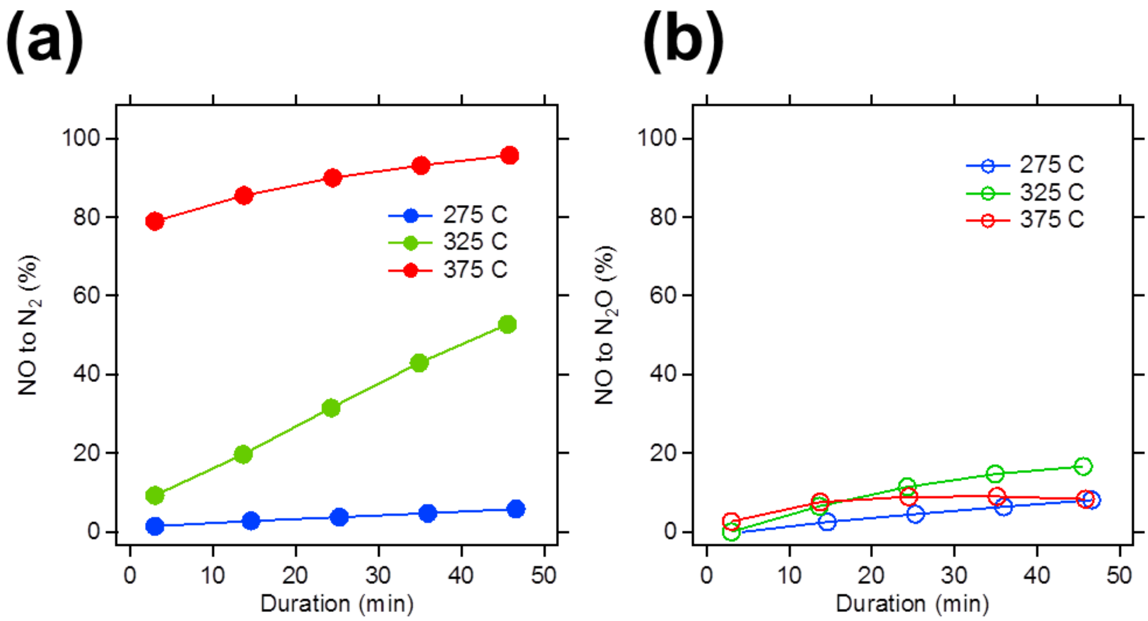


Figure S9. Reaction selectivity of the Cu-Ni@Halloysite to the different reaction paths: (a) NO to N_2 conversion and (b) NO to N_2O conversion.

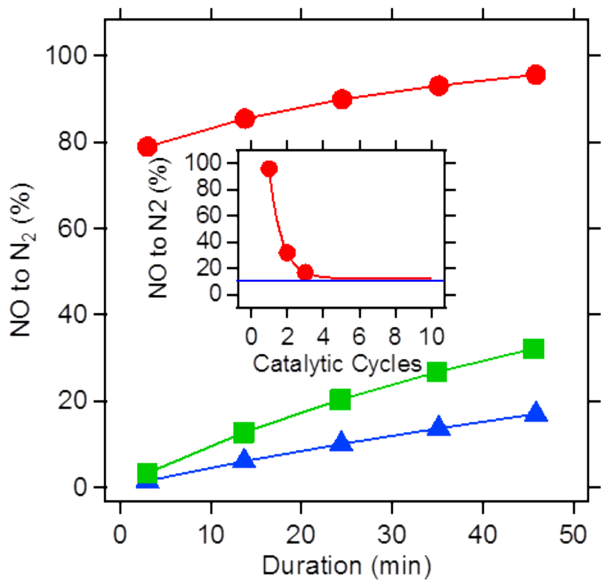
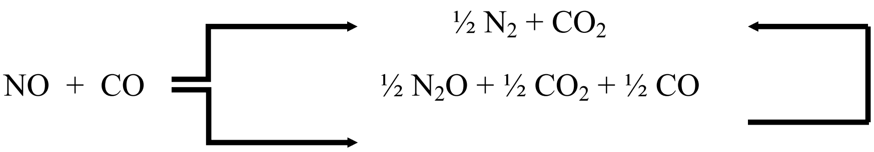


Figure S10. Time courses for the NO remediation (NO to N_2 conversion) through repeated catalysis. The red, green and blue profiles correspond to the 1st, 2nd and 3rd cycles at a reaction temperature of 375 °C. The inset shows the NO-to-N_2 conversion rate at duration time = 45 min as function of catalytic cycles, together with an exponential fitting to the experimental data.

NO remediation catalysis.

The possible reaction paths for the NO remediation are:



The initial number of the NO and CO molecules in the circulating reactor, N (constant), is given by

$$N = N_C = N_N = \frac{1}{2} N_O \qquad (1)$$

where N_C, N_N and N_O denote the number of carbon, nitrogen and oxygen atoms involved in the reaction, respectively.

The numbers of the atoms are always retained in the circulating condition:

$$N_C = N_{CO} + N_{CO2} \qquad (2)$$

$$N_N = 2N_{N2O} + 2N_{N2} + N_{NO} \qquad (3)$$

$$N_O = N_{CO} + 2N_{CO2} + N_{NO} + N_{N2O} \qquad (4)$$

where N_{CO}, N_{CO2}, N_{N2O}, N_{N2} and N_{NO} correspond to the number of CO, CO_2, N_2O, N_2 and NO, respectively, in a given volume of the circulating reactor.

From the equations (1), (2), (3) and (4) we obtain

$$N_{CO} = N - N_{CO2} \qquad (5)$$

$$N_{NO} = N - N_{N2O} - N_{CO2} \qquad (6)$$

$$N_{N2} = \frac{1}{2} N_{CO2} - \frac{1}{2} N_{N2O} \qquad (7)$$

The number of the gas molecules in a given volume of the reactor is proportional to the peak area of the corresponding output signal from the gas chromatograph, Δ_{gas}:

$C\Delta_{gas} = S_{gas}N_{gas}$ (8)

($C = V/RT$; R = gas constant, T = 300 (K), V = volume of the circulating reactor)

Here the proportionality constant, S_{gas}, was determined as the ratio between the known pressure of the gas and the corresponding peak area:

S_{CO} - ratio of the peak area to the partial pressure of CO = 0.22847 kPa^{-1}

S_{NO} - ratio of the peak area to the partial pressure of NO = 0.21674 kPa^{-1}

S_{CO2} - ratio of the peak area to the partial pressure of CO_2 = 0.26502 kPa^{-1}

S_{N2O} - ratio of the peak area to the partial pressure of N_2O = 0.24063 kPa^{-1}

S_{N2} - ratio of the peak area to the partial pressure of N_2 = 0.22516 kPa^{-1}

The output signals from the GC were integrated to obtain the peak area. As given in Chart S1, the area for the first signal, Δ_1, corresponded to a mixture of NO, CO and N_2 gases. The second- and third signals, Δ_2 and Δ_3, corresponded to CO_2 and N_2O, respectively.

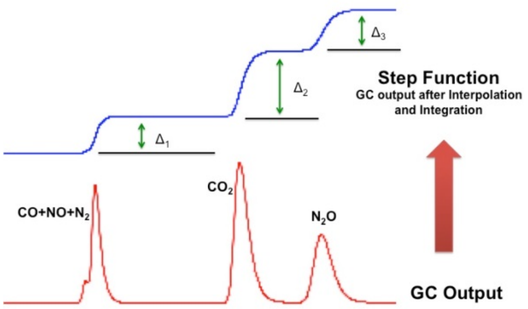


Chart S1. Gas Chromatograph output signal for NO remediation reaction and its corresponding step function graph.

By using equation (5), (6), (7) and (8) we obtain

$C\,\Delta_1 = S_{CO}N_{CO} + S_{NO}N_{NO} + S_{N2}N_{N2}$ (9)

$C\,\Delta_2 = S_{CO2}N_{CO2}$ (10)

$C\,\Delta_3 = S_{N2O}N_{N2O}$ (11)

Combining (6), (7), (10) and (11), we obtain

$N_{CO2} = C\,\varDelta_2/S_{CO2}$ (13)

$N_{N2O} = C\,\varDelta_3/S_{N2O}$ (14)

$N_{N2} = C\,(½\varDelta_2/S_{CO2} – ½\varDelta_3/S_{N2O})$ (15)

From (5) and (9) we obtain

$N = \{C/(S_{CO} + S_{NO})\}\{\varDelta_1 + (S_{CO} + S_{NO} – ½\,S_{N2})\,(\varDelta_2/S_{CO2}) + (S_{NO} + ½\,S_{N2})\,(\varDelta_3/S_{N2O})\}$
(16)

The remediation rates of NO to N_2O and N_2 were finally calculated as $2N_{N2O}/N$ ((14) & (16)) and $2N_{N2}/N$ ((15) & (16)), respectively.