SUPLEMENTARY MATERIAL

Alternate cycles of CO_2 storage and in situ hydrogenation to CH_4 on Ni-Na_2CO_3/Al_2O_3: Influence of promoter addition and calcination temperature

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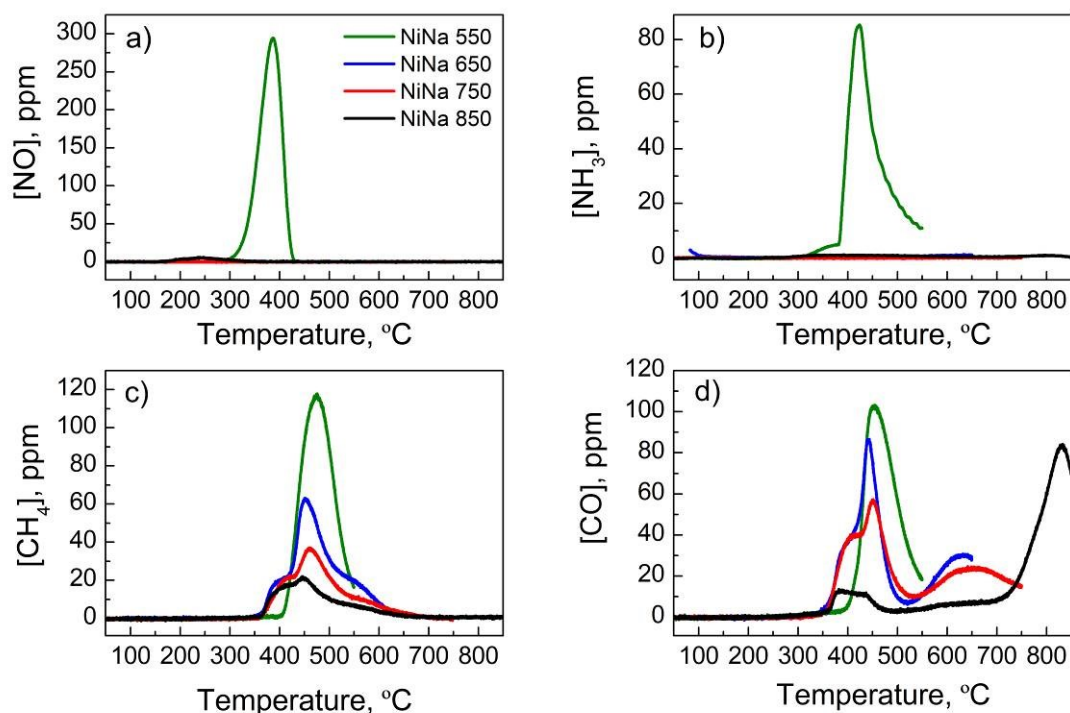
Figure S1. Concentration profiles of NO (a), NH_3 (b), CH_4 (c) and CO (d) at the H_2-TPR reactor outlet measured by the FT-IR for 10NiNa samples calcined at different temperatures (550, 650, 750 and 850 °C).

To explain the new hydrogen consumptions centered at 400-500 °C in the H_2-TPR experiments, the exit gas was analysed in an FTIR. Figure S1 shows the evolution of the compounds of the reduction process with temperature, showing products containing nitrogen and carbon.

The formation of NO (not shown) is related to the decomposition of the residual nitrates belonging to the adsorbent and the nickel precursor that have not completely decomposed during the calcination stage. NH_3 is produced by the reduction of residual nitrates on metallic Ni sites ($NO+5/2H_2{\rightarrow}NH_3+H_2O$) implying the consumption of additional H_2.

The formation of CH_4 and CO was also detected during H_2-TPR. The formation of CH_4 ($CO_2+4H_2{\rightarrow}CH_4+H_2O$), is attributed to the hydrogenation of the CO_2 adsorbed in the samples, due to exposure to the environment before the experiment and the presence of metallic nickel. And these formation also implying the consumption of additional H_2.
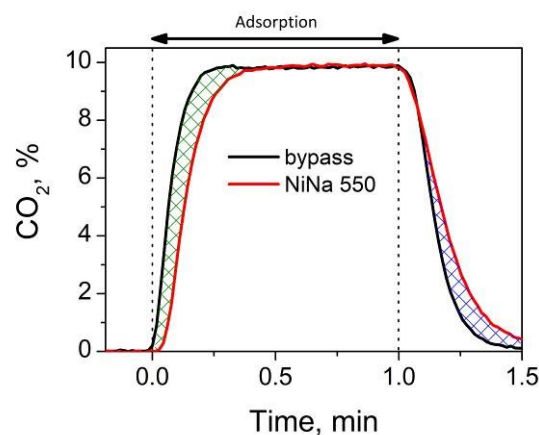
Figure S2. CO_2 concentration profiles, in the adsorption period, during one CO_2 adsorption and hydrogenation cycle at 400 °C with NiNa 550 catalyst, together with the bypass.

The amount of CH_4 or CO produced is obtained directly from the integration of the signal, through Eq. (8-9). Moreover, the CO_2 storage is calculated from the difference between the quantity fed and the quantity leaving the reactor (Eq. 7). For this, the feed is bypassed and the signals are compared. This comparison is recorded in Figure S2, for the sample NiNa 550 operating at 400 °C. In the first seconds of adsorption, it can be seen how the experimental curve is out of phase with the bypass, which indicates that the CO_2 is being adsorbed. The signals are then matched, indicating that the catalyst is saturated, as already mentioned in Figure 4. During the storage period (1 min), 229 µmol of CO_2 are stored. After this period, CO_2 is removed from the feed stream and the catalyst is purged with Ar for two minutes, observing that the CO_2 concentration decreases progressively to practically zero. During this period of time, some of the physically adsorbed CO_2 is released. Consequently, the amount of CO_2 adsorbed before the hydrogenation step is slightly reduced to 190 µmol CO_2.
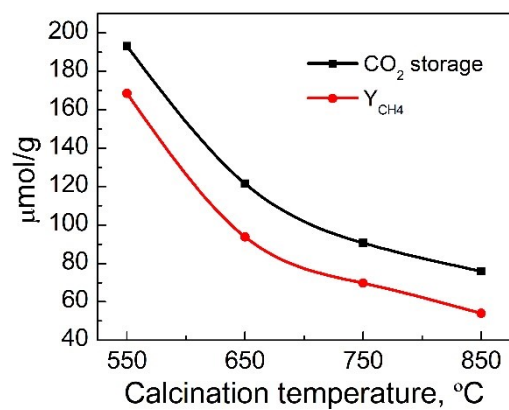
Figure S3. Maximum CO_2 storage and CH_4 production for the 10NiNa samples calcined at different temperatures (550, 650, 750 and 850 °C).

The evolution of the maximum amount of CO_2 stored and CH_4 produced is shown in Figure S3. Both follow a similar trend, descending with the calcination temperature and being the steepest slope at low temperatures.
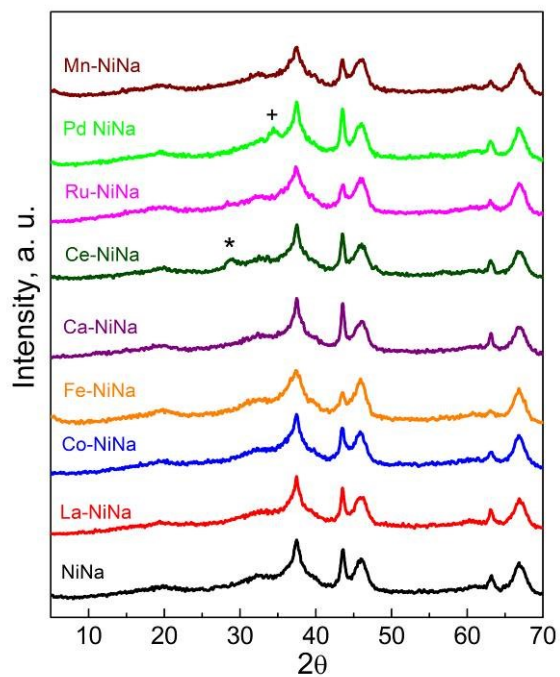
Figure S4. XRD spectra of NiNa promoted samples, were (+) corresponds to PdO and (*) to CeO$_2$.

Figure S4 shows the diffraction profiles of the promoted samples together with the reference sample (NiNa). Diffractograms are quasi-identical to those of the reference sample, only appearing small peaks corresponding to PdO and CeO$_2$.
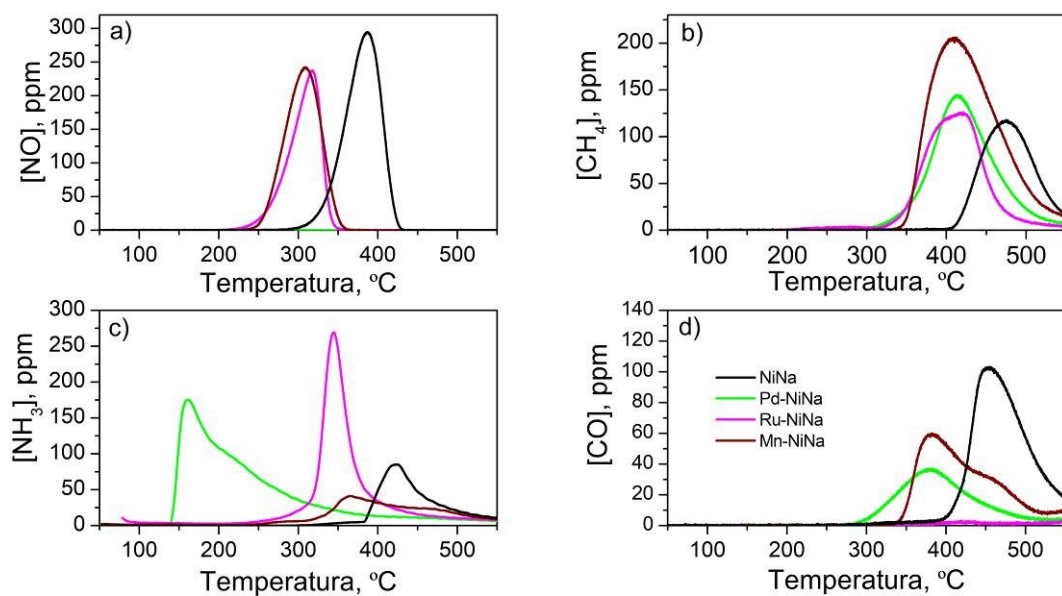
Figure S5. Concentration profiles of NO (a), NH$_3$ (b), CH$_4$ (c) and CO (d) at the H$_2$-TPR reactor outlet measured by the FT-IR for NiNa promoted samples.

Figure S5 shows the evolution, analysed in an FTIR, of the compounds of the reduction process with temperature, showing products containing nitrogen and carbon. The formation of NO is related to the decomposition of the residual nitrates and the formation of CH$_4$ and CO is attributed to the hydrogenation of the CO$_2$ preadsorbed.
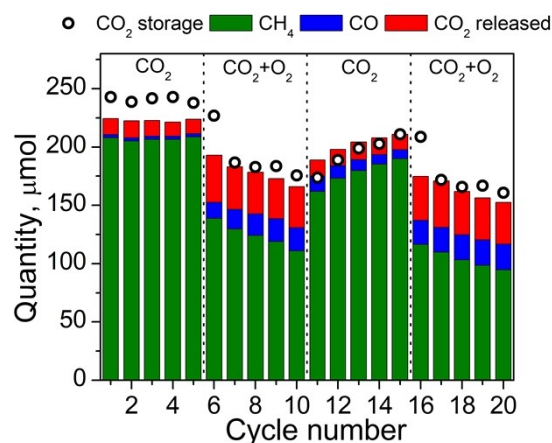
Figure S6. Production of CH$_4$ and CO together with the amount of CO$_2$ leaving the reactor unreacted. The amount of CO$_2$ stored during the adsorption period is also included.

Figure S6 shows the amount of CH$_4$ (green), CO (blue) and CO$_2$ (red) produced during the hydrogenation period for the consecutive 20 cycles. Besides, the amount of CO$_2$ stored in the adsorption period is also included. Note that cycles 1 to 5 are carried out in the absence of oxygen, whereas cycles 6 to 10 in the presence of O$_2$. Then, cycles 11 to 15 are carried out in the absence of oxygen and cycles 16 to 20 in the presence of O$_2$.

The evolution of CH$_4$ and CO shown in Figure S6 is qualitatively similar to that shown in Figure 9 of the manuscript. Specifically, when oxygen is included (cycle 6) the following differences can be observed with respect to the operation in the absence of O$_2$ (cycle 5): i) the amount of CH$_4$ decreases; ii) the amount of CO increases; iii) the amount of CO$_2$ released without being converted increases, and iv) the amount of CO$_2$ stored slightly decreases.

However, the main reason for the progressive diminution of CH$_4$ formation when the CO$_2$ adsorption is carried out in the presence of O$_2$ does not seem to be governed by the lower CO$_2$ adsorption capacity. Note that the CO$_2$ adsorption capacity is only very slightly influenced from cycle 5 to 6 (or cycle 15 to 16). Instead, it seems that the reduction behavior is limiting the overall performance of the catalyst. When some of the Ni species are oxidized to NiO due to the presence of oxygen, the reduction ability of the catalyst during the hydrogenation period is inhibited. Consequently, less CH$_4$ is produced. Besides, due to the fact that the adsorption sites are not fully regenerated, the CO$_2$ adsorption capacity of the subsequent adsorption period is reduced.

Overall, it can be concluded that CH_4 formation decreases when CO_2 adsorption is carried out in the presence of oxygen due to the following facts (sorted by relevance): i) a lower reduction ability; ii) a lower selectivity to CH_4, and iii) a lower CO_2 adsorption capacity.