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

Unravelling the CO_2 Capture and Conversion Mechanism of a NiRu-Na_2O Switchable Dual-function Material in Various CO_2 Utilisation Reactions

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Experimental

Material Preparation

The NiRuNa DFM was synthesised by sequential impregnation, as described in our prior publication.[1] The precursors used were the Ni $(NO_3)_2{\cdot}6H_2O$ (Acros Organics), Ru $(NO)(NO_3)_3$ aqueous solution (1.5 w/v Ru, Alfa Aesar), $NaNO_3$ (Fluka), and CeO_2-Al_2O_3 (SCFa-160 Ce20, Puralox, Sasol). In brief, the required amounts of $NaNO_3$ and CeO_2-Al_2O_3 were mixed with excess deionised water, which was then removed in a rotary evaporator. This suspension was dried overnight at 120°C and calcined at 400°C for 4 hours (5°C min^{-1}). After that, the resulting supported adsorbent was mixed with the Ni and Ru precursors in excess deionised water, which was also removed in a rotary evaporator under reduced pressure. The mixture was then dried overnight at 120°C and calcined at 500°C for 3 hours (5°C min^{-1}). No leaching of Ni-Ru occured, which was confirmed by SEM-EDS and TEM in our previous work.[1]

Material Characterisation

Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) was performed on the reduced DFM in a Talos F200I instrument from ThermoFisher with an electron source of 200 kV. NiRuNa was reduced *ex situ* at 800°C for 1 hour, using a 50 ml min^{-1} total flow rate of a 10% H_2/N_2 mixture. The TEM sample was prepared by dispersing it in ethanol in an ultrasonic bath, dropping it onto copper grids coated with lacey carbon film, and drying it at room temperature for 2 hours. ImageJ software was used to determine the particle size and distribution by measuring *ca*. 170 particles.

X-ray Photoelectron Spectroscopy

XPS measurements were carried out in a SPECS spectrometer equipped with a PHOIBOS 150 MCD analyser, working at fixed pass energy of 40 eV and 0.1 eV resolution for the studied zones. Non-monochromatic source of radiation Al Kα radiation (1486.6 eV) was used at 250 W and 12.5 kV, and the analytical chamber operated at ultra-high vacuum at *ca*. 10^{-10} mbar pressure. Prior to analysis, NiRuNa was reduced *ex situ* at 800°C for 1 hour (50 ml min^{-1} total flow rate of a 10% H_2/N_2 mixture) and pressed into a thin disk. The XPS spectra were recorded at room temperature and the spectra were referenced to the Al2p binding energy of 75.0 eV.

Time-resolved *Operando* DRIFTS-MS

Time-resolved *Operando* DRIFTS-MS measurements were conducted, using a high-temperature reaction cell supported in a Praying Mantis (Harrick) optical system with ZnSe windows. All the spectra were recorded at 4 cm^{-1} resolution and an average of 128 scans via a Thermo Nicolet iS50 FTIR spectrometer with a liquid-nitrogen-cooled MCT detector. The outlet gases were analysed by a mass spectrometer (Prisma plus from Pfeiffer Vacuum), and the data were monitored via Quadera software. Three experiments were performed to test the cyclic performance of NiRuNa in the various CO_2 utilisation reactions, i.e. CO_2 methanation, RWGS, and DRM. The spectrum that was recorded after activation pretreatment was taken as a background. In all the experiments, *ca*. 50 mg was loaded to the cell, which was subsequently reduced *in situ* at 600°C for 1 h (10°C min^{-1}) with a 10% H_2/Ar flow at a rate of 50 mL min^{-1}. Afterwards, the temperature was decreased to 250°C with the same gas mixture in the CO_2 methanation, and to 500°C in the RWGS and DRM reactions. Five (5) cycles of CO_2 capture and conversion were carried out in each experiment and each step (capture or conversion) lasted 10 minutes. A 10% CO_2/Ar mixture was used in the CO_2 capture step, a 10% H_2/Ar mixture in the CO_2 methanation and RWGS steps, and a 10% CH_4/Ar in the DRM step. The total flow rate was 50 mL min^{-1} in all cases. Table S1 summarises the conditions in the time-resolved *operando* DRIFTS-MS experiments.

Table S1: Summary of experimental conditions used in the time-resolved *operando* DRIFTS-MS

	CO_2 methanation		RWGS		DRM	
	Capture	Conversion	Capture	Conversion	Conversion	Capture
Temperature (°C)	250	250	500	500	500	500
Duration (min)	10	10	10	10	10	10

Mixture	10% CO_2/Ar	10% H_2/Ar	10% CO_2/Ar	10% H_2/Ar	10% CH_4/Ar	10% CO_2/Ar

Results & Discussion

X-Ray Photoelectron Spectroscopy

The Ni2p and Ce3d XPS regions are displayed in Figure S1. It was illustrated that only oxidised Ni species (Ni^{2+}) were present in the NiRuNa/CeAl sample. This is attributed to the *ex-situ* treatment of the materials and to the fact that XPS is a surface technique. As mentioned in the “Ex-situ Characterisation: XPS and Particle Size Analysis” section of the article, previously conducted XRD of the reduced NiRuNa sample showed that its bulk consisted of reduced Ni and Ru species,[1] further supporting this explanation and proving that a thin layer of oxidised Ni and Ru was formed after air exposure. The peak fitting of the Ni^{2+} species was not conducted due to the uncertainty of Ni oxide/hydroxide species present and the high-intensity satellite peaks.[2] Similar results were observed for the Ce 3d, whose peaks were mainly attributed to the Ce^{4+} species, evident from the highly increased intensity of the characteristic Ce^{4+} peak at *ca*. 917 eV.[3]

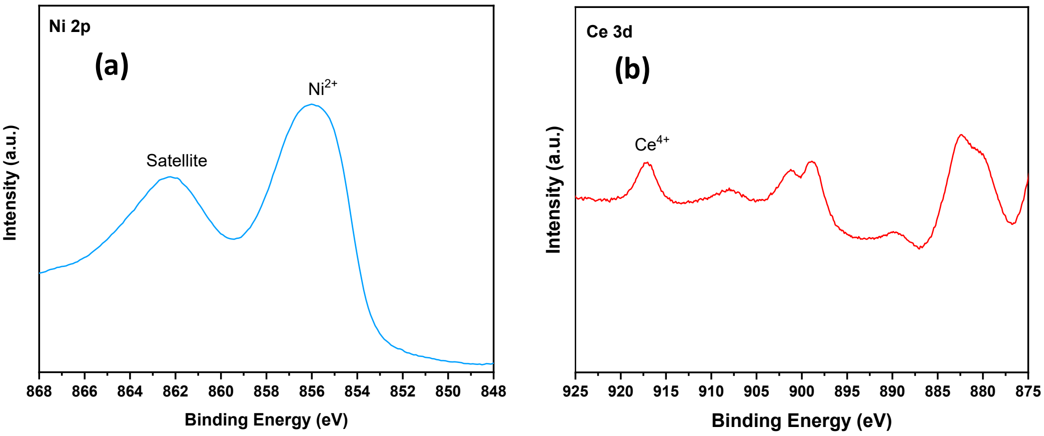

Figure S1: XPS of NiRuNa/CeAl: **(a)** Ni2p region and **(b)** Ce3d region

MS-data during *operando* DRIFTS experiments

Figures S2, S3, and S4 show the recorded MS-data during the operando DRIFTS experiments in CO_2 methanation, RWGS, and DRM respectively.

It is worth noting that the MS signal of CO_2 includes both m/z=44 and m/z=28. In presence of CO_2, CO can only be detected by MS if the concentration is sufficiently high to omit the contribution of m/z=28 from CO_2. Especially during the CO_2 capture-DRM cycles, the CO signal was very weak, and in combination with the DRIFTS data in Figure 4a and 4c, it was demonstrated that no additional CO was formed during the CH_4 reduction steps.

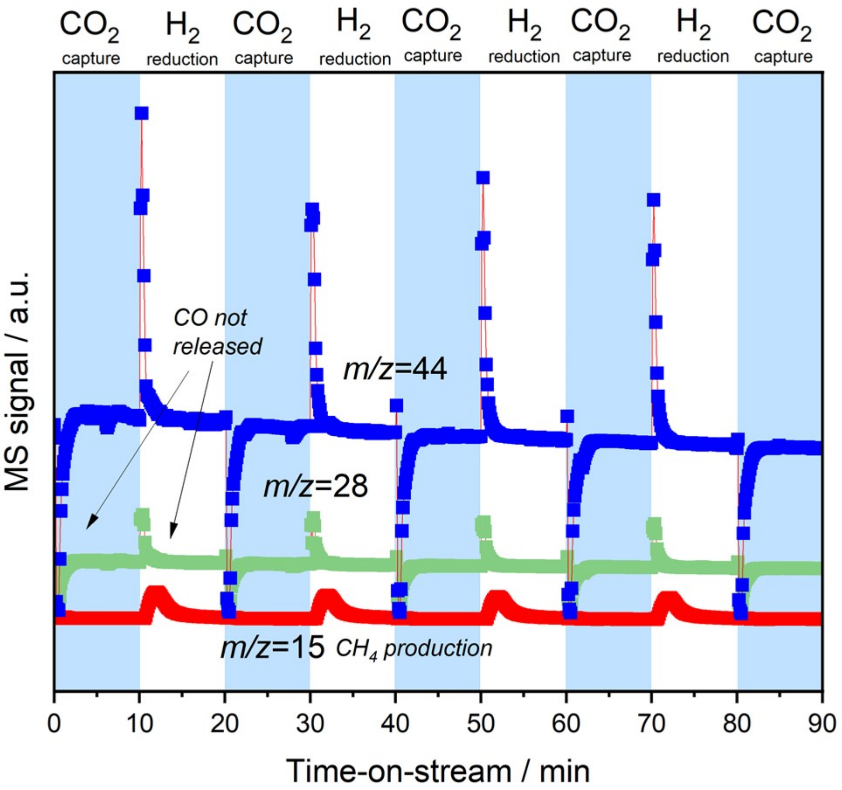

Figure S2: Evolution of selected *m/z* signals during capture/reduction cycles (10% CO_2 in Ar and 10% H_2 in Ar, both at 50 mL min^{-1}) at 250 ºC

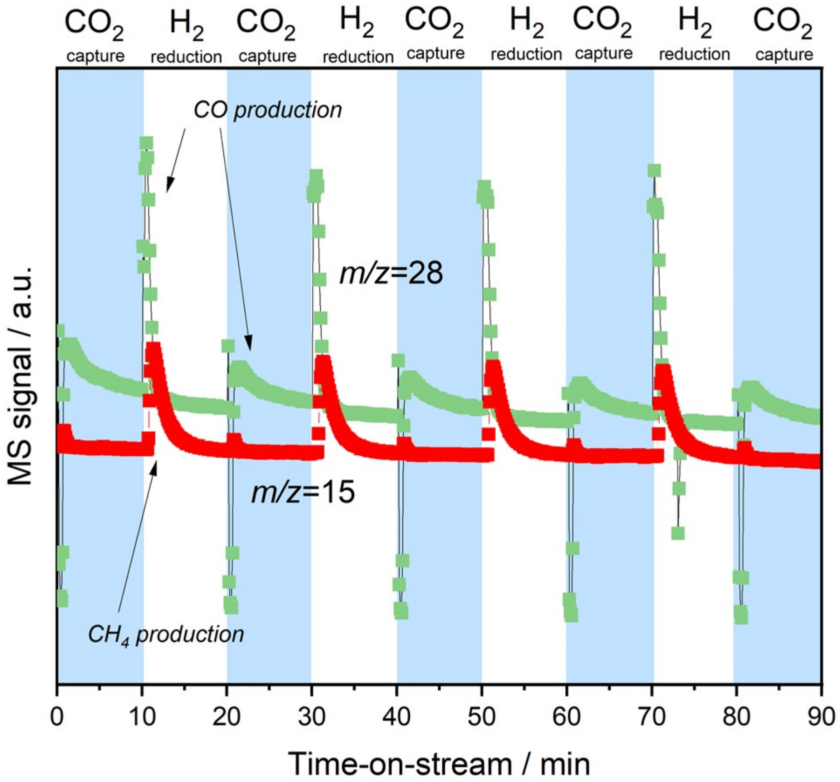

Figure S3: Evolution of selected *m/z* signals during capture/reduction cycles (10% CO_2 in Ar and 10% H_2 in Ar, both at 50 mL min^{-1}) at 500ºC

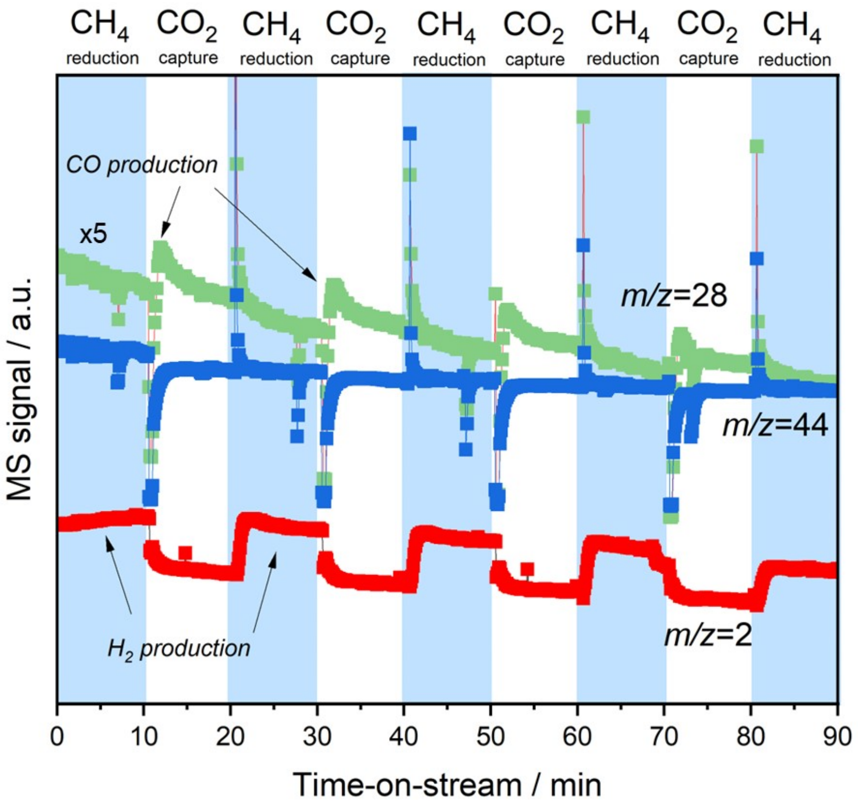

Figure S4: Evolution of selected *m/z* signals reduction/capture cycles (10% CH_4 in Ar and 10% CO_2 in Ar, both at 50 mL min^{-1}) at 500ºC

References

1 L.-P. Merkouri, R. Reina and M. S. Duyar, *Nanoscale*, 2022, **14**, 12620–12637.

2 A. I. Tsiotsias, N. D. Charisiou, A. Alkhoori, S. Gaber, V. Sebastian, S. J. Hinder, M. A. Baker, K. Polychronopoulou and M. A. Goula, *J. CO2 Util.*, 2022, **61**, 102046.

3 J. W. Allen, *J. Magn. Magn. Mater.*, 1985, **47–48**, 168–174.