ChemSusChem

Supporting Information

Butane Dry Reforming Catalyzed by Cobalt Oxide Supported on Ti_2AlC MAX Phase

Maria Ronda-Lloret, Vijaykumar S. Marakatti, Willem G. Sloof, Juan José Delgado, Antonio Sepúlveda-Escribano, Enrique V. Ramos-Fernandez, Gadi Rothenberg, and N. Raveendran Shiju*This publication is part of a Special Issue entitled “Green Carbon Science: CO_2 Capture and Conversion”. Please visit the issue at .

SUPPORTING INFORMATION

This document contains supplementary data on the characterization of the catalysts (XRD patterns, STEM-HAADF images, nitrogen adsorption-desorption isotherms, temperature programmed reduction profiles, thermogravimetric analysis and XPS data). The results of the control catalytic tests, as well as the selectivity and carbon balance plots of Co_3O_4/Ti_2AlC, Co_3O_4/Al_2O_3 and Co_3O_4/TiO_2 are also included.

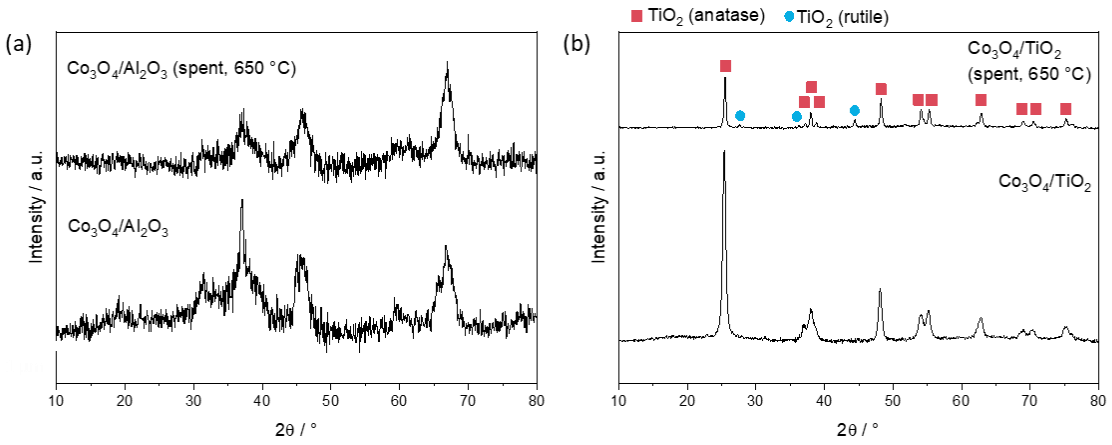

Figure S1. XRD patterns of (a) as-prepared Co_3O_4/Al_2O_3 and Co_3O_4/Al_2O_3 after stability test (spent, 650 °C), (b) as-prepared Co_3O_4/TiO_2 and Co_3O_4/TiO_2 after stability test (spent, 650 °C).

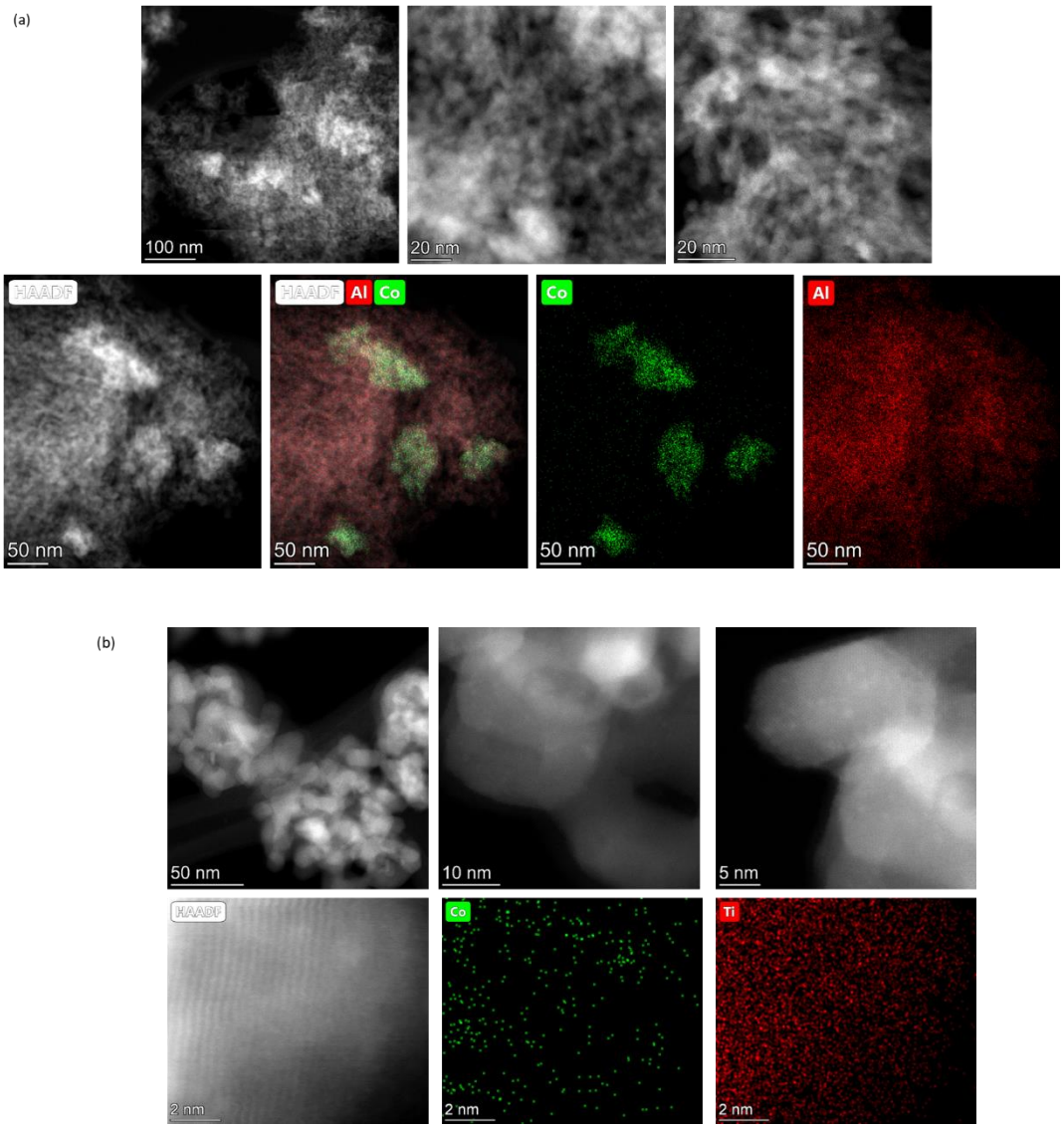

Figure S2. HAADF-STEM images of (a) Co_3O_4/Al_2O_3 and (b) Co_3O_4/TiO_2 catalysts, including Co, Al and Ti elemental distribution maps.

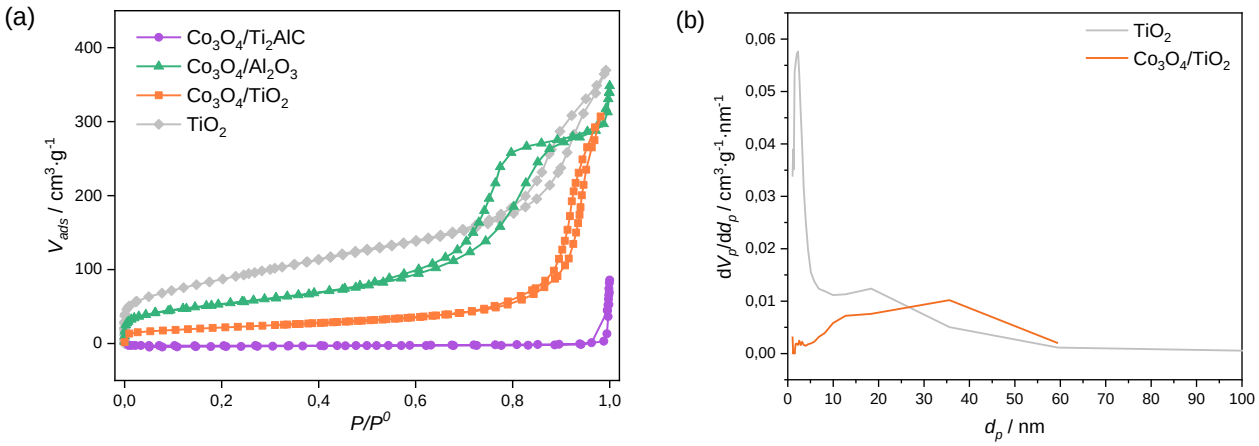

Figure S3. a) Nitrogen adsorption-desorption isotherms of the studied catalysts. b) BJH pore size distribution of TiO_2 and Co_3O_4/TiO_2 materials.

Table S1. BET surface area (S_{BET}), total pore volume (V_t), micropore volume (V_0), mesopore volume (V_{meso}) and average pore diameter values of the studied catalysts.

Catalyst	S_{BET} / $m^2 \cdot g^{-1}$	V_t / $cm^3 \cdot g^{-1}$	V_0 / $cm^3 \cdot g^{-1}$	V_{meso} / $cm^3 \cdot g^{-1}$	Average pore diameter (nm)
Co_3O_4/Ti_2AlC[a]	-	-	-	-	-
Co_3O_4/Al_2O_3	187	0.43	0.05	0.38	9
Co_3O_4/TiO_2	76	0.48	0.06	0.42	22
TiO_2	316	0.57	0.10	0.47	6

[a] Co_3O_4/Ti_2AlC values are not reported because this sample is not accessible for N_2.

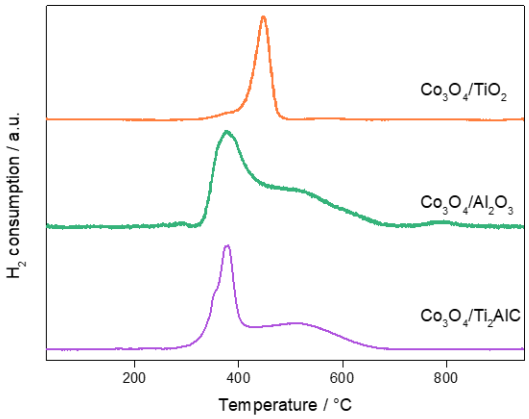

Figure S4. Temperature programmed reduction profiles of Co_3O_4/Ti_2AlC, Co_3O_4/Al_2O_3 and Co_3O_4/TiO_2 catalysts, under a flow of 5% H_2/N_2 mixture.

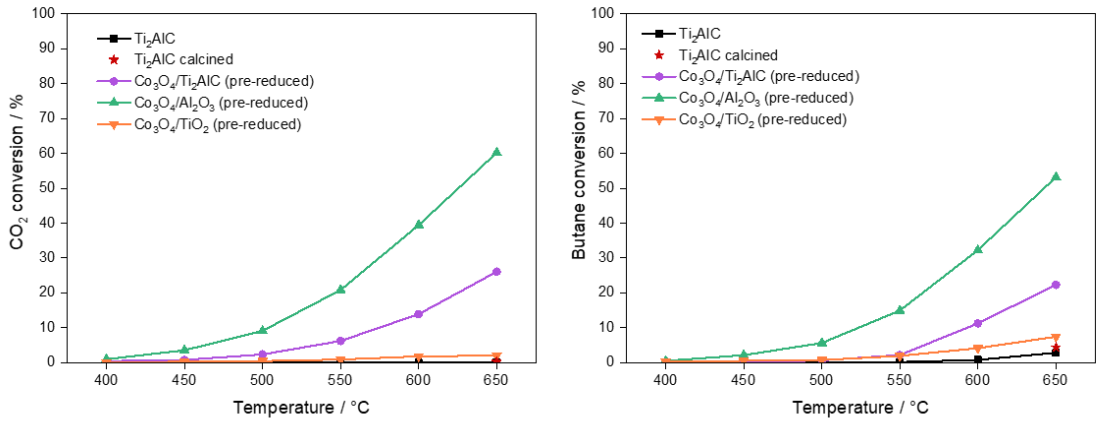

Figure S5. CO_2 and butane conversion during temperature screening of Ti_2AlC, Ti_2AlC calcined at 450 °C and the pre-reduced 5 wt% catalysts. Reduction conditions: 650 °C, 1h, 70% H_2 and 30% Ar mixture,10 mL·min^{-1}. Reaction conditions: 100 mg of catalyst, CO_2:C_4H_{10} = 4:1, total flow 20 mL·min^{-1}, atmospheric pressure.

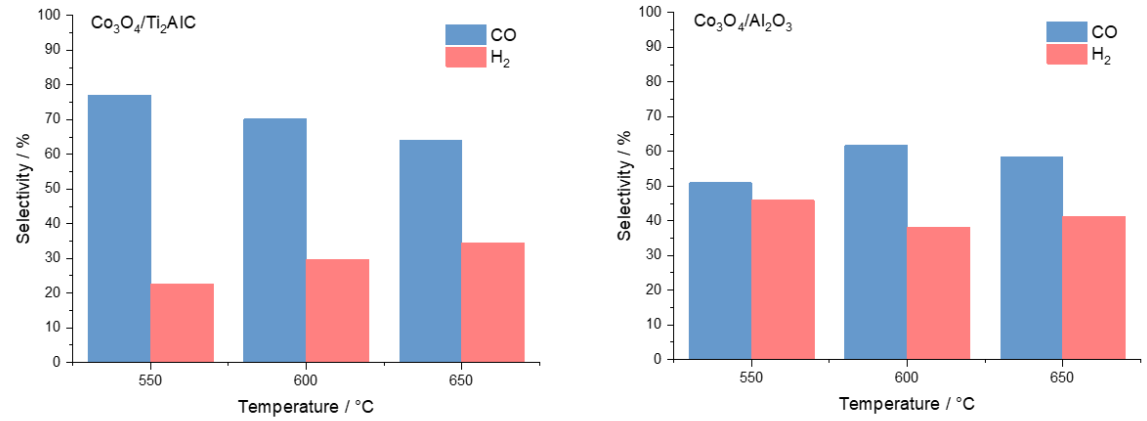

Figure S6. Selectivity during temperature screening of 5 wt.% Co_3O_4/Ti_2AlC and Co_3O_4/Al_2O_3 catalysts. Reaction conditions: 100 mg of catalyst, CO_2:C_4H_{10} = 4:1, total flow 20 mL·min^{-1}, atmospheric pressure.

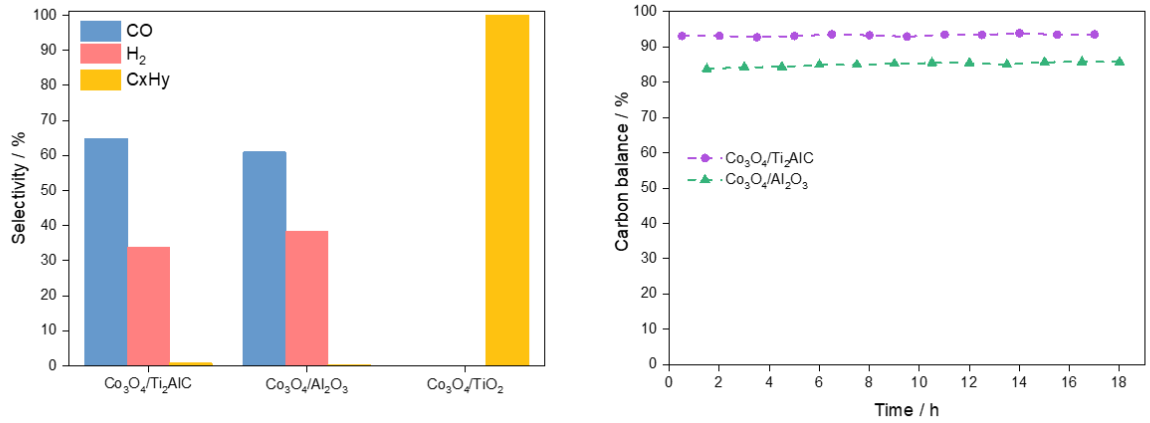

Figure S7. Selectivity (at 12 h) and carbon balance during stability test of 5 wt% catalysts. Reaction conditions: 100 mg of catalyst, CO_2:C_4H_{10} = 4:1, total flow 20 mL·min^{-1}, atmospheric pressure.

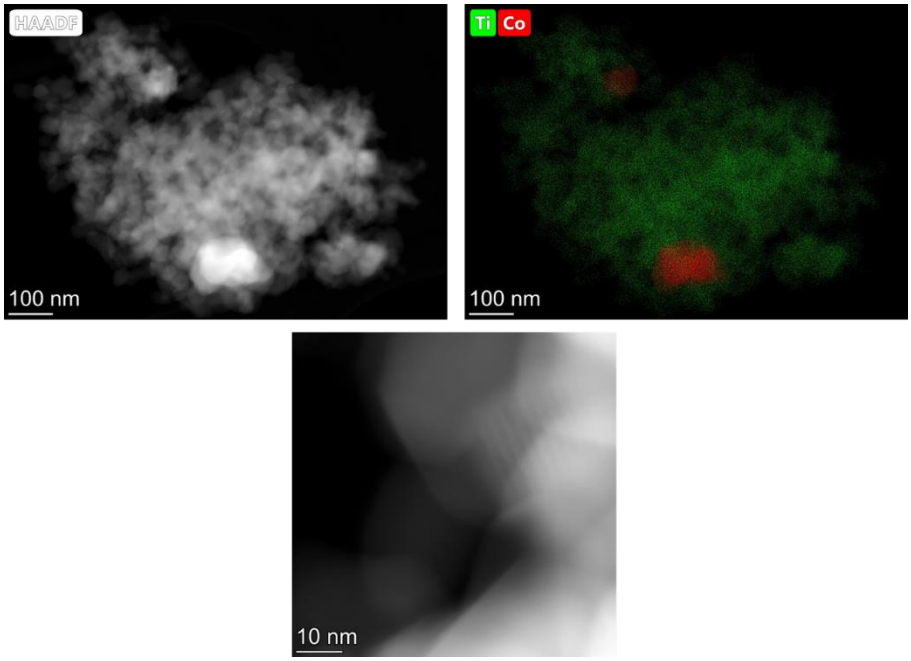

Figure S8. HAADF-STEM images of Co_3O_4/TiO_2 catalyst after stability test at 650 °C, which show the agglomeration of Co_3O_4 particles on the support. The HRTEM image shows the absence of small particles as in the fresh catalyst.

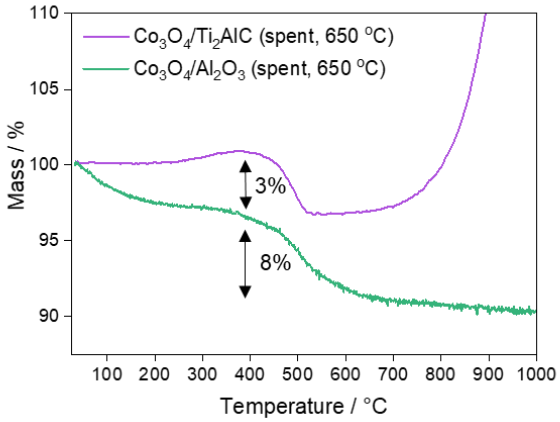

Figure S9. Thermogravimetric analysis of the samples after stability test at 650 °C for 18 hours. Coke combustion takes place at temperatures between 300 and 600 °C. Co_3O_4/Ti_2AlC catalyst experiences mass gain corresponding to the oxidation of Ti_2AlC to TiO_2 and Al_2O_3 during the measurement.

Table S2. NH_3 adsorption-desorption measurements of Co_3O_4/Ti_2AlC and Co_3O_4/Al_2O_3 catalysts.

Catalyst	NH_3 desorption / µmol $NH_3 \cdot g\ catalyst^{-1}$
Co_3O_4/Ti_2AlC	11
Co_3O_4/Al_2O_3	128

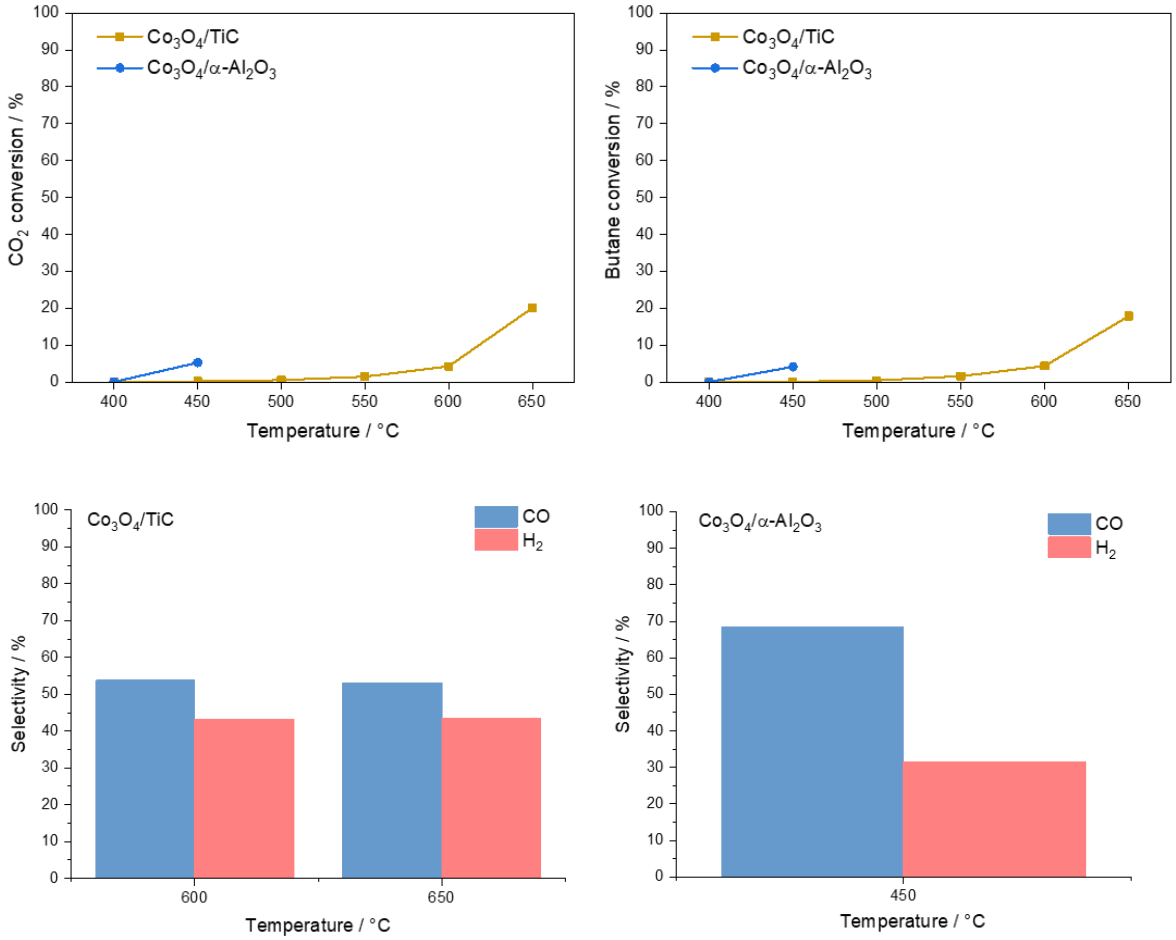

Figure S10. CO_2 and butane conversion and selectivity during temperature screening of Co_3O_4/TiC and Co_3O_4/α-Al_2O_3. Reaction conditions: 100 mg of catalyst, CO_2:C_4H_{10} = 4:1, total flow 20 mL·min^{-1}, atmospheric pressure.

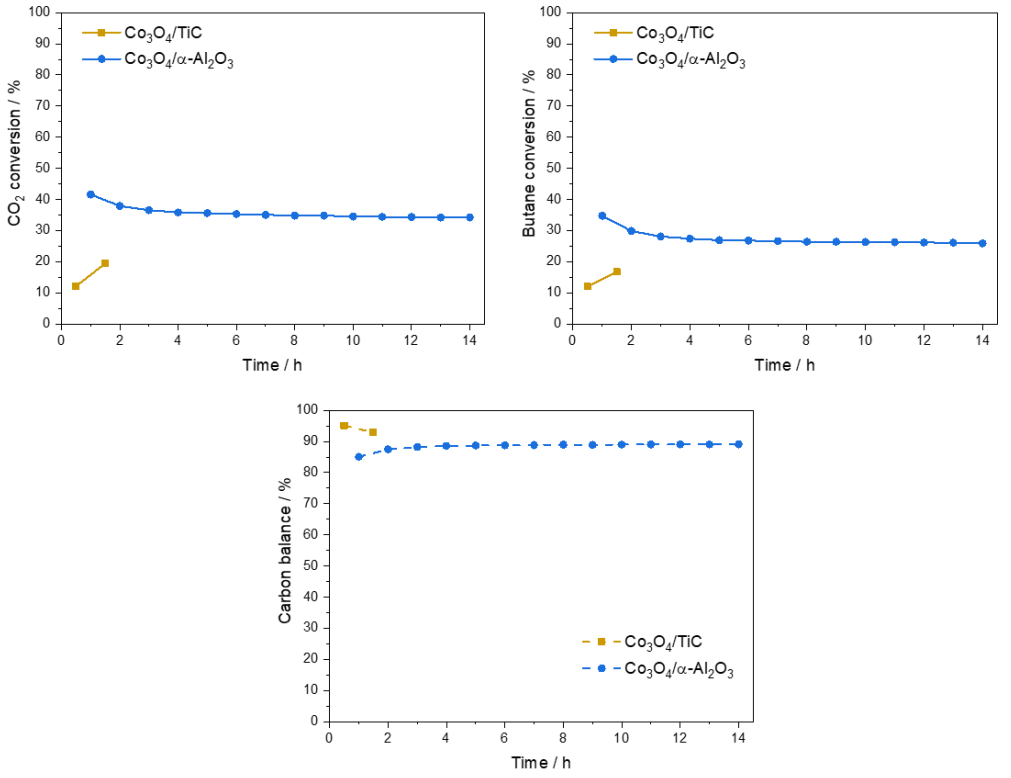

Figure S11. Conversion and carbon balance values during stability test of Co_3O_4/TiC and Co_3O_4/α-Al_2O_3. Reaction conditions: 650 °C, 100 mg of catalyst, CO_2:C_4H_{10} = 4:1, total flow 20 mL·min^{-1}, atmospheric pressure.

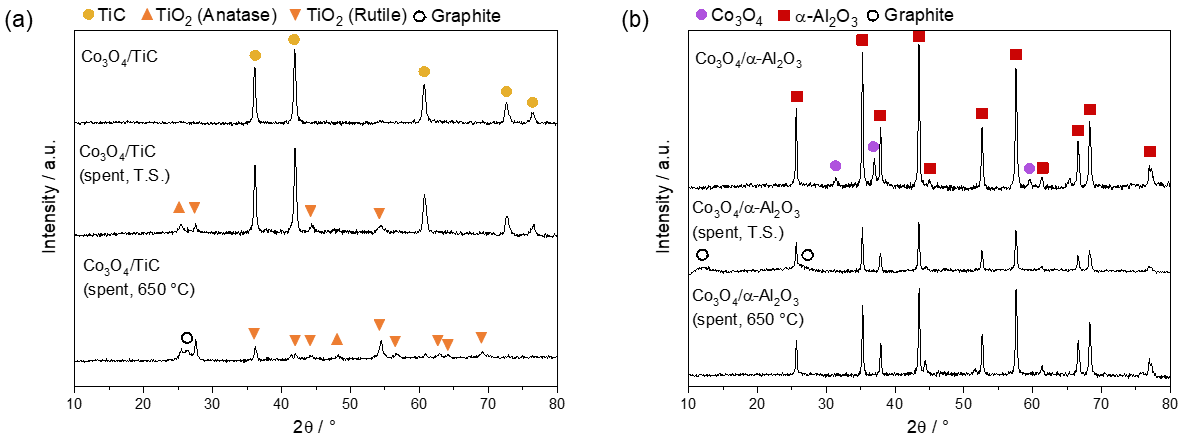

Figure S12. XRD patterns of Co_3O_4/TiC and Co_3O_4/α-Al_2O_3 as-prepared, after temperature screening tests (spent, T.S.) and after stabiliy tests (spent, 650 °C).

Table S3. Atomic percentage of Co, Ti, Al, C and O on the surface of the catalysts and the intensity ratios between cobalt and support particles, obtained from XPS analysis.

Catalyst	Atom fraction (%) on the surface					I_{Co}/I_{Al} ratio	I_{Co}/I_{Ti} ratio
	Co	Ti	Al	C	O		
Co_3O_4/Ti_2AlC	12.86	6.39	9.08	15.09	56.58	1.42	2.01
Co_3O_4/Ti_2AlC (spent, 650 °C)	3.62	3.64	6.93	59.91	25.9	0.52	0.99
Co_3O_4/TiO_2	2.33	16.37	-	27.45	54.26	-	0.14
Co_3O_4/Al_2O_3	0.55	-	25.24	23.77	50.44	0.02	-

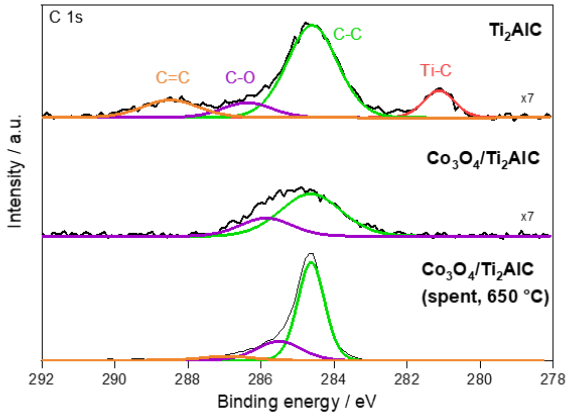

Figure S13. C 1s photoelectron spectra of Ti_2AlC, fresh Co_3O_4/Ti_2AlC and Co_3O_4/Ti_2AlC after stability test (spent, 650 °C).

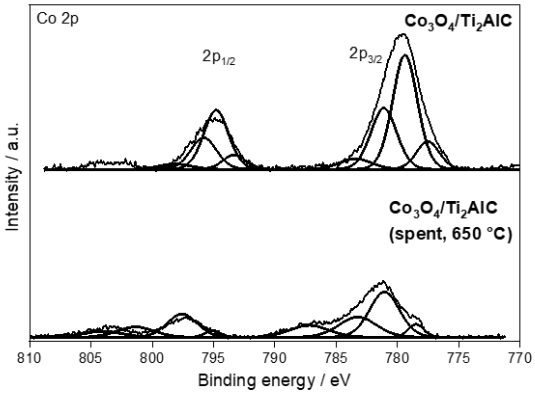

Figure S14. Co 2p photoelectron spectra of fresh Co_3O_4/Ti_2AlC and Co_3O_4/Ti_2AlC after stability test (spent, 650 °C).

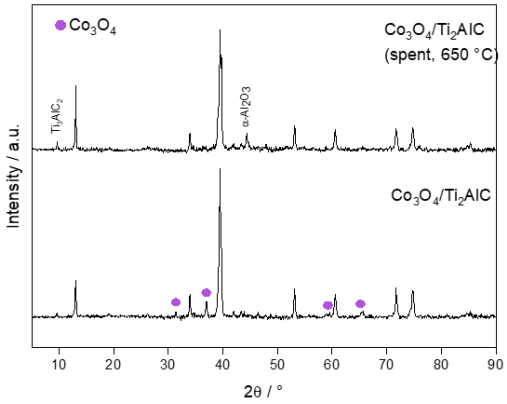

Figure S15. Comparison of the XRD patterns of as-prepared Co_3O_4/Ti_2AlC and Co_3O_4/Ti_2AlC catalyst after stability test (spent, 650 °C).

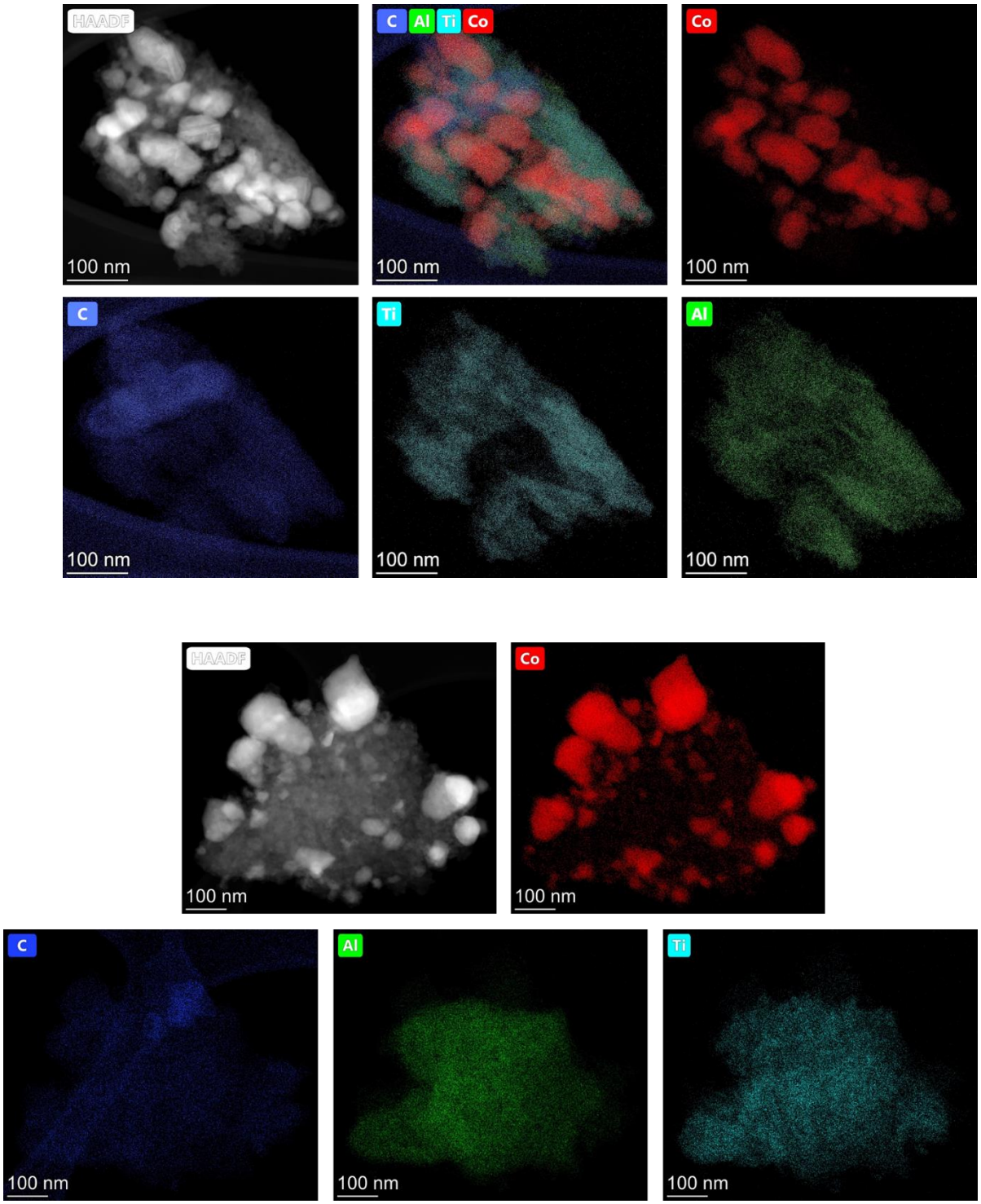

Figure S16. HAADF-STEM images of Co_3O_4/Ti_2AlC catalyst after stability test at 650 °C.

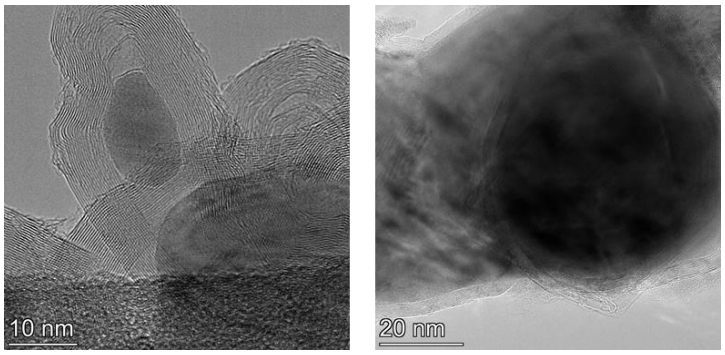

Figure S17. TEM images of Co_3O_4/Ti_2AlC catalyst after stability test at 650 °C, showing the formation of carbon nanotubes covering some Co_3O_4 particles.