Development of In-Cu binary oxides catalysts for hydrogenating CO_2 via thermocatalytic and electrocatalytic routes

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Supplementary Materials

1. Test bench scheme

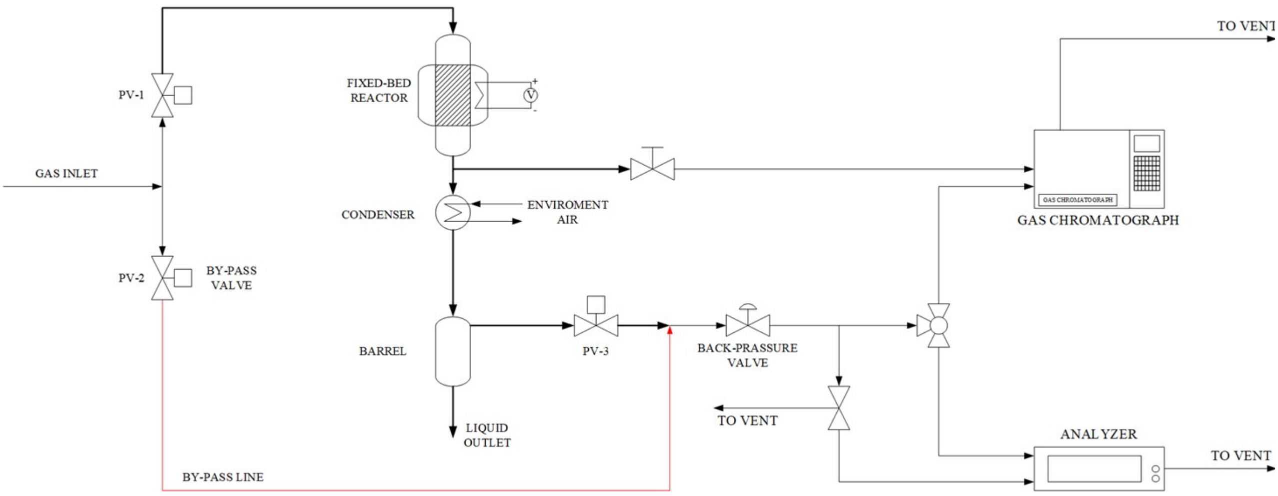


Figure S1. Simplified scheme of the thermochemical test bench.

2. N_2 physisorption measurements of the fresh samples

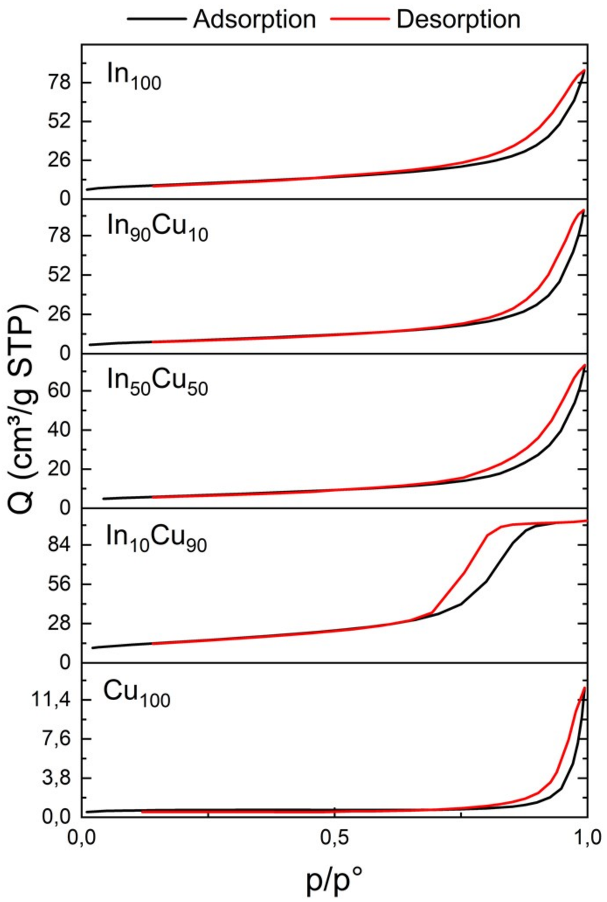


Figure S2. N_2 adsorption-desorption isotherms of each fresh catalysts.

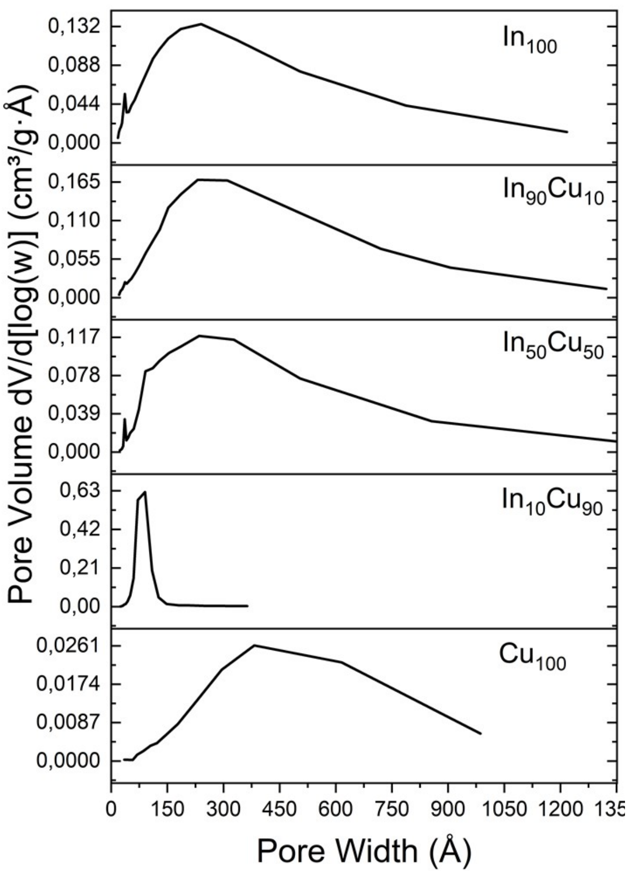


Figure S3. N_2 adsorption-desorption pores distribution of each fresh catalysts.

3. Raman spectroscopy of the fresh samples

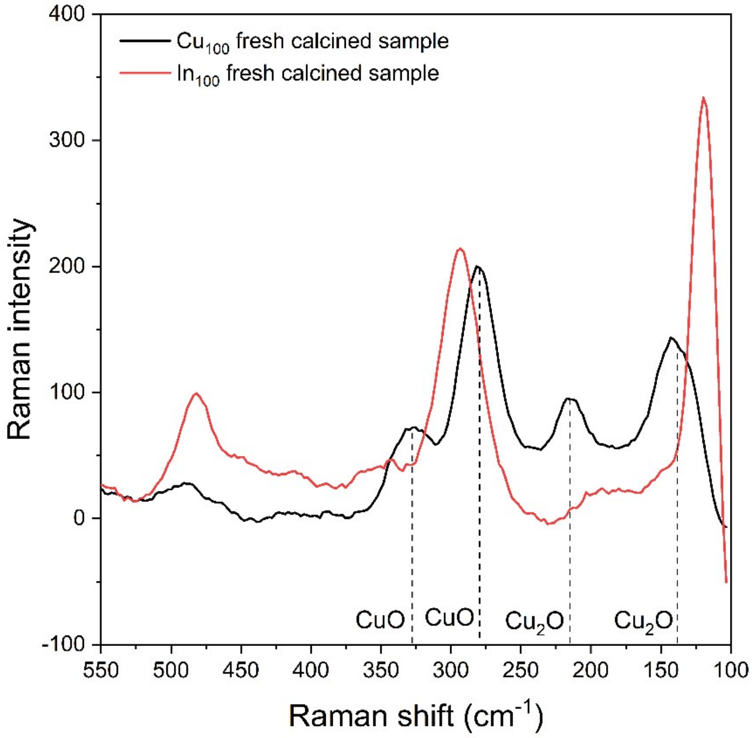


Figure S4. Raman spectra of non-binary fresh catalysts.

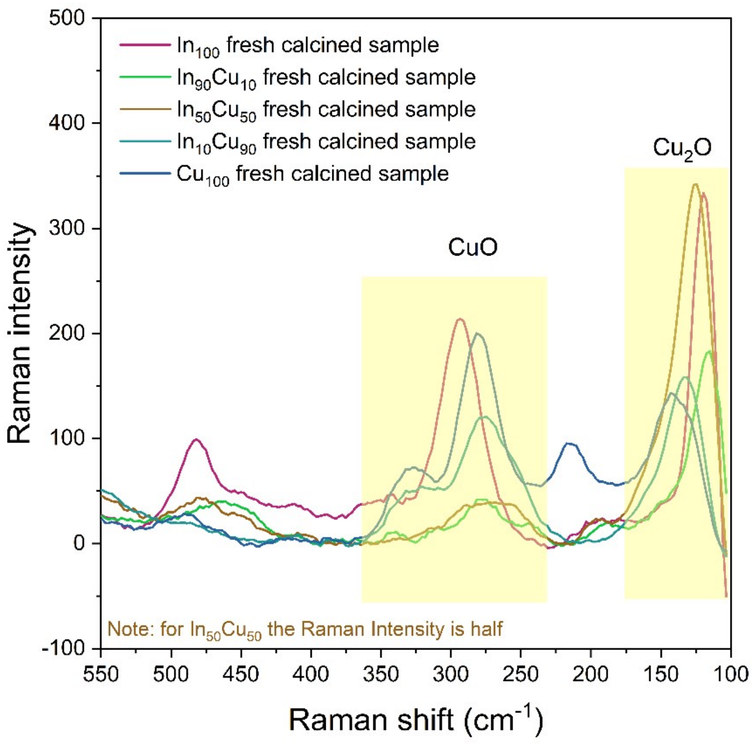
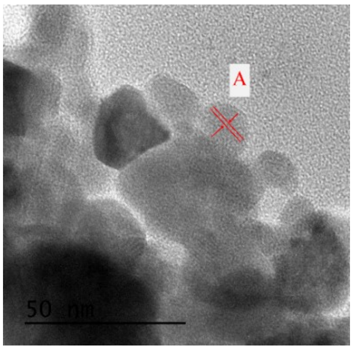
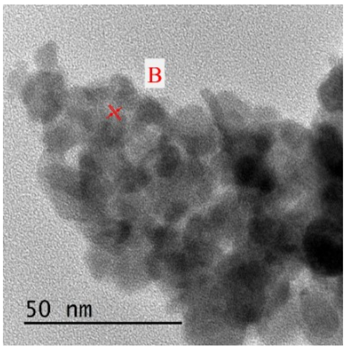


Figure S5. Raman spectra of all fresh samples. Yellow regions refer to the main peaks of CuO and Cu_2O.

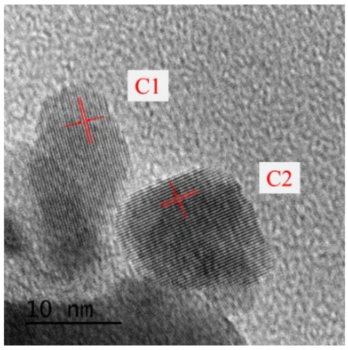
4. *Transmission electron microscopy results*



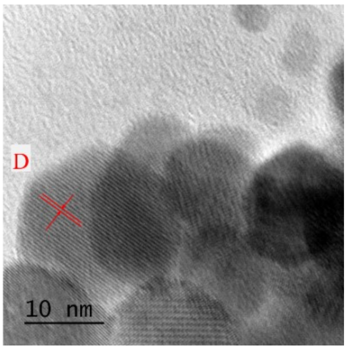
(a) In_{100} fresh



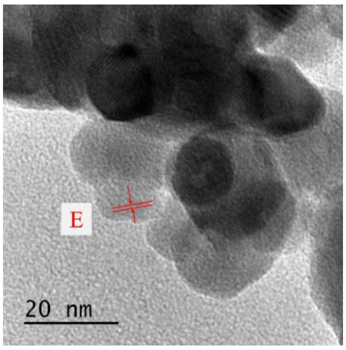
(b) In_{100} fresh



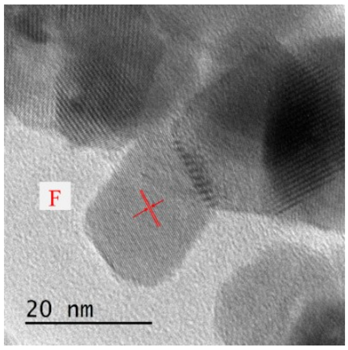
(c) In_{100} fresh



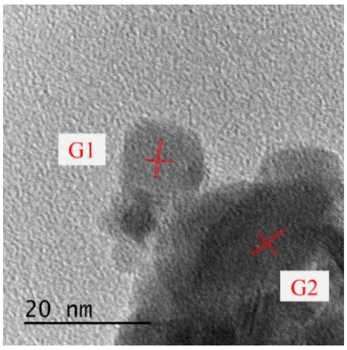
(d) In_{100} spent



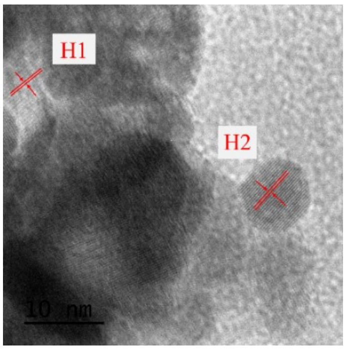
(e) In_{100} spent



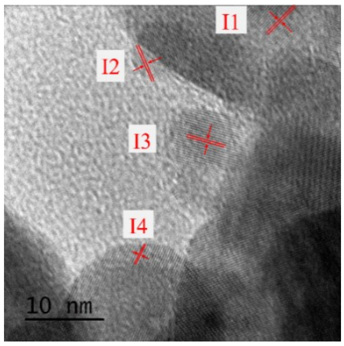
(f) In_{100} spent



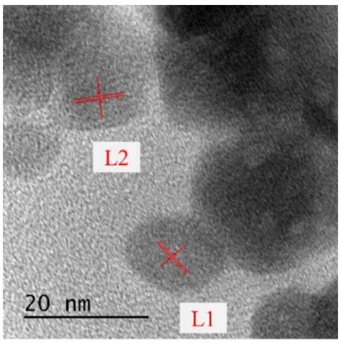
(g) $In_{90}Cu_{10}$ fresh



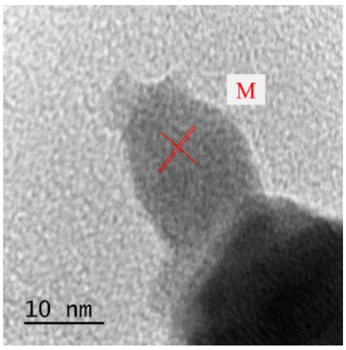
(h) $In_{90}Cu_{10}$ fresh



(i) $In_{90}Cu_{10}$ fresh



(l) $In_{90}Cu_{10}$ spent



(m) $In_{90}Cu_{10}$ spent

Figure S6. TEM images of the fresh calcined and TC spent samples. The crystal planes (in red) and the associated data are reported in Table S1.

Table S1. Crystalline planes obtained from the TEM analysis shown in Figure S6.

Sample		Plane name	d observed [Å]	d reference [Å]	Miller indexes h	k	l	Reference substance
In_{100}	Fresh	A	4.165	4.140	2	1	1	In_2O_3
In_{100}	Fresh	B	2.777	2.704	3	2	1	In_2O_3
In_{100}	Fresh	C1	2.821	2.821	2	2	0	$In(OH)_3$
In_{100}	Fresh	C2	2.941	2.920	2	2	2	In_2O_3
In_{100}	TC spent	D	4.210	4.140	2	1	1	In_2O_3
In_{100}	TC spent	E	2.685	2.704	3	2	1	In_2O_3
In_{100}	TC spent	F	2.956	2.920	2	2	2	In_2O_3
$In_{90}Cu_{10}$	Fresh	G1	2.863	2.821	2	2	0	$In(OH)_3$
				2.865	3	-2	1	Cu_7In_3 – alloy
$In_{90}Cu_{10}$	Fresh	G2	4.103	4.140	2	1	1	In_2O_3
$In_{90}Cu_{10}$	Fresh	H1	3.961	3.990	2	0	0	$In(OH)_3$
$In_{90}Cu_{10}$	Fresh	H2	2.849	2.821	2	2	0	$In(OH)_3$
				2.865	3	-2	1	Cu_7In_3 – alloy
$In_{90}Cu_{10}$	Fresh	I1	2.710	2.704	3	2	1	In_2O_3
$In_{90}Cu_{10}$	Fresh	I2	2.697	2.704	3	2	1	In_2O_3
$In_{90}Cu_{10}$	Fresh	I3	2.836	2.821	2	2	0	$In(OH)_3$
$In_{90}Cu_{10}$	Fresh	I4	2.794	2.754	1	1	0	CuO
$In_{90}Cu_{10}$	TC spent	L1	2.893	2.898	2	-1	2	Cu_7In_3 – alloy
$In_{90}Cu_{10}$	TC spent	L2	2.914	2.910	2	0	2	Cu_7In_3 – alloy
$In_{90}Cu_{10}$	TC spent	M	2.766	2.774	1	-3	1	Cu_7In_3 – alloy

5. Raman spectroscopy of the TC spent samples

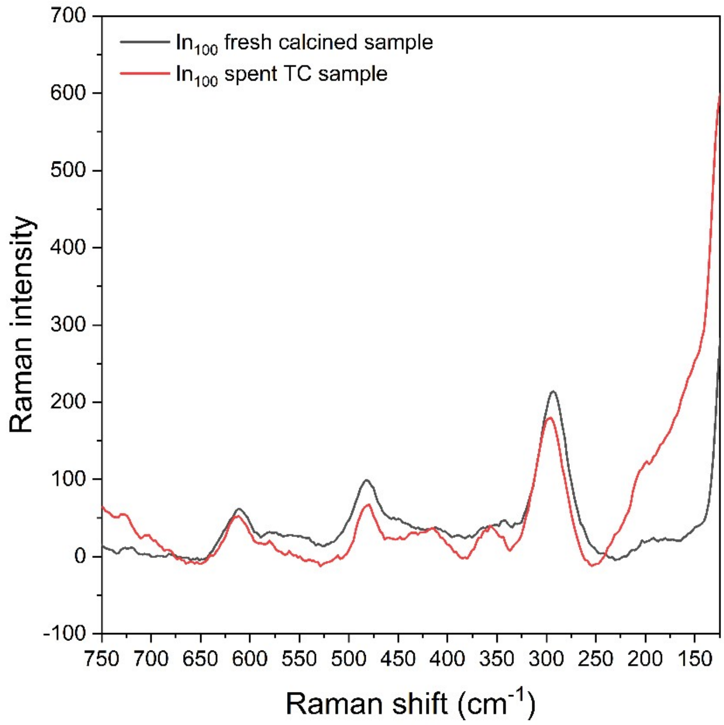


Figure S7. Raman spectra of In_{100} sample (fresh and spent).

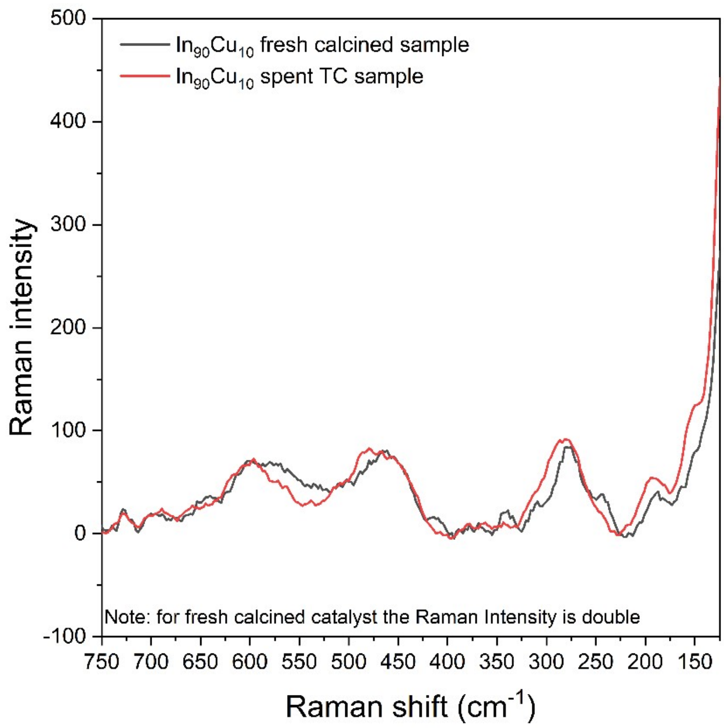


Figure S8. Raman spectra of $In_{90}Cu_{10}$ sample (fresh and spent).

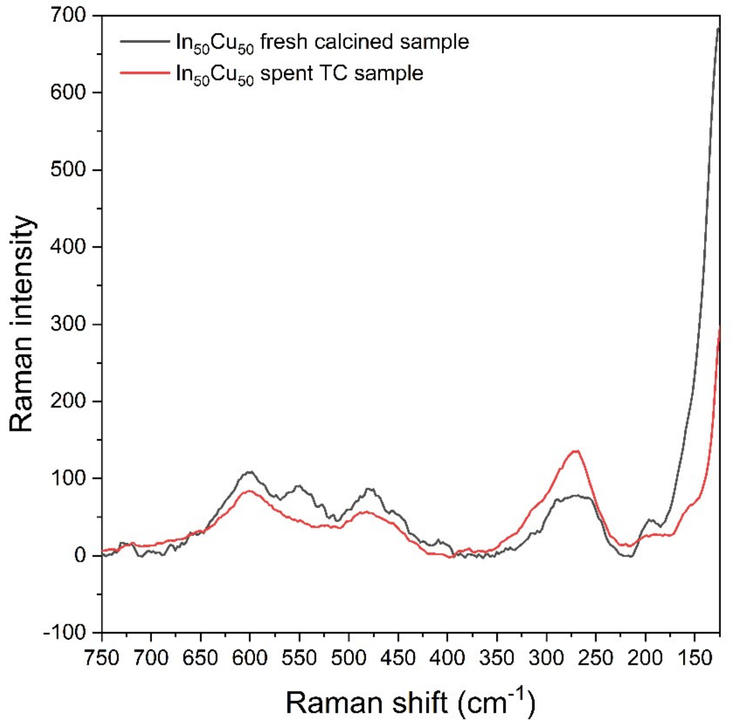


Figure S9. Raman spectra of $In_{50}Cu_{50}$ sample (fresh and spent).

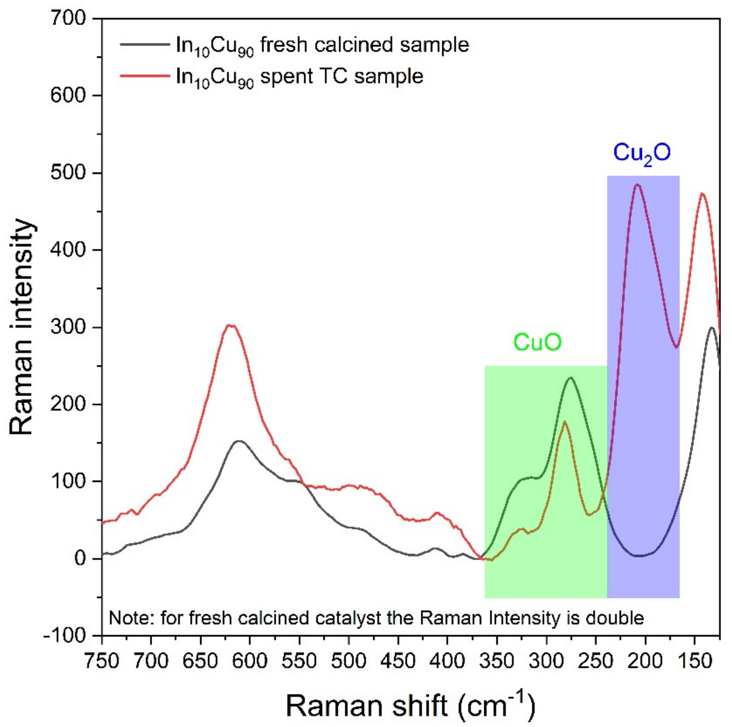


Figure S10. Raman spectra of $In_{10}Cu_{90}$ sample (fresh and spent). Cu_2O formation is appreciable in the spent TC catalyst.

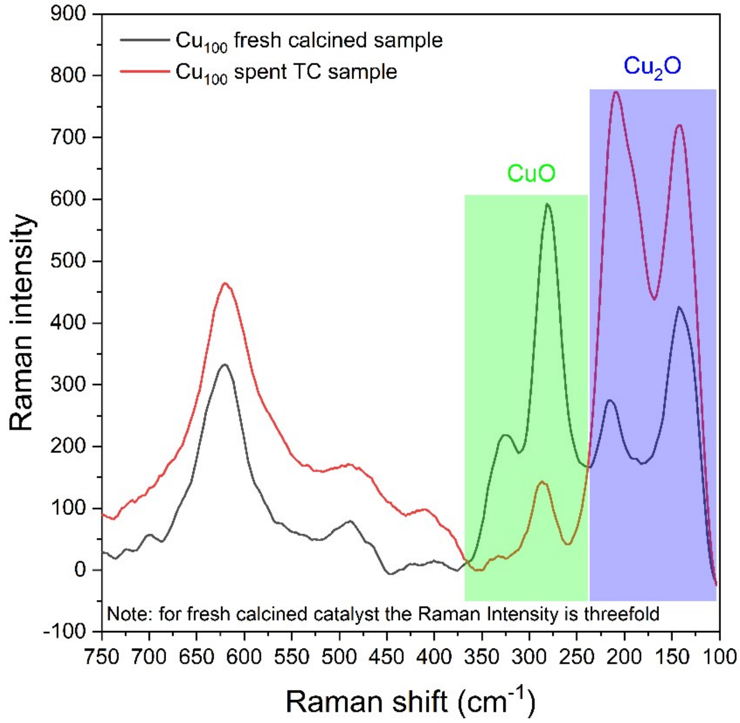


Figure S11. Raman spectra of Cu_{100} sample (fresh and spent). Cu_2O formation is appreciable in the spent TC catalyst. Otherwise, CuO reduction is found.

6. XPS measurements

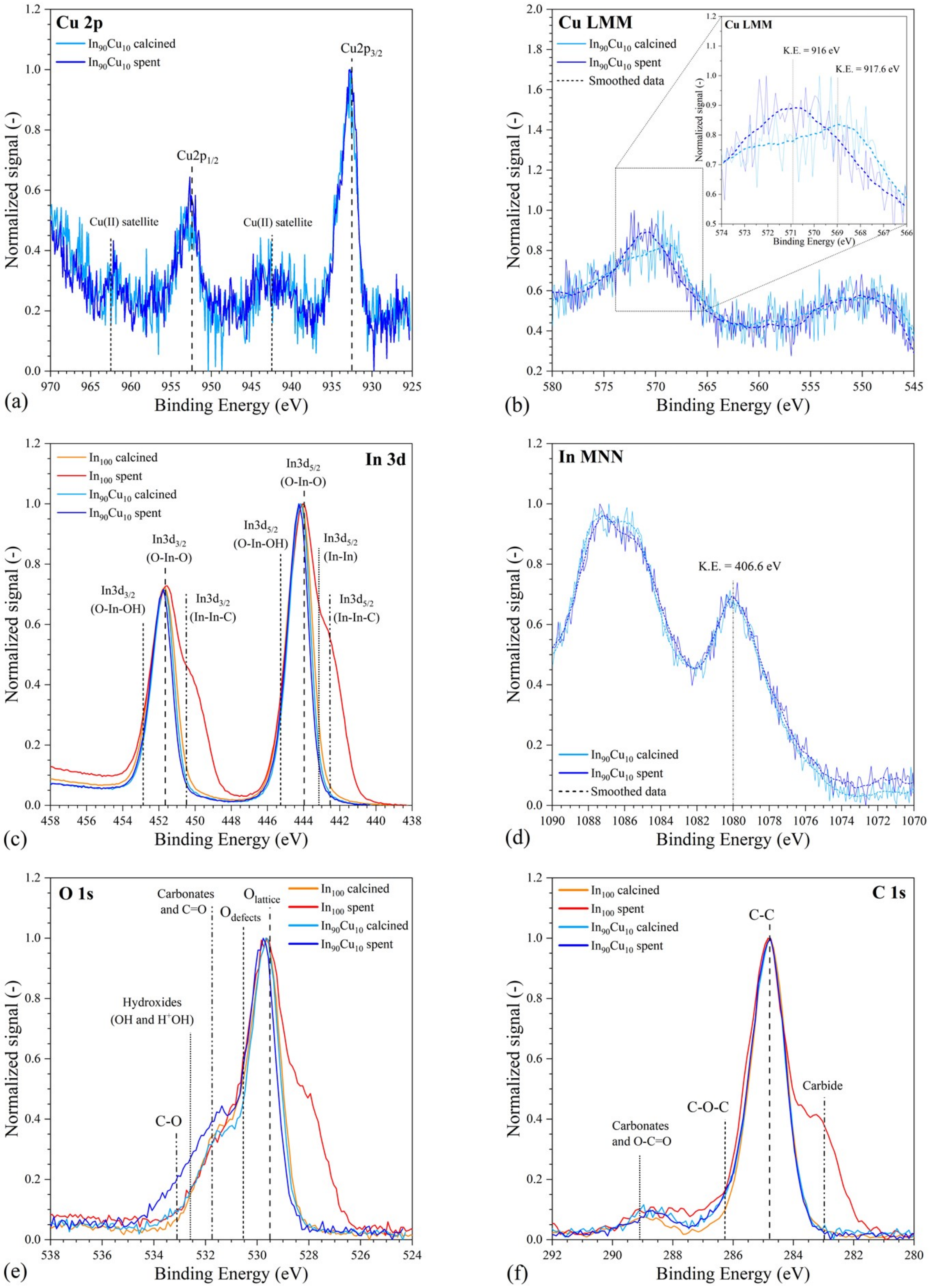


Figure S12. XPS spectra of both fresh calcined and TC spent In_{100} and $In_{90}Cu_{10}$ samples: (a) Cu2p, (b) Cu LMM, (c) In3d, (d) In MNN, (e) O1s and (f) C1s.

Table S2. Results of the XPS measurements on the fresh calcined and TC spent samples.

Catalyst	Superficial atomic composition[(a)]			Cu oxidation state[(b)]		Modified Auger parameters[(c)]		O defects[(d)]
	Cu (at %)	In (at %)	O (at %)	Cu^{2+}/Cu (at %)	(Cu^0+Cu^{1+})/Cu (at %)	Cu (eV)	In (eV)	$O_{defects}$/O (at %)
In_{100} fresh	-	39.1	60.9	-	-	-	849.6	24.5
In_{100} TC spent	-	43.5	56.5	-	-	-	850.7	17.1
$In_{90}Cu_{10}$ fresh	1.6	49.2	49.3	73.3	26.7	1850.1	850.8	26.8
$In_{90}Cu_{10}$ TC spent	2.3	46.1	51.6	65.2	34.8	1848.5	850.9	30.1

[(a)] Evaluated using $Cu2p_{3/2}$, $In3d_{5/2}$ and O1s HR XPS spectra.

[(b)] Evaluated using the deconvolution of the $Cu2p_{3/2}$ HR XPS spectra.

[(c)] Evaluated using Cu LMM and In MNN HR XPS spectra.

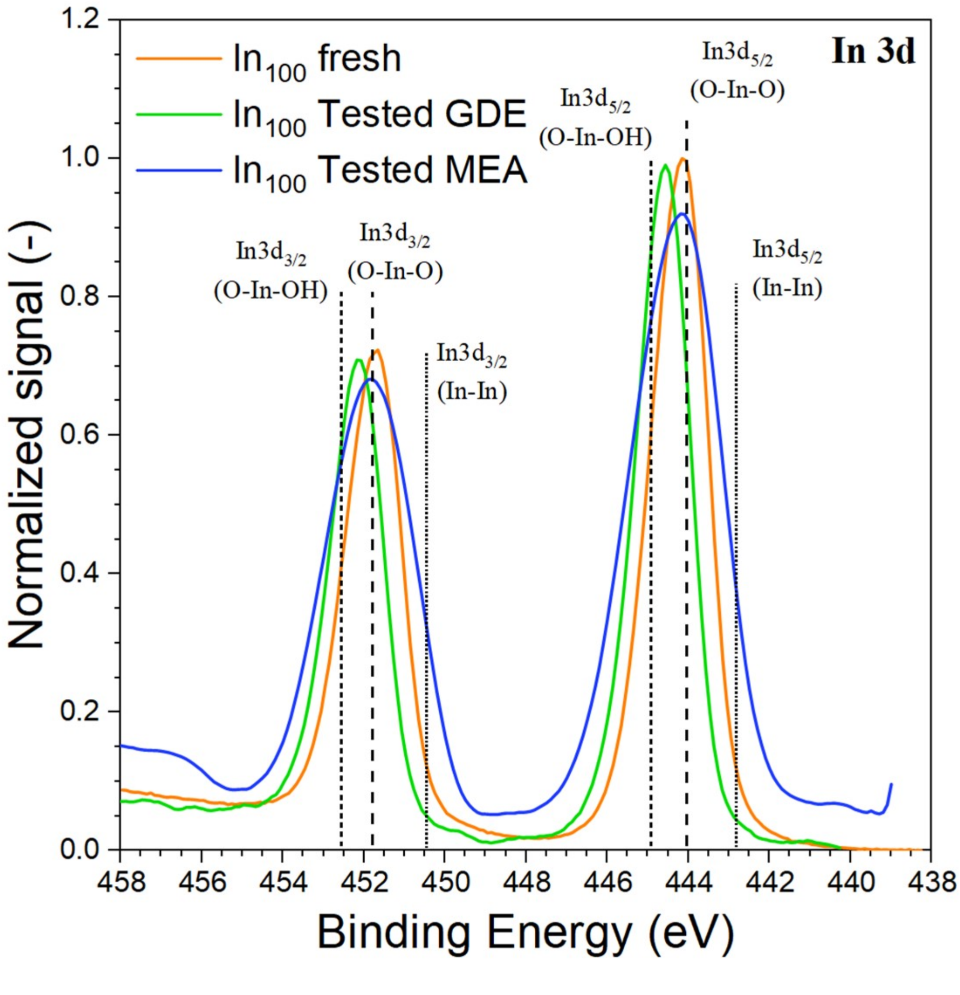


Figure S13. XPS spectra around the In 3d region of the fresh, tested in GDE and tested in MEA In_{100} samples.

7. Deactivation study

The results of equation (11) are reported in this section.

$$\ln \ln \frac{1}{1-\zeta_A} = \ln\left[\tau^{'} k^{'}\right] - k_d t \quad (11)$$

Equation (11) is valid for reactions with first-order kinetics; deactivation is independent from reagents or products concentration and the order of deactivation is unity. Table S3 reports the fittings results.

Table S3. Deactivation kinetic parameters were obtained from fitting experimental data with equation (11).

Sample	k'	Deactivation constant k_d	Correlation coefficient R^2
	$Nm^3 \cdot kg^{-1} \cdot h^{-1}$	h^{-1}	-
In_{100}	0.380	0.010	0.836
$In_{90}Cu_{10}$	0.511	0.014	0.768
$In_{50}Cu_{50}$	0.133	0.086	0.990
$In_{10}Cu_{90}$ [(a)]	-	-	-
Cu_{100}	0.118	0.022	0.884

[(a)] Catalyst with zero conversion, so the data obtained from the interpolation is meaningless and subject to physical errors.

8. *Kinetic study*

Equation used for data fitting reported in Table S4:

$$\ln\left(R_i\right) = \ln\left(k^{*}_{\infty,i}\right) - \frac{E_{a,i}}{R} \cdot \frac{1}{T} \tag{1}$$

Table S4. Kinetic data obtained from data fitting with equation (14).

Sample	CO_2 hydrogenation			CO synthesis			CH_3OH synthesis		
	E_a (kJ/mol)	(+) ln(k^*_∞)	R^2	E_a (kJ/mol)	(+) ln(k^*_∞)	R^2	E_a (kJ/mol)	(+) ln(k^*_∞)	R^2
In_{100}	78.3	25.2	1.00	103.1	29.7	1.00	65.3	21.7	1.00
$In_{90}Cu_{10}$	93.7	29.0	1.00	105.6	30.5	1.00	89.8	27.7	1.00
$In_{50}Cu_{50}$	91.3	25.8	1.00	100.7	26.8	0.99	85.9	24.1	1.00
Cu_{100}	70.9	22.2	1.00	91.3	26.3	1.00	28.5	11.4	0.98

(+) [k^*_∞] = $mmol \cdot kg^{-1} \cdot h^{-1}$