energies

MDPI

Article

Supplementary Material for Manuscript

A Use-Store-Reuse [USR] Concept in Catalytic HCOOH Dehydrogenation: Case-Study of a Ru-based Catalytic System for Long-Term USR under Ambient O_2

Marinos Theodorakopoulos [1], Maria Solakidou [2], Yiannis Deligiannakis [2,3] and Maria Louloudi [1,3,*]

[1] Laboratory of Biomimetic Catalysis and Hybrid Materials, Department of Chemistry, University of Ioannina, GR45110 Ioannina, Greece
[2] Laboratory of Physical Chemistry of Materials and Environment, Department of Physics, University of Ioannina, GR45110 Ioannina, Greece
[3] Institute of Environment & Sustainable Development, University Research Center of Ioannina, GR45110 Ioannina, Greece

1. GC-TCD Analysis

A representative chromatograph for the catalytic system [Ru:PP3], shows that the only products were H_2 and CO_2 in 1:1 ratio, during whole catalytic procedure.

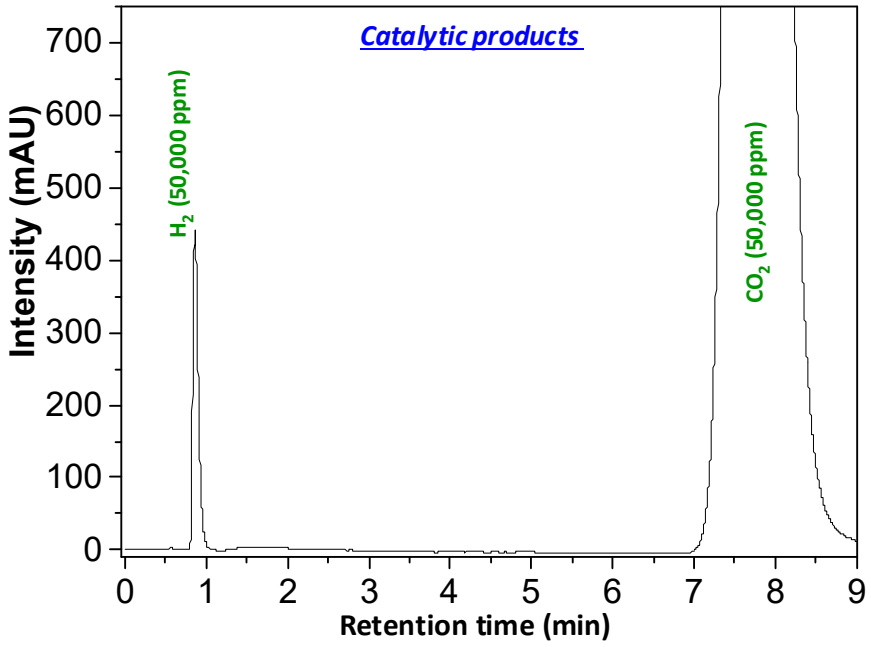

Figure S1. Representative GC-TCD chromatogram for the catalytic gas products, detected by a Shimadzu GC-2014 GC-TCD with a Carboxen-1000 column.

2. Catalytic Data

Table S1. Turn Over Numbers (TONs) and Turn Over Frequencies (TOFs) for each ratio of Ru:PP3. For 1:0 ratio there is no hydrogen production. Each day was added 5 ml of FA, except the 1:1 ratio, which it was not necessary, due to slow rate production of gasses.

Operating days	Ru:PP3 (9 μmol of catalyst)									
	1:1		1:2		1:3		1:4		1:5	
	TONs	TOFs (h^{-1})	TONs	TOFs (h^{-1})	TONs	TOFs (h^{-1})	TONs	TOFs (h^{-1})	TONs	TOFs (h^{-1})
1st day	5710	2855 ***(2)***	11468	6267 ***(1.83)***	11468	6266 ***(1.83)***	11693	7043 ***(1.66)***	11918	7179 ***(1.66)***
2nd day	5028	2514 ***(2)***	11513	6291 ***(1.83)***	11516	6291 ***(1.83)***	11579	6977 ***(1.66)***	11693	7041 ***(1.66)***
3rd day	6096	3048 ***(2)***	11648	6365 ***(1.83)***	11652	6366 ***(1.83)***	11693	7046 ***(1.66)***	10859	7191 ***(1.66)***
4th day	6300	3150 ***(2)***	11806	6451 ***(1.83)***	11811	6452 ***(1.83)***	11738	7073 ***(1.66)***	11965	7205 ***(1.66)***
5th day	5914	2080 ***(2.83)***	11491	4931 ***(2.3)***	11493	4982 ***(2.3)***	11579	5346 ***(2.16)***	11693	5393 ***(2.16)***
6th day	5732	2016 ***(2.83)***	11468	4922 ***(2.3)***	11470	4972 ***(2.3)***	11465	5293 ***(2.16)***	11579	5341 ***(2.16)***
7th day	5684	1992 ***(2.83)***	11693	5018 ***(2.3)***	11698	5072 ***(2.3)***	11534	5401 ***(2.16)***	11579	5341 ***(2.16)***
30th day	5187	1136 ***(4.5)***	10119	2529 ***(4)***	10335	2548 ***(4)***	10557	2717 ***(3.83)***	10443	2682 ***(3.83)***

Table S2. Maximum rate of gas production for each Ru:PP3 ratio every day.

Operating days	Ru:PP3 (9 μmol of catalyst)									
	1:1		1:2		1:3		1:4		1:5	
	ml/min	ml/min* μmol catalyst	ml/min	ml/min* μmol catalyst	ml/min	ml/min*μmol catalyst	ml/min	ml/min* μmol catalyst	ml/min	ml/min *μmol catalyst
1st day	19	2.1	73	8.1	76	8.4	86	9.5	88	9.7
2nd day	23.5	2.6	62	6.8	81	9	73	8.1	75	8.3
3rd day	29	3.2	80	8.8	77	8.5	80	8.8	80	8.8
4th day	27.5	3.05	68	7.5	64	7.1	68	7.5	65	7.2
5th day	17.2	1.9	42	4.6	40	4.4	50	5.5	55	6.1
6th day	15.8	1.7	48	5.3	50	5.5	45	5	43	4.7
7th day	17.1	1.9	55	6.1	55	6.1	51	5.6	56	6.2
30th day	13	1.4	31	3.4	21	2.3	26	2.8	27	3

3. Raman and ATR Spectroscopy

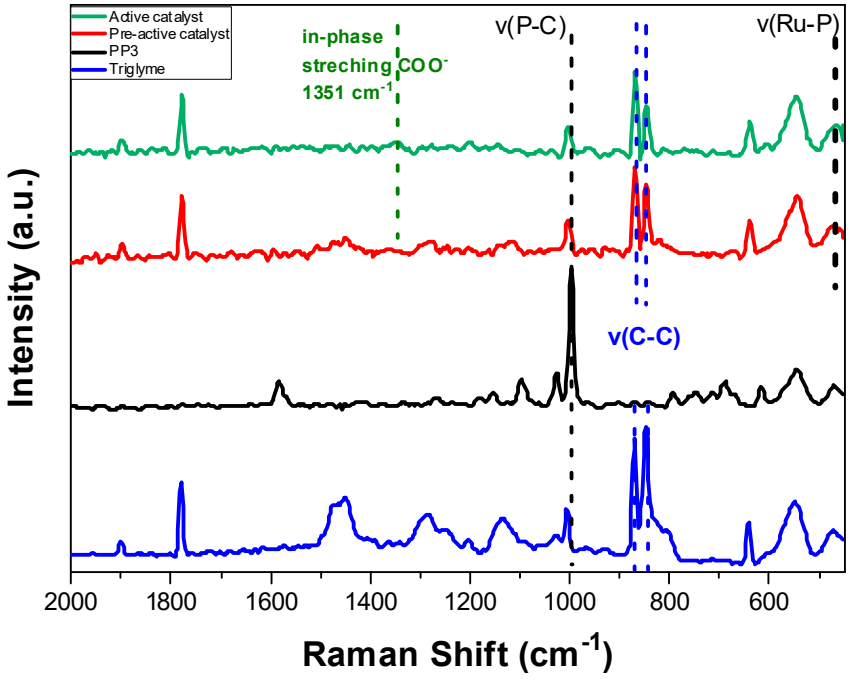

Figure S2. Raman spectrum for all components in the catalytic system.

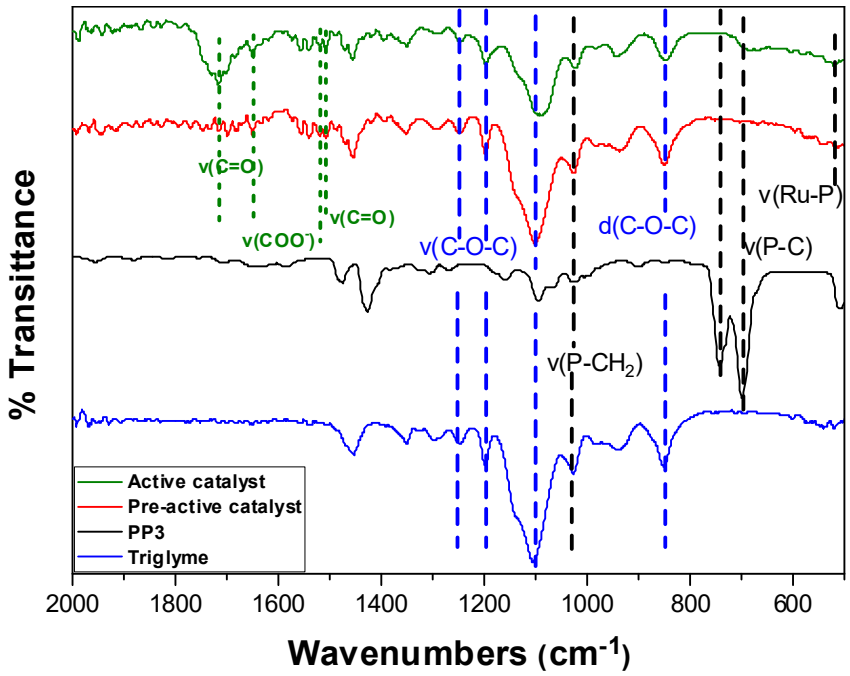

Figure S3. ATR spectrum for all components in the catalytic sytstem.

4. EPR Spectroscopy

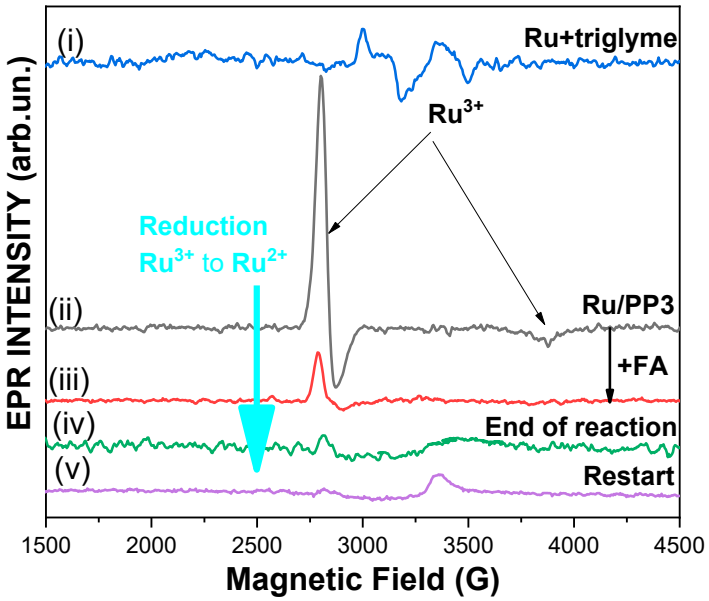

Figure S4. EPR spectra of the catalytic system. (i) only the Ru-precursor in triglyme (ii) [Ru/PP3] catalyst in triglyme after 10 min (iii) catalytic reaction ([Ru/PP3]/FA/KOH in triglyme:water solution) during evolution (iv) after the end of the catalytic reaction and (v) restart of catalytic reaction by adding 1 ml of FA on the next day.