



Highly Selective CO₂ Hydrogenation to Methanol over Complex In/Co Catalysts: Effect of Polymer Frame

Svetlana A. Sorokina ¹, Nina V. Kuchkina ¹, Stepan P. Mikhailov ², Alexander V. Mikhilchenko ¹, Alexey V. Bykov ², Valentin Yu. Doluda ², Lyudmila M. Bronstein ^{3,*} and Zinaida B. Shifrina ^{1,*}

¹ A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov St., 119991 Moscow, Russia; sorokinas@ineos.ac.ru (S.A.S.); kuchkina@ineos.ac.ru (N.V.K.); koal2702@yandex.ru (A.V.M.)

² Department of Biotechnology and Chemistry, Tver State Technical University, 22 A. Nikitina St., 170026 Tver, Russia; stefan.oblivion@mail.ru (S.P.M.); bykovav@yandex.ru (A.V.B.); doludav@yandex.ru (V.Y.D.)

³ Department of Chemistry, Indiana University, 800 E. Kirkwood Av., Bloomington, IN 47405, USA

* Correspondence: lybronst@indiana.edu (L.M.B.); shifrina@ineos.ac.ru (Z.B.S.)

Table S1. Summary of the catalysts synthesized. All catalysts contain SiO₂-Fe₃O₄-PPP as a support, unless otherwise is stated.

Sample notation	Metal content, wt%			
	by loading		by elemental analysis	
	In	Co	In	Co
3In	3	0	3.2	0
1.5In	1.5	0	1.8	0
3In/3Co	3	3	3.1	3.0
3In/1.5Co	3	1.5	3.3	1.6
3In/0.3Co	3	0.3	3.2	0.3
1.5In/1.5Co	1.5	1.5	1.6	1.7
1.5In/0.9Co	1.5	0.9	1.7	1.0
1.5In/0.6Co	1.5	0.6	1.6	0.6
1.5In/0.3Co	1.5	0.3	1.6	0.4
1.5In/0.1Co	1.5	0.1	1.7	0.2
1.0In/0.5Co	1.0	0.5	1.2	0.5
0.7In/0.7Co	0.7	0.7	0.8	0.8
1.5In/0.3Co without Fe ₃ O ₄	1.5	0.3	1.7	0.4
1.5In/0.3Co without PPP	1.5	0.3	1.6	0.4
3In/3Co without PPP	3	3	3.3	3.2

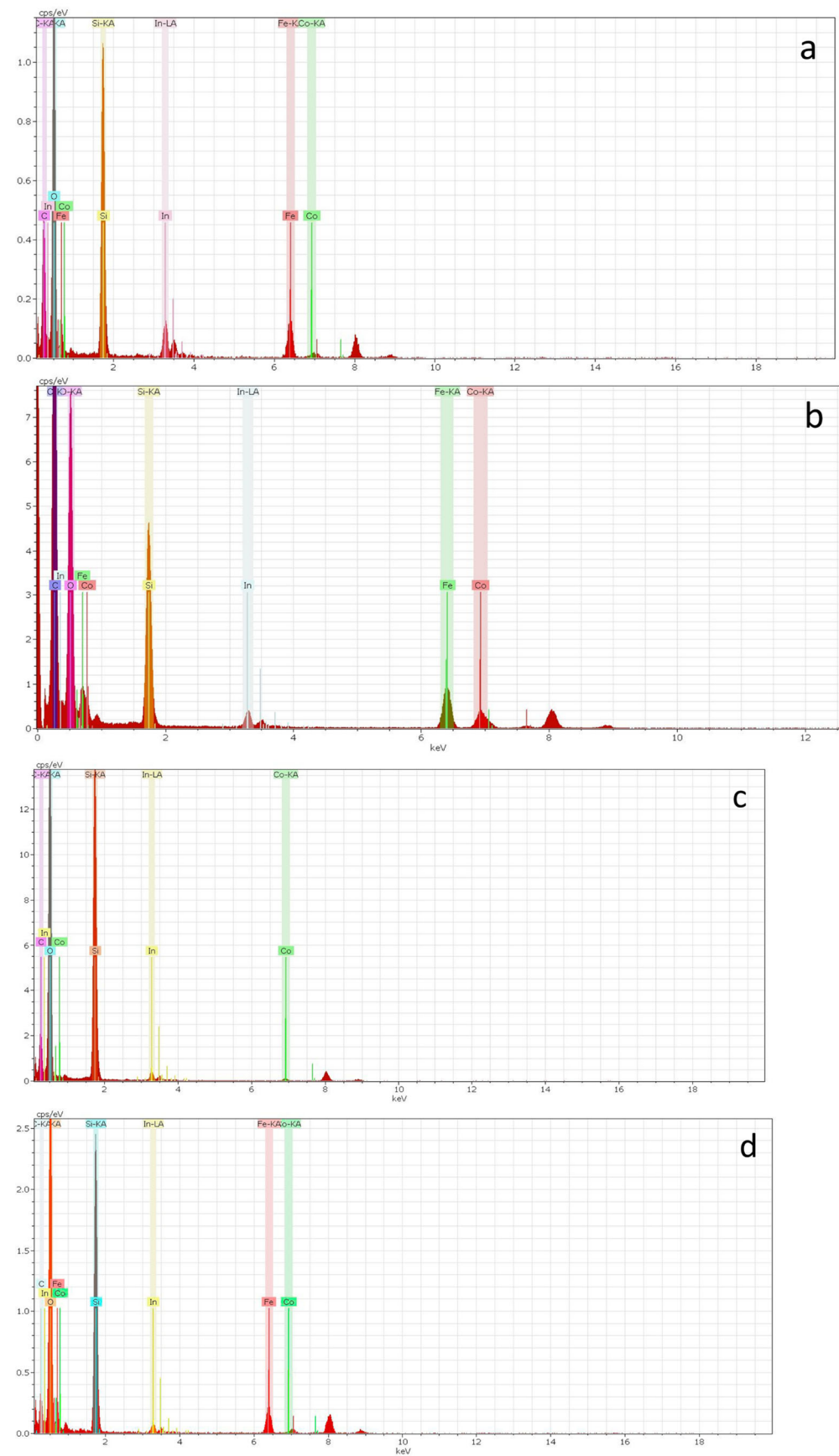


Figure S1. EDX spectra of 1.5In/0.3Co (a), 3In/3Co (b), 1.5In/0.3Co without Fe₃O₄ (c) and 1.5In/0.3Co without PPP (d).

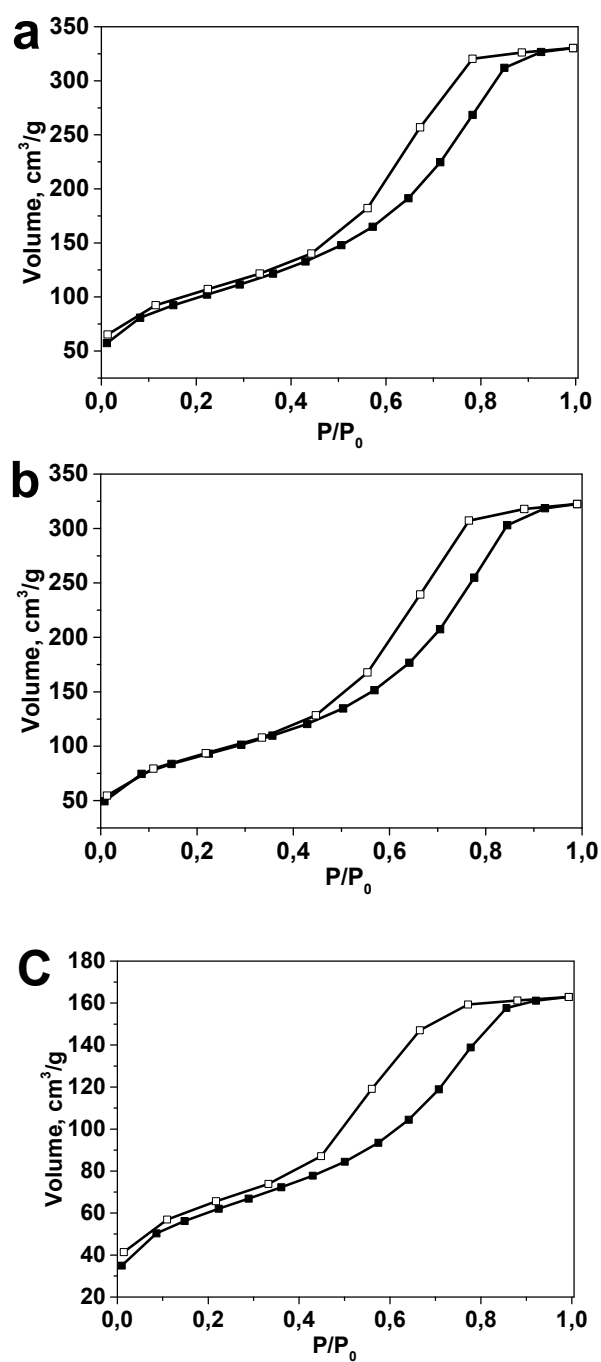


Figure S2. N_2 adsorption-desorption isotherms of 1.5In (a), 1.5In/0.3Co (b) and 3In/3Co (c) catalysts.

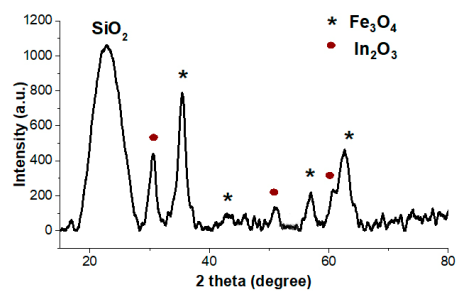


Figure S3. XRD pattern of 1.5In/0.3 Co without PPP.

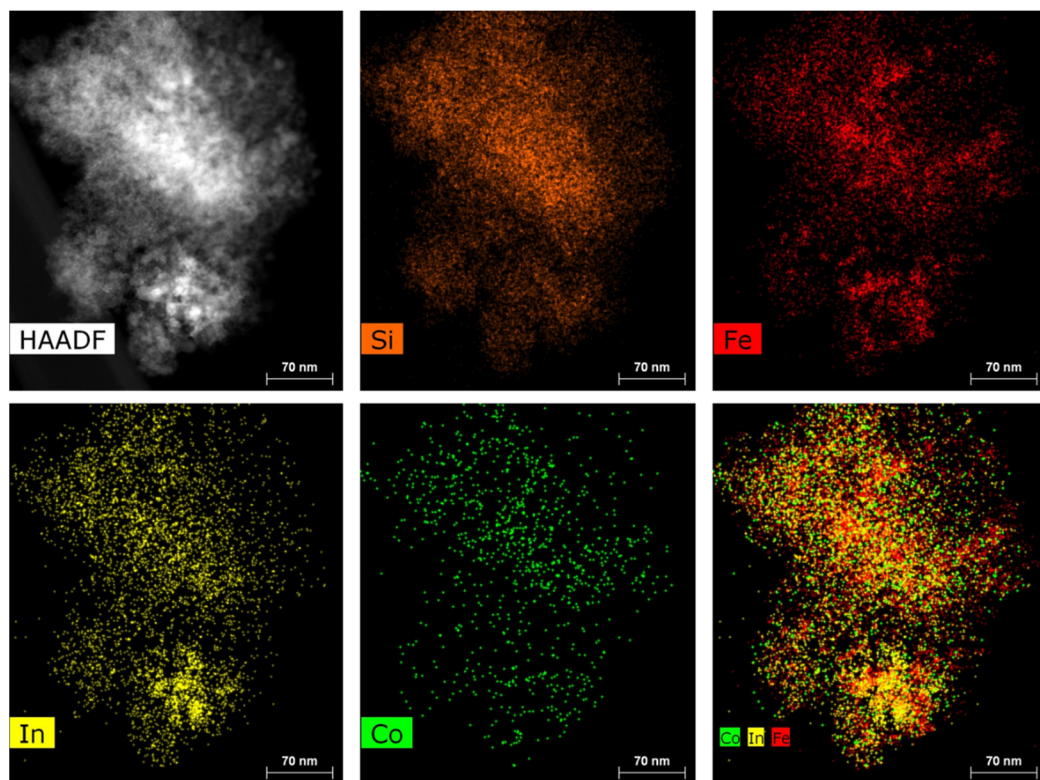


Figure S4. STEM dark field image and EDS maps of Si, Fe, In, Co and their superpositions of the 1.5In/0.3Co catalyst without the polymer layer.

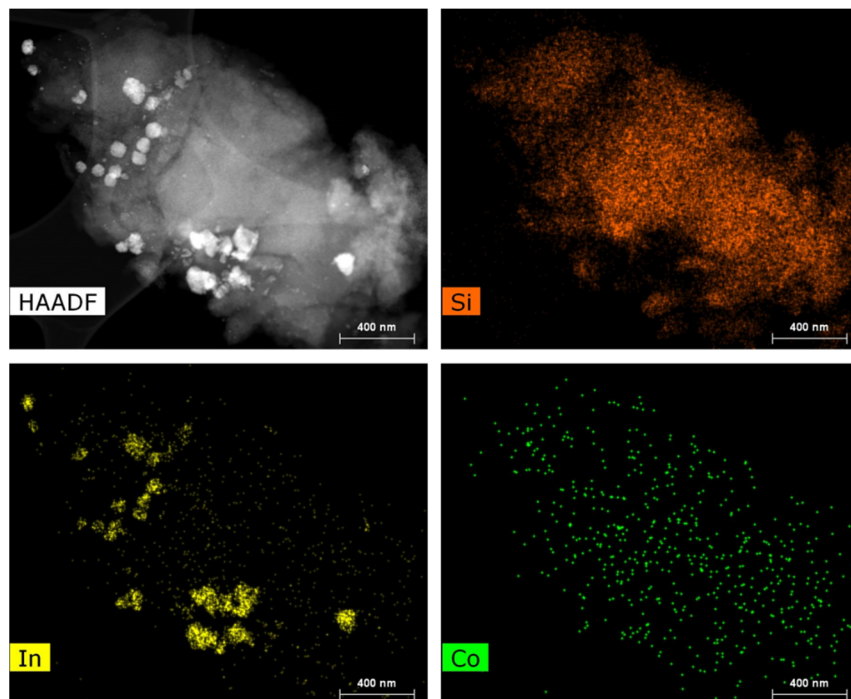


Figure S5. STEM dark field image and EDS maps of Si, In, Co and their superpositions of the 1.5In/0.3Co without magnetic NPs.

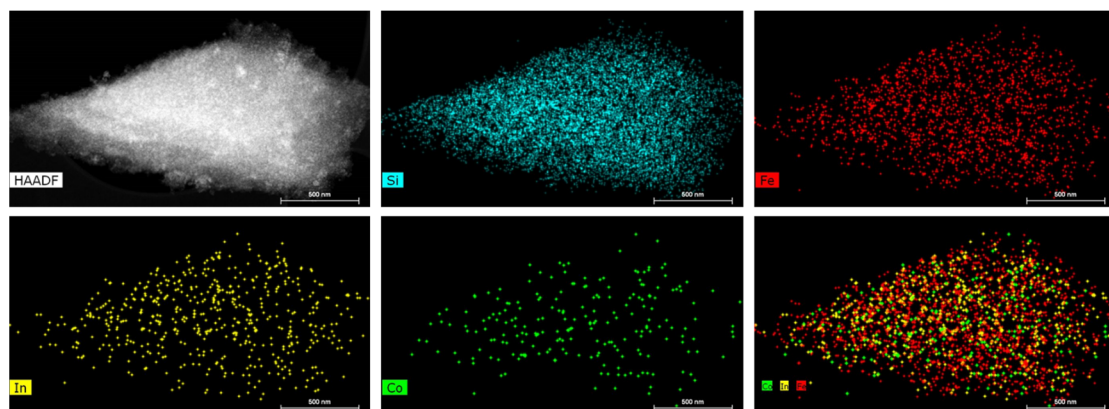


Figure S6. STEM dark field image and EDS maps of Si, Fe, In, Co and their superpositions of the 1.5In/0.3Co catalyst after the catalytic experiments.

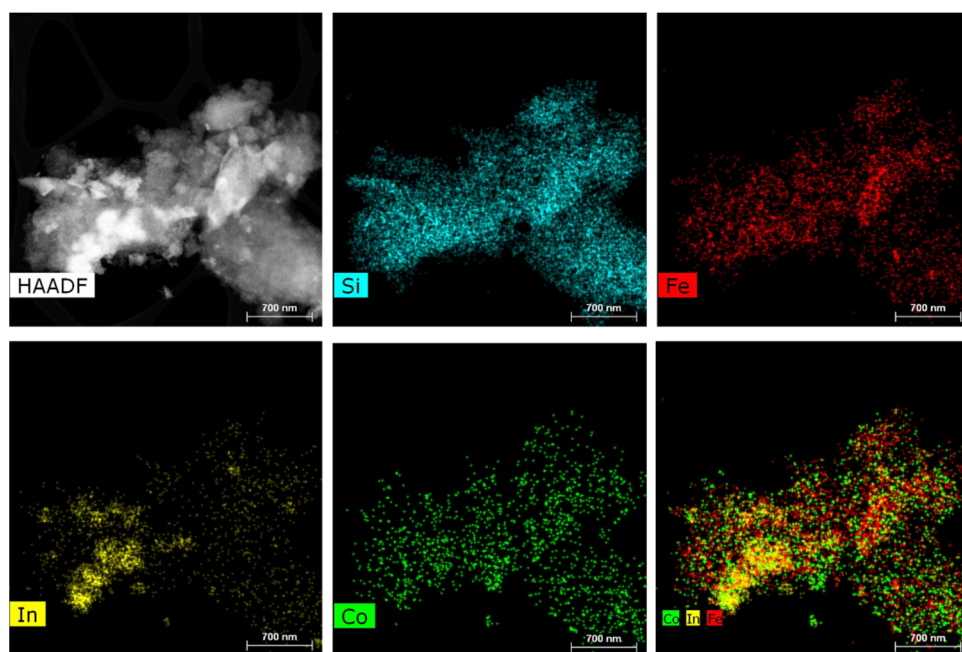
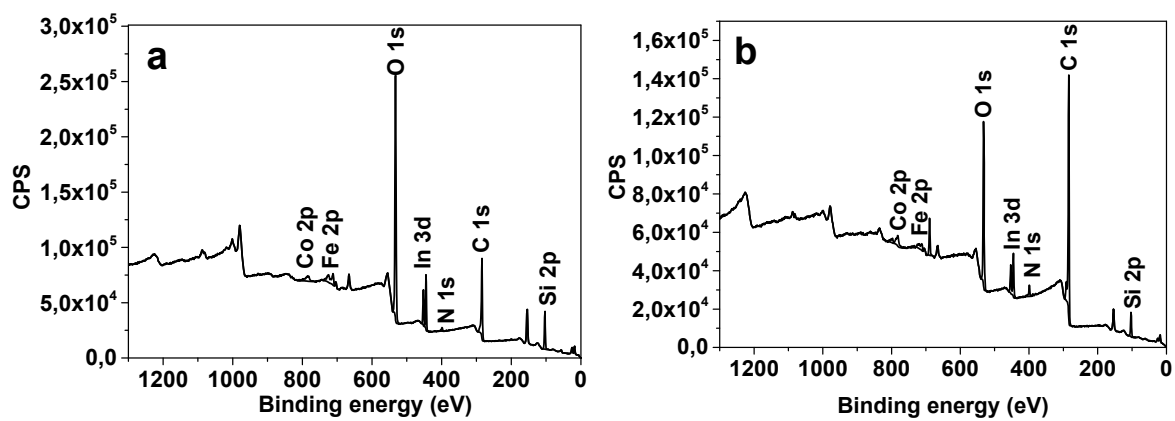


Figure S7. STEM dark field image and EDS maps of Si, Fe, In, Co and their superpositions of the 3In/3Co catalyst after the catalytic experiments.



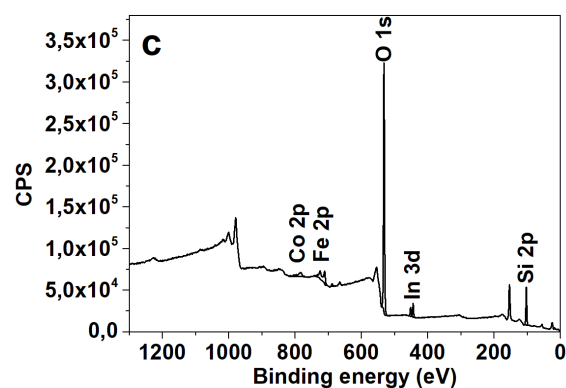


Figure S8. XPS survey spectra of 1.5In/0.3Co (a), 3In/3Co (b) and 1.5In/0.3Co without PPP (c).

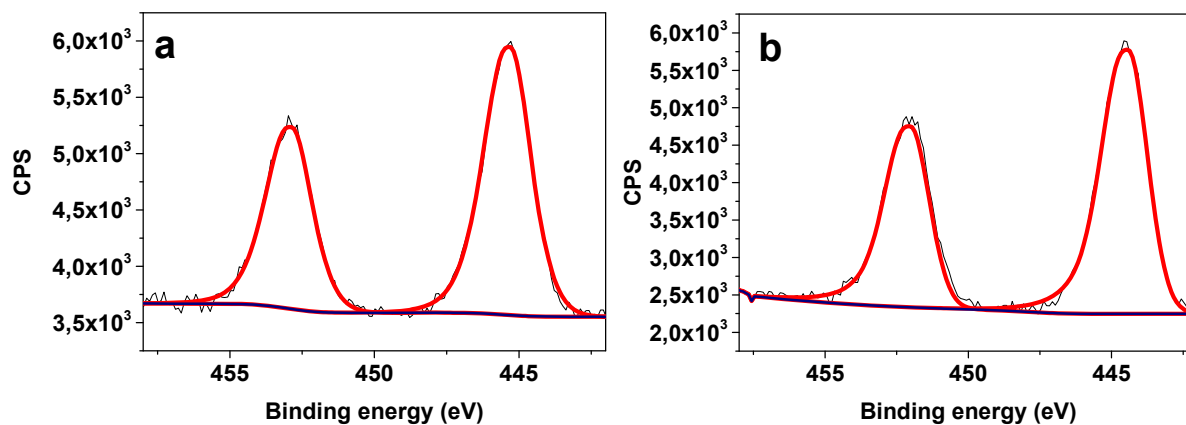


Figure S9. HR XPS spectra of In 3d of 3In/3Co catalyst (a) and 1.5In/0.3Co without PPP (b).

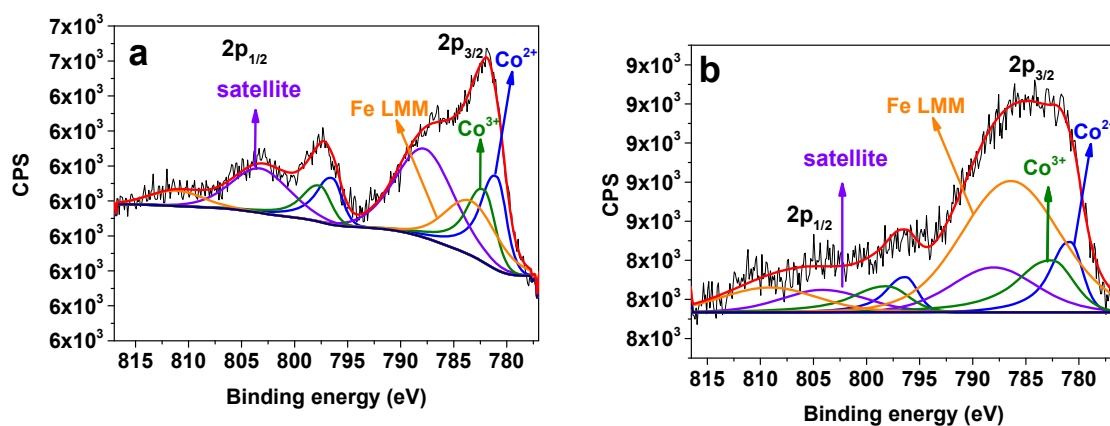


Figure S10. HR XPS spectra of Co 2p of 3In/3Co catalyst (a) and 1.5In/0.3Co without PPP (b).

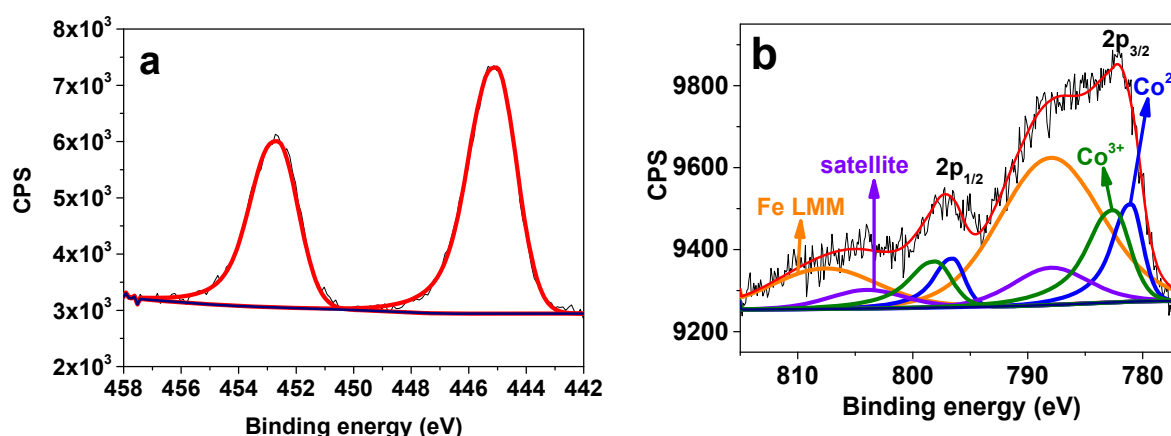


Figure S11. HR XPS spectra of In 3d (a) and Co 2p (b) of 1.5In/0.3Co after catalysis.

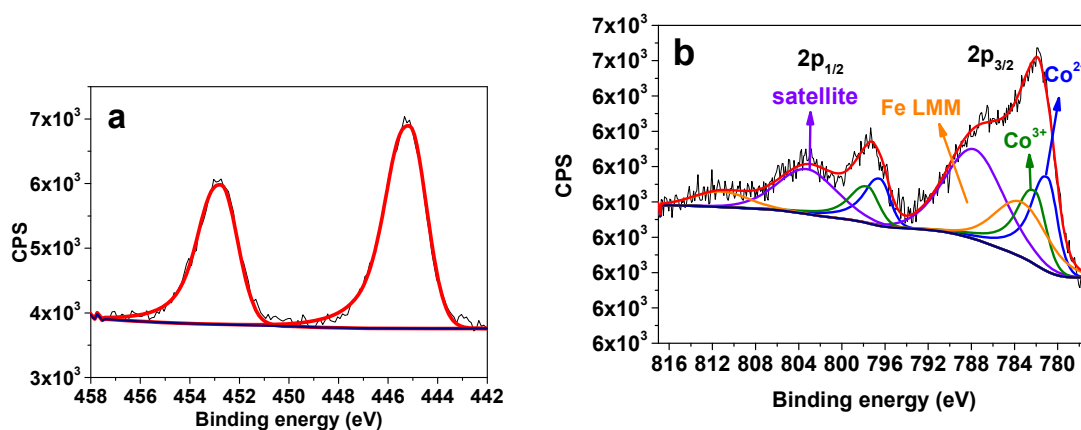


Figure S12. HR XPS spectra of In 3d (a) and Co 2p (b) of 3In/3Co after catalysis.

Table S2. Fitting parameters for HR XPS of Fe 2p of 1.5In/0.3Co before catalytic experiments.

	Pos.	FWHM	%Area
In 3p _{1/2}	704.52	3.11	13.53
Fe 2p _{3/2} (Fe ²⁺)	711.20	2.33	13.12
Fe 2p _{1/2} (Fe ²⁺)	724.80	2.56	6.56
Fe 2p _{3/2} (Fe ²⁺) Satellite	720.83	8.00	14.99
Fe 2p _{1/2} (Fe ²⁺) Satellite	734.43	8.00	7.50
Fe 2p _{3/2} (Fe ³⁺)	712.80	2.87	14.85
Fe 2p _{1/2} (Fe ³⁺)	726.40	2.87	7.43
Co LMM	717.00	12.00	8.78
Fe 2p _{3/2} (Fe ³⁺) Satellite	715.32	3.93	8.83
Fe 2p _{1/2} (Fe ³⁺) Satellite	728.92	3.93	4.42

Table S3. Fitting parameters for HR XPS of Fe 2p of 1.5In/0.3Co after catalytic experiments.

	Pos.	FWHM	%Area
In 3p _{1/2}	704.26	2.69	6.18
Fe 2p _{3/2} (Fe ²⁺)	711.17	2.92	25.90
Fe 2p _{1/2} (Fe ²⁺)	724.77	3.21	12.95
Fe 2p _{3/2} (Fe ²⁺) Satellite	717.96	8.06	14.42
Fe 2p _{1/2} (Fe ²⁺) Satellite	731.56	8.06	7.21
Fe 2p _{3/2} (Fe ³⁺)	713.50	4.12	15.94
Fe 2p _{1/2} (Fe ³⁺)	727.10	4.12	7.97

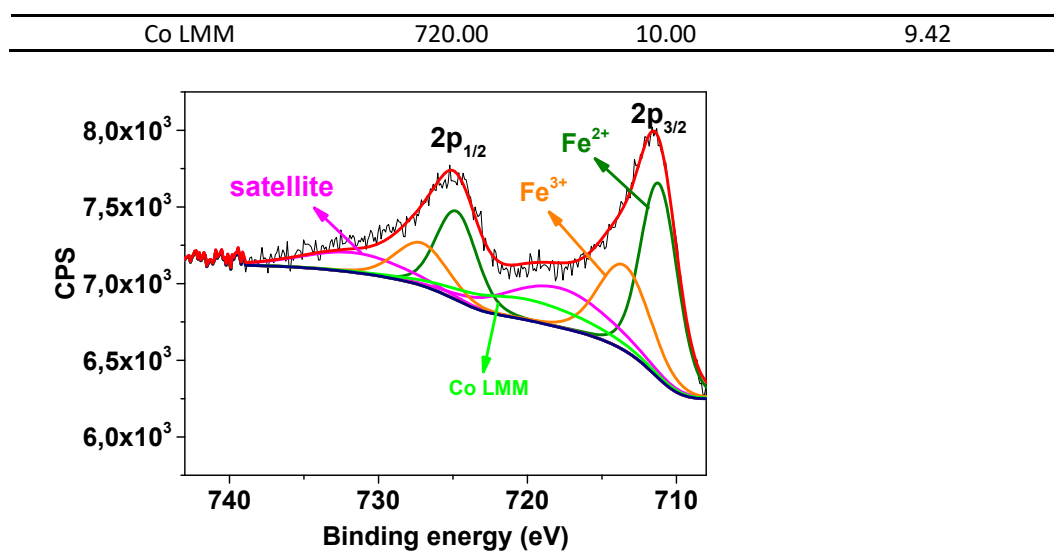


Figure S13. HR XPS spectra of Fe 2p of 1.5In/0.3Co after catalysis.

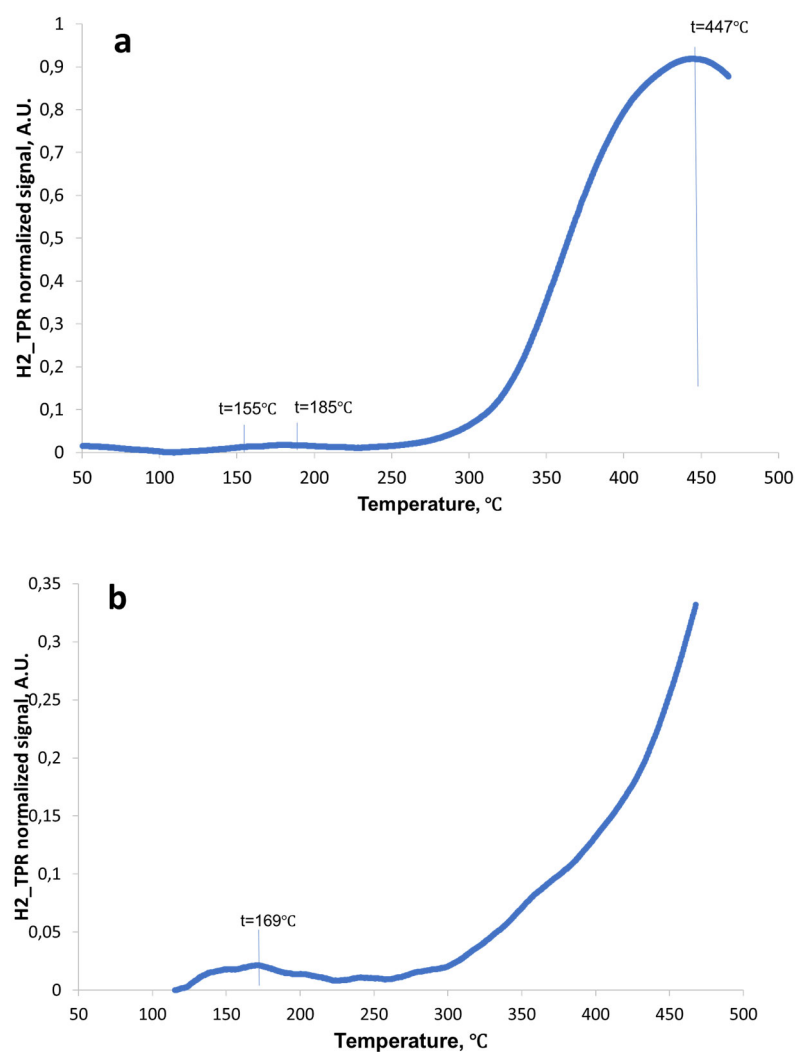


Figure S14. H₂ TPR profiles of 1.5In/0.3Co without PPP (a) and without Fe₃O₄ (b).

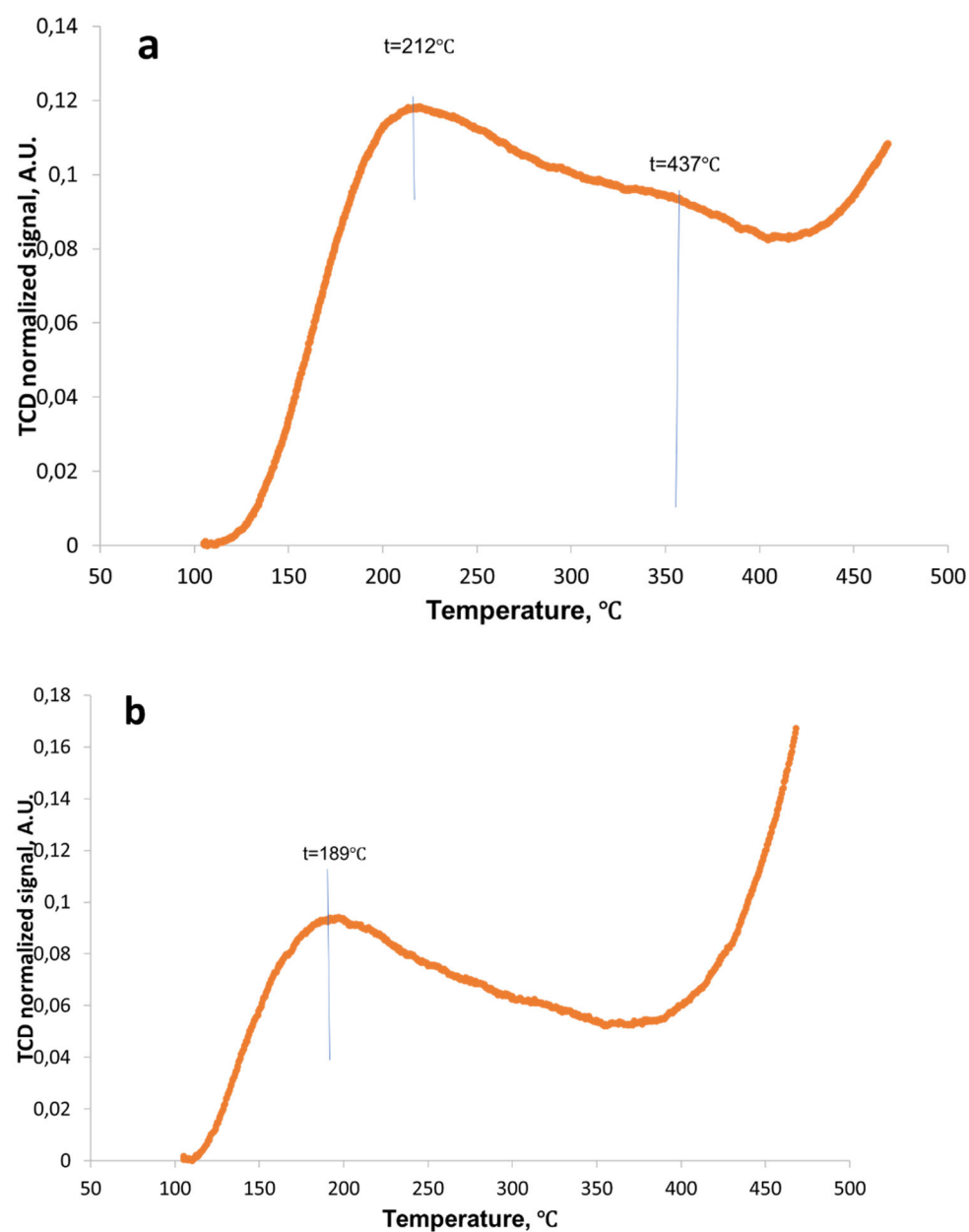


Figure S15. CO₂ TPD profiles of 1.5In/0.3Co without PPP **(a)** and without Fe₃O₄ **(b)**.