SUPPLEMENTARY MATERIALS

Unsupported shaped cobalt nanoparticles as efficient and recyclable catalysts for the solvent-free acceptorless dehydrogenation of alcohols.

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Content

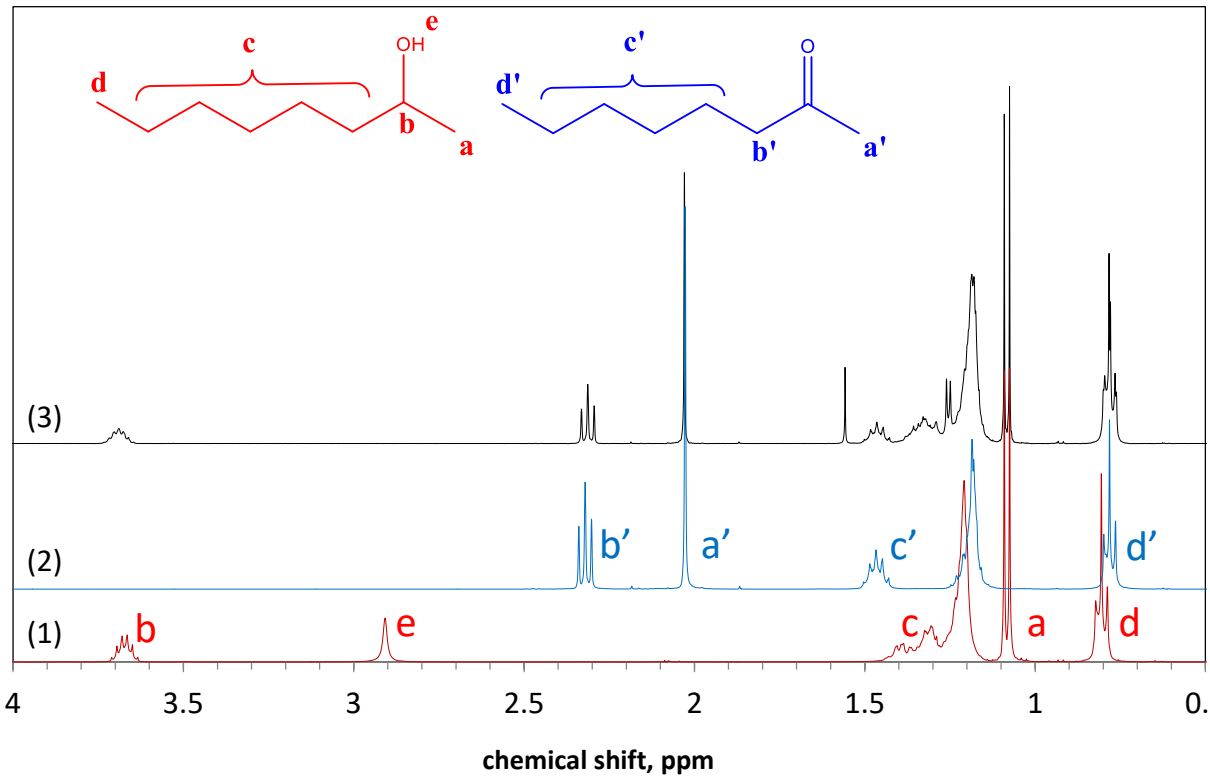

Figure S1. ^{1}H NMR spectra of (1) commercial octan-2-ol, (2) octan-2-one and of (3) the liquid phase after 6h of reaction using Co NRs and octan-2-ol (the conversion of octan-2-ol into octan-2-one at 175 °C is of 56% with a selectivity > 90%).

The conversion was calculated using the peaks located at 0.8 ppm, 1.1 ppm, 1.15-1.4 ppm and 3.65 ppm corresponding to H_d, H_a, H_c and H_b from the initial 2-octanol, respectively, H_e fluctuating. Protons from the resulting octan-2-one are attributed as follows: 0.8 ppm: $H_{d'}$, 1.15-1.4 ppm: $H_{c'}$, 2.05 ppm: $2H_{a'}$, 2.42 ppm: $H_{b'}$.

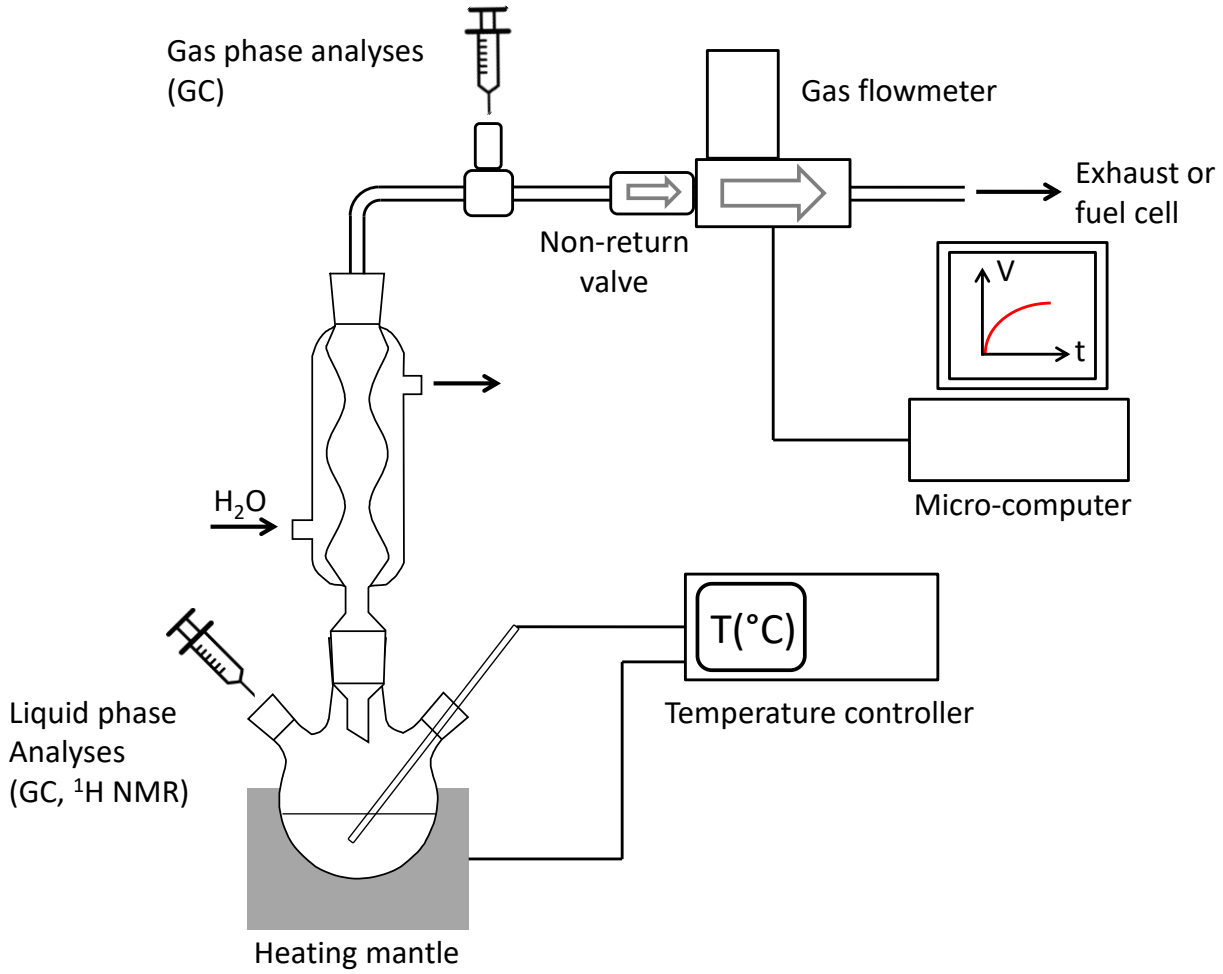

Figure S2. Experimental setup used for the catalytic tests.

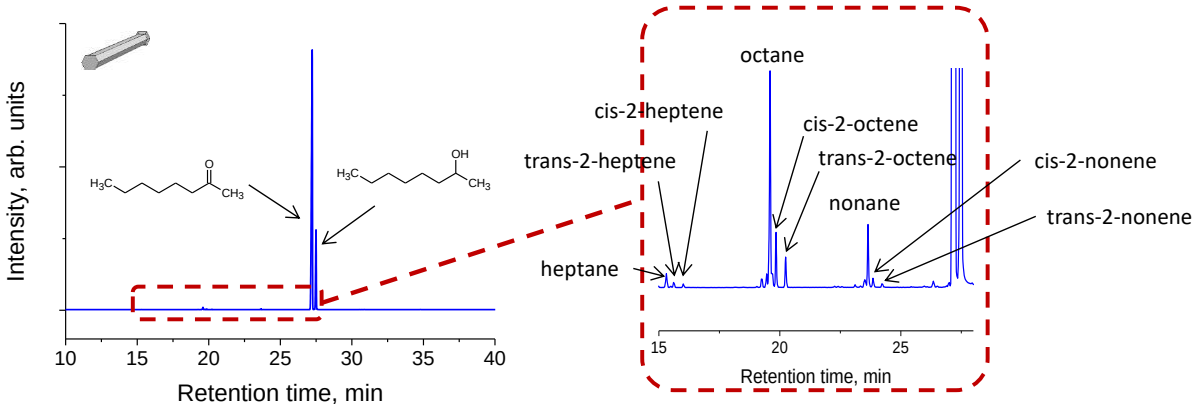

Figure S3. Gas chromatogram (right) recorded after 24h reaction time with sample Co-A showing that octan-2-one is the main oxidation product and b) magnification showing the other compounds detected during the ADA of octan-2-ol.

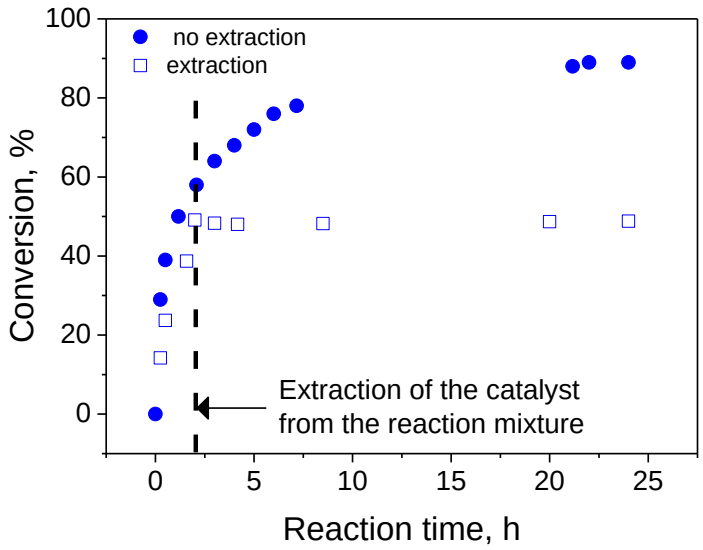

Figure S4. Conversion of octan-2-ol into octan-2-one as a function of time for sample Co-A without (●) and with (□) extraction of the particles after 2 h reaction time.

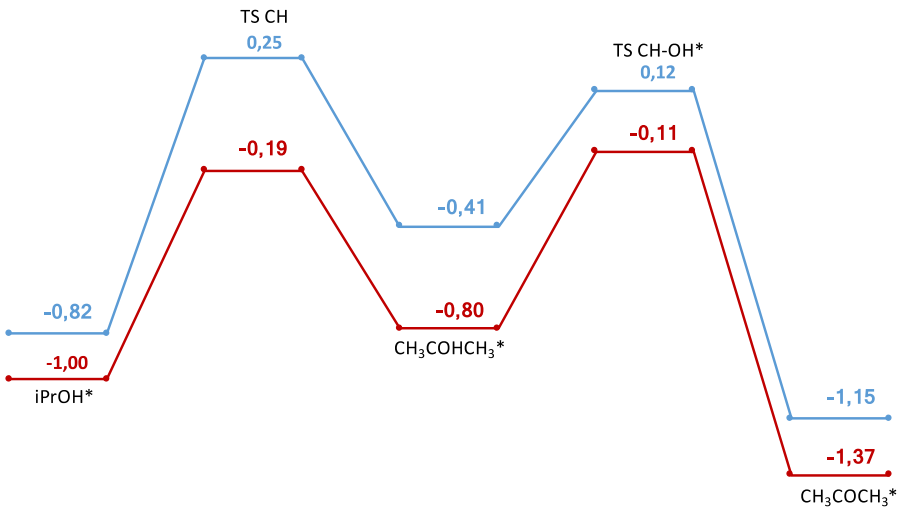

Figure S5. iPrOH dehydrogenation energetic profiles on (11$\bar{2}$0) (red) and (0001) (blue) surfaces. Reaction proceeding *via* alkyl path. The sum of energies of free surface and iPrOH in gas phase is taken as the reference energy. Asterisks stand for adsorbed species. TS: transition state.

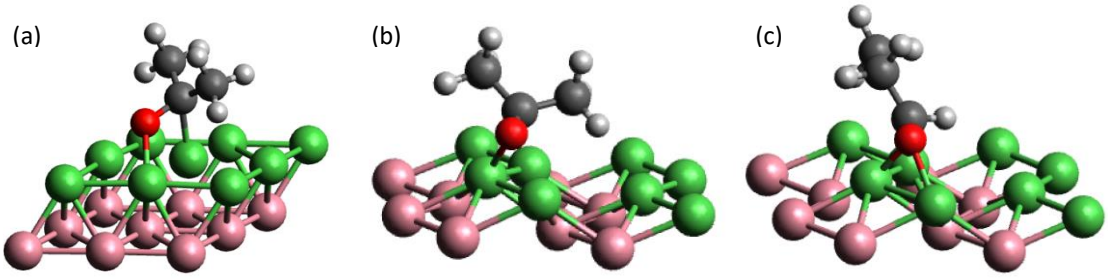

Figure S6. Carbonyl product for iPrOH dehydrogenation on (a) (0001) surface and (b) (11$\bar{2}$0) surface and for 1-PrOH dehydrogenation on (c) (11$\bar{2}$0) surface.

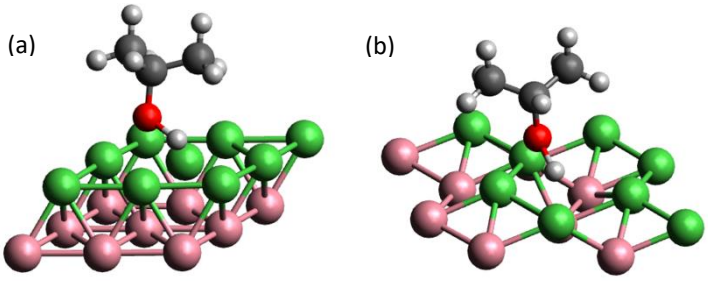

Figure S7. O-H bond breaking transition states for iPrOH on (a) (0001) and (b) (11$\bar{2}$0) surfaces *via* alkoxy path.

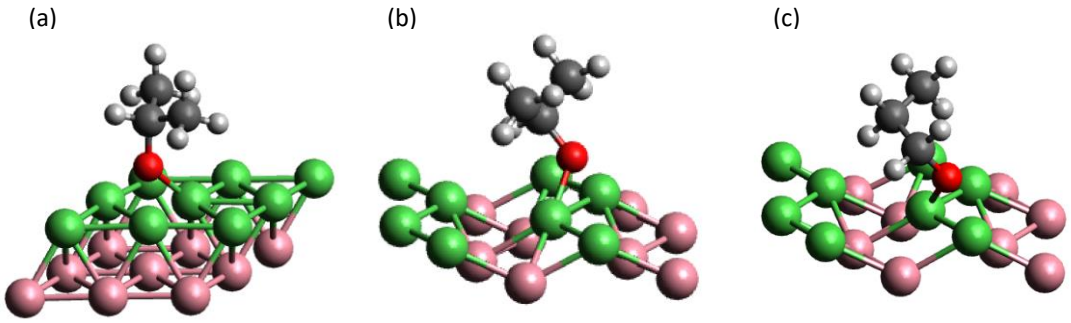

Figure S8. Alkoxy intermediates for (a) iPrOH on (0001) surface, (b) iPrOH on (11$\bar{2}$0) surface, (c) 1-PrOH on (11$\bar{2}$0) surface.

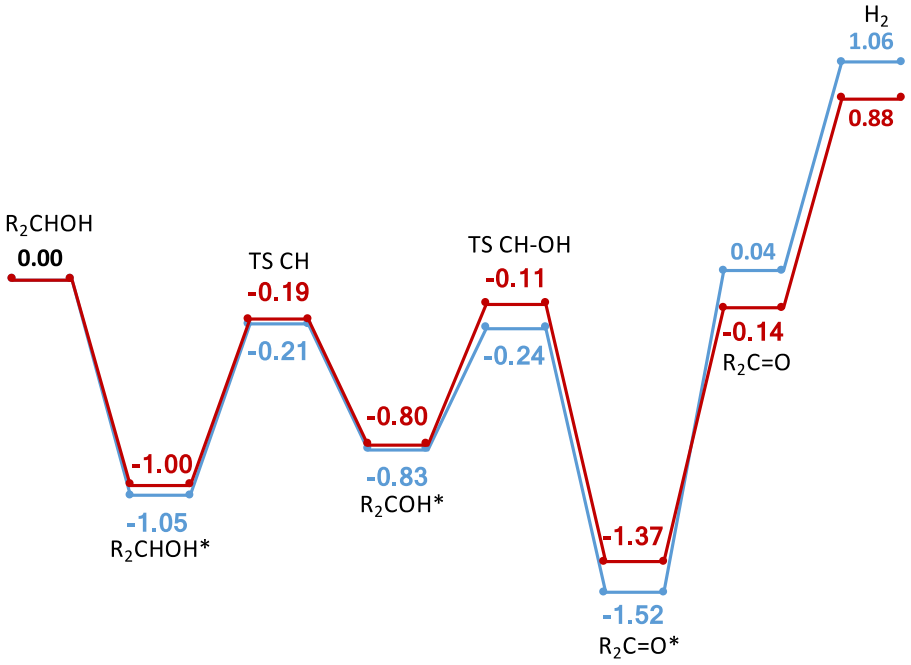

Figure S9. 1-PrOH (blue) and iPrOH (red) alcohol dehydrogenation on (11$\bar{2}$0) surface. Reaction *via* alkyl path. Asterisks stand for adsorbed species.

Table S1. Activation energies and effective barriers for alcohols dehydrogenation *via* alkyl and alkoxy pathways on $(11\bar{2}0)$ and (0001) surfaces.

Surface	Alcohol	Alkyl pathway			Alkoxy pathway		
		E_{act} TS CH (eV)	E_{act} TS OH (eV)	Effective barrier (eV)	E_{act} TS OH (ev)	E_{act} TS CH (eV)	Effective barrier (eV)
$(11\bar{2}0)$	**iPrOH**	0.81	0.69	0.89	0.50	0.98	0.98
(0001)	**iPrOH**	1.07	0.53	1.07	0.72	0.88	0.88
$(11\bar{2}0)$	**1-PrOH**	0.84	0.59	0.84	0.48	0.87	0.87

TS: transition state

Table S2. Key bond lengths in transition states for alcohols dehydrogenation *via* alkyl and alkoxy pathways on $(11\bar{2}0)$ and (0001) surfaces.

Surface	Alcohol	Alkyl pathway		Alkoxy pathway	
		TS CH C-H	TS OH O-H	TS OH O-H	TS CH C-H
$(11\bar{2}0)$	**iPrOH**	1.575	1.379	1.303	1.525
(0001)	**iPrOH**	1.602	1.212	1.292	1.581
$(11\bar{2}0)$	**1-PrOH**	1.537	1.388	1.305	1.612

TS: transition state

Molecular hydrogen produced along ADA is used to operate a fuel cell.

Experimental

The gas outlet of the catalysis setup was connected to a fuel cell. The fuel cell used was purchased at PaxiTech Fuel Cell and is part of the PaxiTech Fuel Cell and Electrolyser Educational Kit. The Kit PAC#2, having a 50 µm thick membrane and 40% Pt/C and a catalyst Loading of 0.5 mg Pt /cm² both at the anode and the cathode was used. The fuel cell was first connected to an electronic load which consists of an electronic variable resistor and can work in constant current or constant voltage mode. A display panel shows the fuel cell current and voltage. The fuel cell was then connected to a RF-300CA311440 DC motor.

Videos S1 and S2

As shown in video S1, after connecting the gas outlet to the fuel cell, the voltage increased rapidly up to 1 V which is the voltage typically obtained when connecting hydrogen gas tank to this cell. The cables were then disconnected from the electronic load and connected to a small fan which started immediately and was able to run all along the catalytic reaction (video S2). From an industrial point-of-view, the use of Co nanoparticles as catalyst for the ADA of alcohols is of high interest since they allow to produce corresponding ketones with a high yield and a high selectivity, they can be easily recovered using a simple magnet and they allow for the production of H_2 which can be directly used in a fuel cell to produce electricity.