Supplementary information

Experimental section

Materials
Levulinic acid (LA) (98%, Sigma-Aldrich) was used as delivered.

Catalyst preparation
Platinum, ruthenium and palladium catalysts in 1% loading were prepared by incipient wet impregnation from $Pt(acac)_2$, $Ru(acac)_3$ $Pd(acac)_2$ (Sigma-Aldrich, 97%, 97% and 99.9% respectively) methanolic solutions respectively on TiO_2 (P-25; Degussa). Catalysts were calcined in air at 200°C and reduced at the same temperature for 1 h in hydrogen.

Characterization
Transmission Electron Microscopy (TEM) has been carried out on a Jeol 2100 microscope operating at a 200 kV voltage, equipped with a LaB6 filament as electron source and an Orius camera, and allowing a point-to-point resolution of 0.2 nm. Prior to analysis, the samples have been dispersed in ethanol using an ultrasound bath, and 1 to 3 drops of the suspension have been deposited on a 300 mesh copper grid coated holey carbon film. Afterwards, the samples have been left to dry in air at room temperature for 30 min.

Catalytic tests - Hydrogenation of levulinic acid (LA)
In a typical experiment, 1 g of levulinic acid, 0.3 g of a catalyst and 30 ml of water or THF were combined in a stainless steel autoclave from Berghof, equipped with teflon insert allowing the reaction volume of 70 mL. The reactor was pressurized with hydrogen to 50 bar and the temperature was maintained at 70°C for 1 h.

After the end of the reaction the reactor was cooled down, the remaining pressure was released and the reaction mixture was centrifuged to separate the solid catalyst and the product solution. The products were analyzed or by HPLC equipped with RID detector and Rezex ROA column, 0.005N H_2SO_4 was used as an eluent. The liquid after reaction was analyzed by ICP-MS or by Shimadzu GCMS-QP2010 with the agilent column VF-5ms (30m, 0.25mm, 0.25μm)

TEM images

TEM images of the tested catalysts are presented below (Fig 1a, b, c) and it is possible to observe that the metal distribution was rather homogeneous, which was especially visible in the case of Pd/TiO_2 and Pt/TiO_2 (Fig S1. a,b). Also the average crystallite sizes were very similar (Tab. S1).

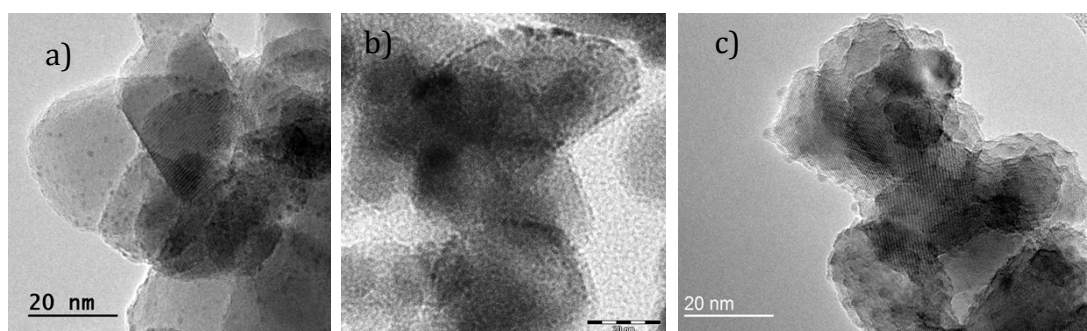*Figure S1:* TEM images of a)Pt/TiO_2, b)Ru/TiO_2, c)Pd/TiO_2

Catalyst	Size [nm]
1%Ru/TiO$_2$ (P25)	2.3
1%Pd/TiO$_2$ (P25)	2.1
1%Pt/TiO$_2$ (P25)	3.2

Table S1 The average crystallite size of tested catalysts

Theoretical section

1- Computational details

Metallic catalysts were modeled using a periodic slab model of the most stable close-pack facet for each of them (Ru(0001), Co(0001), Rh(111), Ir(111), Ni(111), Pd(111), Pt(111), Cu(111)). The supercell is a p(3x3) cell containing 4 metallic layers separated by a vacuum equivalent to five layers. The two bottom layers are kept fixed in the optimal bulk position while the two upper layers and the adsorbed molecule are free to relax till forces lower than 0.01eV/Å. The electronic density is computed in the Generalized Gradient Approximation using the PW91 functional.[1] The periodic DFT calculations were performed using the VASP package.[2,3] Electron-ions interactions were described in the Projector-Augmented-Wave formalism.[4] The planewave cutoff was set at 400eV using a 3x3x1 grid of K points generated using the Monkhorst-Pack scheme[5] To ensure a quick electronic convergence to 10^{-6}eV, the smearing method of Methfessel-Paxton[6] is used with a width of 0.2 eV. The magnetic properties of Co and Ni are taken into account using the unrestricted formalism.

The transition states (TS) were obtained by a combination of nudged elastic band method[7,8], and dimer method[9] and were characterized by the presence of a unique imaginary frequency corresponding to the reaction coordinate.

Calculations on Ru(0001) have been repeated modeling water as a continuum solvent using the VASPsol package developed by K. Mathew and R.G. Hennig.[10]

Structures are drawn using VESTA.[11]

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[1] J.P. Perdew, Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244

[2] G. Kresse, J. Hafner, *Phys. Rev. B*, 1993, **47**, 558

[3] G. Kresse, J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169

[4] G. Kresse, D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758

[5] H.J. Monkhorst, J.D. Pack, *Phys. Rev. B* 1976, **13**, 5188

[6] M. Methfessel and A.T. Paxton, *Phys. Rev. B* 1989, **40**, 3616

[7] G. Henkelman, B.P. Uberuaga, and H. Jónsson, *J. Chem. Phys.*, 2000, **113**, 9901

[8] G. Henkelman and H. Jónsson, *J. Chem. Phys.*, 2000, **113**, 9978

[9] A. Heyden, A. T. Bell, and F. J. Keil, *J. Chem. Phys.*, 2005, **123**, 224101

[10] K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T. A. Arias, and R. G. Hennig. *J. Chem. Phys.* 2014, **140**, 084106

[11] K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272.

2- Energetic span

The concept of energetic span[1] is defined for a catalytic cycle. The reaction starts with an initial state (IS) in gas phase, which adsorbs on the catalysts (IS*), and proceeds through an radical intermediate (Int.). The latter, gives the final product FS*, that is adsorbed on the surface and finally goes in gas phase (FS). Since it is a cycle, after the final product desorption, another reactant from the gas phase binds to the catalyst and the process restarts.

The energetic span δE is defined through the two determining states: the TOF-determining intermediate (TDI) and the TOF-determining transition state (TDTS). TDTS and TDI are defined as the states maximizing the energetic span.[1] The latter is determined such as:

$$\delta E = \begin{cases} (a)\ E_{TDTS} - E_{TDI} & \text{if TDTS appears after TDI} \\ (b)\ E_{TDTS} - E_{TDI} + \Delta G_r & \text{if TDTS appears before the TDI} \end{cases}$$

where E_{TDTS} and E_{TDI} are respectively the energies of the TDTS and the TDI, and where ΔG_r is the overall reaction energy (see Fig. S2)
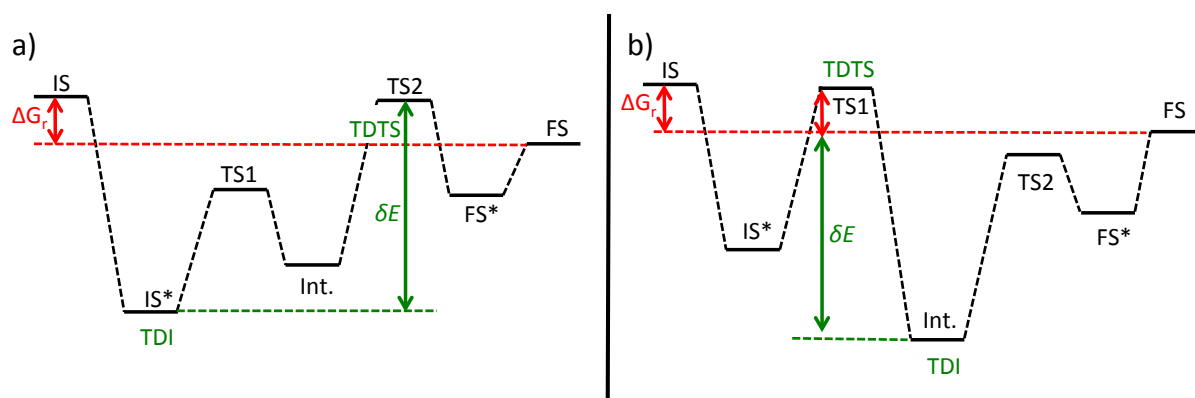
Figure S2: Two different catalytic cycles represented with their corresponding energetic spans δE. TDTS and TDI are respectively the TOF-determining TS and the TOF-determining Intermediate. IS* and FS* denote the initial and final state adsorbed on the surface, whereas IS and FS correspond to the gas phase.

In the following tables we present the complete list of the various energetic span related to acetone hydrogenation on metallic catalysts, both in gas phase and in aquaeous medium.

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[1] S. Kozuch and S. Shaik, *Accounts of Chemical Research*, 2011, **44**, 101

	Alkyl route			Alkoxy route		
	TDI	**TDTS**	**δE**	**TDI**	**TDTS**	**δE**
Ru	IS*	OH-CH	1.37	Int	CH-OH	1.40
Ru sol	*IS**	*OH-CH*	*1.39*	*Int*	*CH-OH*	*1.45*
Co	IS*	OH	1.43	Int	CH-OH	1.50
Rh	IS*	OH-CH	1.19	IS*	CH-OH	1.14
Ir	IS*	OH-CH	0.94	IS*	CH-OH	0.82
Ni	IS*	OH-CH	1.32	Int	CH-OH	1.37
Pd	IS*	OH-CH	1.36	IS*	CH-OH	1.57
Pt	IS*	OH-CH	0.88	IS*	CH-OH	1.00
Cu	IS*	OH-CH	1.02	Int	CH-OH	1.19

Table S2: Energetic span for acetone hydrogenation. For both alkyl and alkoxy route we mentioned the TOF-determining state (TDTS and TDI). IS* denotes the initial state that is adsorbed on the catalyst. "CH-OH" means CH bond formation followed by OH bond formation. Ru sol corresponds to the calculations modeling the water as a continuum medium. Energies are given in eV.

	Alkyl route			Alkoxy route		
	TDI	**TDTS**	**δE**	**TDI**	**TDTS**	**δE**
Ru	IS*	OH-CH	1.57	Int	CH-OH	0.99
Ru sol	*IS**	*OH-CH*	*1.66*	*Int*	*CH-OH*	*1.00*
Co	IS*	OH-CH	1.46	Int	CH-OH	1.00
Rh	IS*	OH-CH	1.20	IS*	CH-OH	0.78
Ir	IS*	OH-CH	0.88	Int	CH-OH	0.55
Ni	IS*	OH	1.44	Int	CH-OH	0.86
Pd	IS*	OH-CH	1.47	IS*	CH-OH	1.30
Pt	IS*	OH-CH	1.18	IS*	CH-OH	0.89
Cu	IS*	OH-CH	1.31	IS*	CH	0.87

Table S3: Energetic span for acetone hydrogenation in presence of one water molecule. For both alkyl and alkoxy route we mentioned the TOF-determining state (TDTS and TDI). IS* denotes the initial state that is adsorbed on the catalyst. "CH-OH" means CH bond formation followed by OH bond formation. Ru sol corresponds to the calculations modeling the water as a continuum medium. Energies are given in eV.

We have also increased the number of surrounding water molecules up to eleven for the TD-I and TS-TS of the alkoxy route on Ru. The energetic span does not change much: 0.99eV using one water molecule, 1.18eV using 3 water molecules and 1.03eV using 11 water molecules. The corresponding transition state structures are provided in Figure S3.
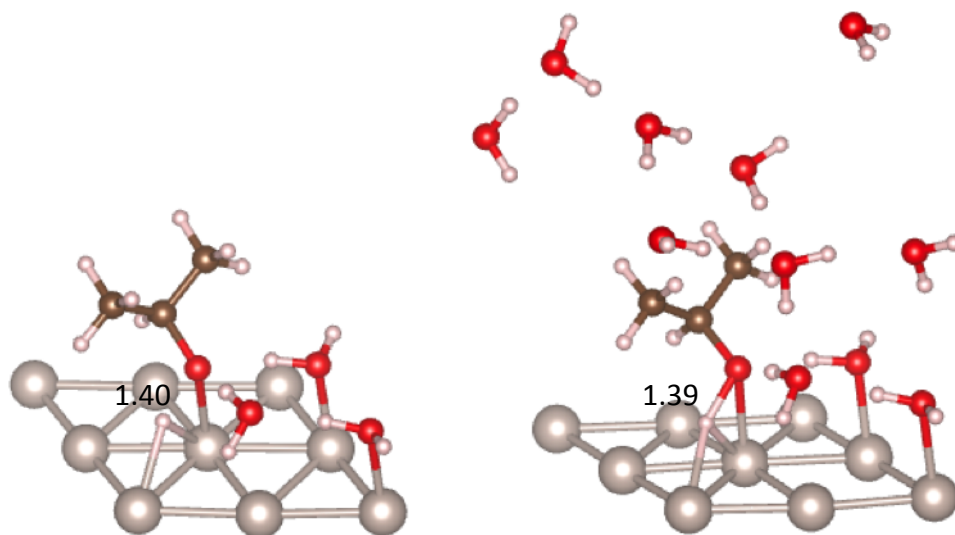
Figure S3. Transition states structures of the TS_{CH-OH} for the hydrogenation of acetone on Ru(0001) in presence of three water molecules (left structure) and 11 water molecules (right structure).

Last, we have also explored an alternative route that includes the splitting/regeneration of a water molecule (Figure S4). However, the transition state of hydrogenation of the surface hydroxy is comparable in energy to the hydrogenation of the alkoxy . It is the TD-TS of this alternative route.
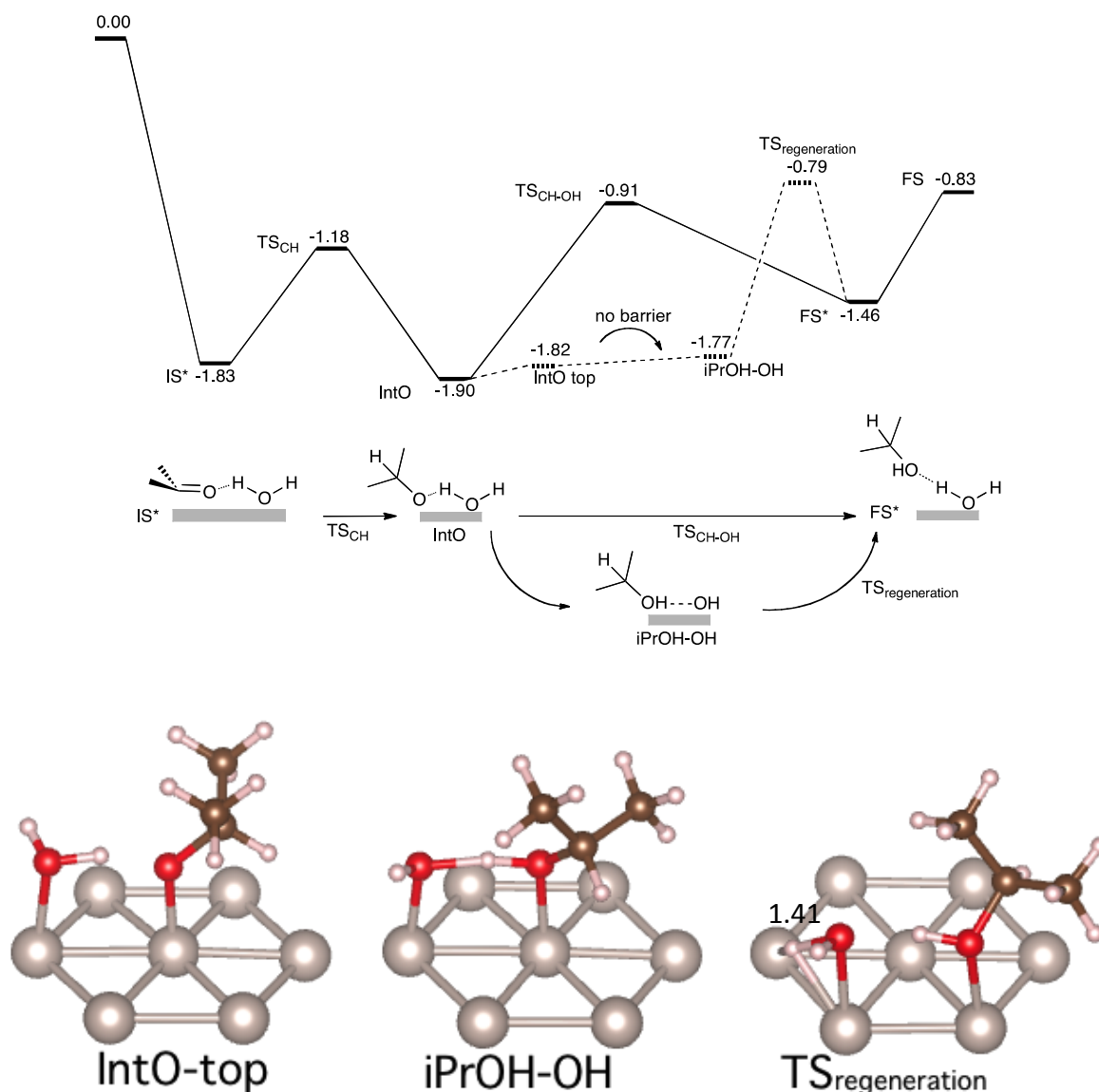
Figure S4. Alkoxy reactions paths for the hydrogenation of acetone on Ru(0001) in presence of a water molecule. The reference energy is common and includes the acetone and a H_2

molecule in gas phase, three bare Ru(0001) slabs and a 'hydrated' slab bearing a chemisorbed water molecule. The straight line corresponds to the Alkoxy mechanism presented in the Communication, Figure 3. The dash line corresponds to an alternative route. First, the alkoxy is lifted up in a top position. Then, it is protonated directly by the H-bonded water in a barrierless process. Last, the H-bonded hydroxyl is protonnated by a surface hydrogen to regenerate water and avoid hydroxyl accumulation at the catalyst surface. The structures corresponding to this alternative path are represented below. The others structures are given later in this ESI, part 4.
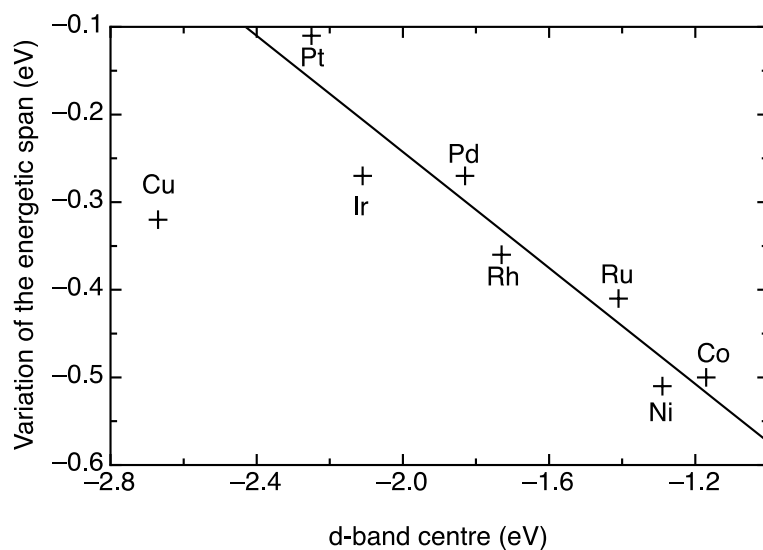
Figure S5. Variation of the energetic span of the alkoxy route upon water assistance in function of the d-band centre as computer by Hammer and Norskov *in Advances in Catalysis* 45, 71-129 (2000). As expected, the Cu is not on the linear relation since the d-band is full and as a consequence, the d-band model is not applicable.

3- Energies of some important species

a) Energies of the metallic slabs and of some adsorbed species

Metal	H @ slab (hollow) (eV)	H₂O @ slab (O top) (eV)	Bare slab (eV)
Co	-243.67	*-254.37*	-239.77
Ni	-189.27	*-199.92*	-185.33
Cu	-130.12	-141.00	-126.52
Ru	-314.93	*-325.63*	-310.95
Rh	-249.28	*-260.01*	-245.32
Pd	-181.35	*-191.83*	-177.24
Ir	-304.19	*-314.94*	-300.35
Pt	-210.68	*-221.36*	-206.81

b) Energies of the corresponding species in gas phase

Gas phase (eV)	
Acetone	-56.15
iPrOH	-63.76
iPrO	-57.95
MeCOHMe	-58.53
iPrOH.H₂O	-78.32
Acetone.H₂O	-70.73
iPrO.H₂O	-72.51
MeCOHMe.H₂O	-73.01
H₂O	-14.27
H₂	-6.78

4- Structures corresponding to hydrogenation of acetone in gas phase

Hydrogenation of acetone in gas phase on Co (0001)

Alkoxy route

	IS	*TS*	*FS*
CHα	-296.32608 eV	299.812393 eV	-300.650426 eV
CHαOH	-300.715143 eV	-303.050673 eV	-303.897567 eV

Alkyl route

	IS	*TS*	*FS*
OH	-296.32608 eV	-298.795913 eV	-299.454975 eV
OHCHα	-299.454975 eV	-302.708119 eV	-303.889627 eV

Hydrogenation of acetone in gas phase on Ni (111)

Alkoxy route

	IS	TS	FS
CHα	-241.855653 eV	1.61 -245.035938 eV	1.10 -246.002494 eV
CHαOH	-246.002494 eV	1.55 -248.574612 eV	0.98 -249.458336 eV

Alkyl route

	IS	TS	FS
OH	-241.855653 eV	1.40 -244.549353 eV	0.98 -245.160052 eV
OHCHα	-245.156238 eV	1.79 -248.426644 eV	1.10 -249.455466 eV

Hydrogenation of acetone in gas phase on Cu (111)

	Alkoxy route		
	IS	*TS*	*FS*

CHα

-182.855169 eV   -185.595156 eV   -186.784468 eV

CHαOH

-186.784468 eV   -189.195468 eV   -190.519320 eV

	Alkyl route		
	IS	*TS*	*FS*

OH

-182.855169 eV   -185.524675 eV   -185.669631 eV

OHCHα

-185.669631 eV   -189.06020102 eV   -190.519320 eV

Hydrogenation of acetone in gas phase on Ru (0001)

Alkoxy route

	IS	*TS*	*FS*
CHα	-367.561910 eV	1.77 -370.794092 eV	1.10 -371.788612 eV
CHαOH	-371.761665 eV	1.47 -374.373565 eV	0.98 -375.163441 eV

Alkyl route

	IS	*TS*	*FS*
OH	-367.561910 eV	1.42 -370.307606 eV	0.98 -371.032118 eV
OHCHα	-371.032118 eV	1.51 -374.151798 eV	1.10 -375.147328 eV

Hydrogenation of acetone in gas phase on Rh (111)

Alkoxy route

	IS	TS	FS
CHα	-301.950535 eV	1.67 -305.167493 eV	1.10 -305.812811 eV
CHαOH	-305.812811 eV	1.58 -308.722177 eV	0.98 -309.559483 eV

Alkyl route

	IS	TS	FS
OH	-301.950535 eV	1.52 -304.883719 eV	0.98 -305.57362 eV
OHCHα	-305.566593 eV	1.52 -308.667107 eV	1.11 -309.555802 eV

Hydrogenation of acetone in gas phase on Pd (111)

Alkoxy route

	IS	TS	FS
CHα	-233.773822 eV	1.55 / -236.724203 eV	1.10 / -237.326776 eV
CHαOH	-237.326776 eV	1.59 / -240.419159 eV	0.98 / -241.393403 eV

Alkyl route

	IS	TS	FS
OH	-233.773822 eV	1.53 / -236.794680 eV	0.99 / -237.466329 eV
OHCHα	-237.469869 eV	1.63 / 2.60 / -240.628223 eV	1.11 / -241.392006 eV

Hydrogenation of acetone in gas phase on Ir (111)

Alkoxy route

	IS	*TS*	*FS*
CHα	-356.814976 eV	1.56 -360.028068 eV	1.10 -360.385909 eV
CHαOH	-360.385909 eV	1.55 -363.667166 eV	0.98 -364.494878 eV

Alkyl route

	IS	*TS*	*FS*
OH	-356.814976 eV	1.49 -359.709233 eV	0.98 -360.417012 eV
OHCHα	-364.493856 eV	1.96 -363.541364 eV	1.11 -364.467600 eV

Hydrogenation of acetone in gas phase on Pt (111)

	Alkoxy route		
	IS	*TS*	*FS*

CHα

-263.262361 eV | **-2**66.318966 eV | -266.393520 eV

CHαOH

-266.393520 eV | **-2**69.995990 eV | -270.922080 eV

	Alkyl route		
	IS	*TS*	*FS*

OH

-263.262361 eV | -266.306334 eV | -267.113866 eV

OHCHα

-267.113866 eV | -270.119551 eV | -270.922080 eV

5- Structures corresponding to hydrogenation of acetone in water

Water assisted hydrogenation of acetone on Co (0001)

Alkoxy route

	IS	*TS*	*FS*
CHα	-310.994503 eV	1.63 -314.399657 eV	1.12 -315.145104 eV
CHαOH	1.12 -315.145104 eV	1.43 -318.046455 eV	0.99 -318.752454 eV

Alkyl route

	IS	*TS*	*FS*
OH	-310.994503 eV	1.38 -313.569919 eV	0.98 -314.110173 eV
OHCHα	-314.110173 eV	1.64 -317.339776 eV	1.11 -318.752454 eV
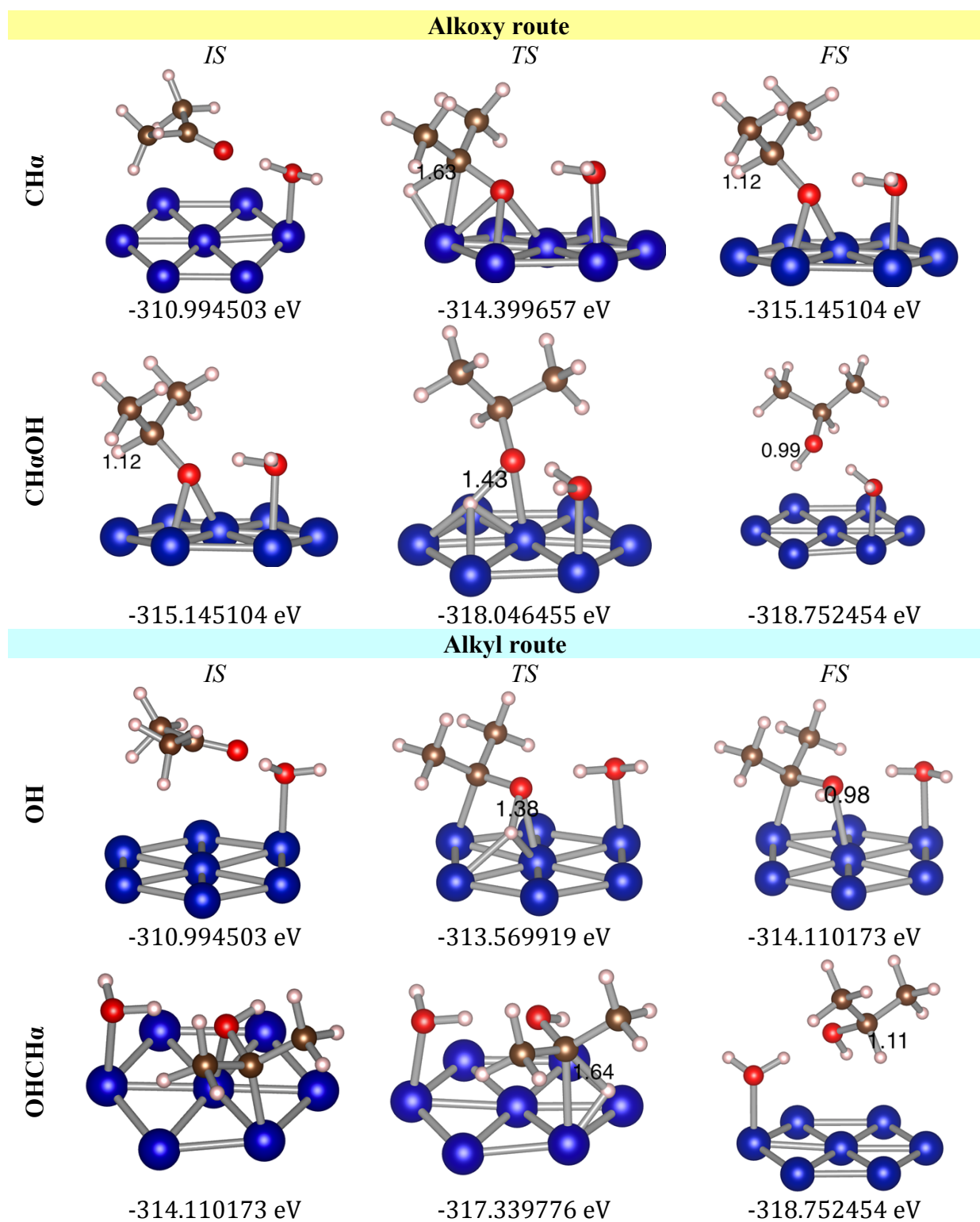
Water assisted hydrogenation of acetone on Ni (111)

Alkoxy route		
IS	*TS*	*FS*

CHα

-259.774676 eV

1.62

-262.982929 eV

1.12

-260.474738 eV

CHαOH

-260.474738 eV

1.44

-263.554388 eV

0.98

-264.279038 eV

Alkyl route		
IS	*TS*	*FS*

OH

-256.593318 eV

1.37

-258.972214 eV

0.99

-259.603795 eV

OHCHα

-259.774676 eV

1.63

-262.982929 eV

1.10

-264.279038 eV

Acetone hydrogenation on Cu (111)

Alkoxy route

	IS	TS	FS
CHα	-197.634794 eV	-200.373908 eV (1.66)	-201.304666 eV (1.11)
CHαOH	-201.304666 eV	-204.189267 eV (1.59)	-205.327075 eV (0.99)

Alkyl route

	IS	TS	FS
OH	-197.634794 eV	-200.179352 eV (1.22)	-200.326660 eV (0.98)
OHCHα	-200.325039 eV	-203.405704 eV (2.09)	-205.290247 eV (1.11)

Water assisted hydrogenation of acetone on Ru (0001)

Alkoxy route

	IS	*TS*	*FS*
CHα	-382.431397 eV	1.57 -385.760225 eV	1.12 -386.478028 eV
CHαOH	-386.478448 eV	1.40 -389.468023 eV	0.99 -390.037614 eV

Alkyl route

	IS	*TS*	*FS*
OH	-382.431397 eV	1.40 -385.190877 eV	0.98 -385.778848 eV
OHCHα	-385.760883 eV	1.56 -388.828879 eV	1.11 -390.018826 eV

Water assisted hydrogenation of acetone on Rh (111)

Alkoxy route

	IS	*TS*	*FS*
CHα		1.57	1.12
	-316.713461 eV	-319.944825 eV	-320.549926 eV
CHαOH		1.47	0.99
	-320.549926 eV	-323.797039 eV	-324.418112 eV

Alkyl route

	IS	*TS*	*FS*
OH		1.43	0.98
	-316.752484 eV	-319.672178 eV	-320.277549 eV
OHCHα		1.57	1.11
	-320.212106 eV	-323.379600 eV	-324.418112 eV

Water assisted hydrogenation of acetone on Pd (111)

Alkoxy route

	IS	*TS*	*FS*
CHα	-248.501623	1.62 -251.562635 eV	1.14 -251.929310
CHαOH	-251.958979	1.54 -255.370960 eV	0.99 -256.203132 eV

Alkyl route

	IS	*TS*	*FS*
OH	-248.516013 eV	1.47 -251.460339 eV	0.99 -252.088957 eV
OHCHα	-252.114783 eV	1.64 -255.200371 eV	1.11 -256.224068 eV

Water assisted hydrogenation of acetone on Ir (111)

Alkoxy route

	IS	*TS*	*FS*
CHα	-371.615299 eV	-374.776338 eV	-375.323088 eV
CHαOH	-375.323088 eV	-378.607285 eV	-379.356367 eV

Alkyl route

	IS	*TS*	*FS*
OH	-371.615299 eV	-374.348891 eV	-374.999867 eV
OHCHα	-375.049251 eV	-378.096703 eV	-379.356367 eV

Water assisted hydrogenation of acetone on Pt (111)

Alkoxy route

	IS	*TS*	*FS*
CHα	-278.039190 eV	1.50 -281.048319 eV	1.11 -281.375524 eV
CHαOH	-281.380458 eV	1.61 -284.884280 eV	0.99 -285.731543 eV

Alkyl route

	IS	*TS*	*FS*
OH	-278.039190 eV	1.47 -281.111213 eV	0.99 -281.760109 eV
OHCHα	-281.760109 eV	1.72 -284.597112 eV	1.11 -285.759984 eV