Effect of Cu and Sb active sites on acid-base properties and reactivity of the hydrated alumina for glycerol conversion by dehydrogenation and dehydration reactions

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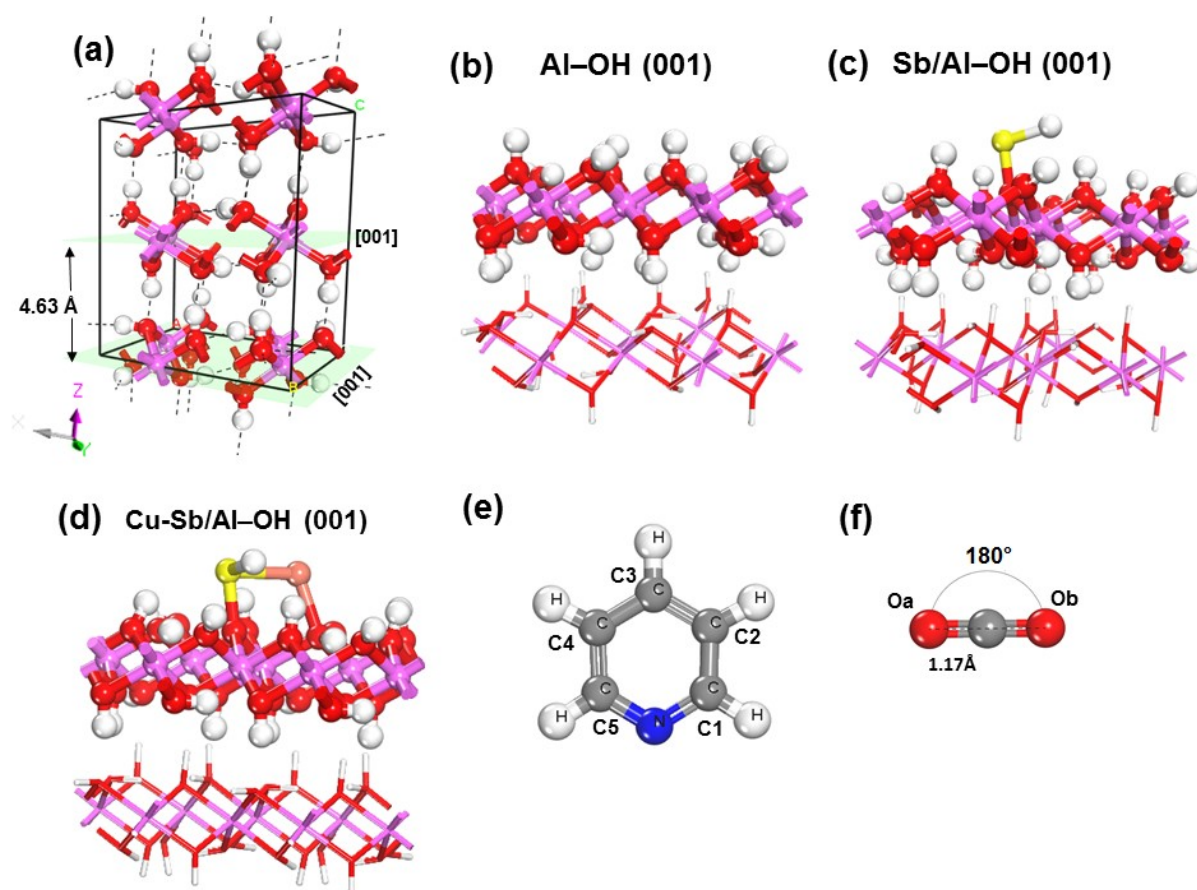
Supplementary Information

Fig. S1. Optimized structures of (a) Bayerite β-Al(OH)$_3$, (b) side view of the (2 × 1) supercell of the bayerite Al–OH (001) surface, (c) doped with Sb atom; (d) doped with Cu-Sb atoms and (e and f) Free pyridine and CO$_2$ molecules. Pink, red, white, grey, light brown, blue and yellow balls are Al, O, H, C, Cu, N and Sb atoms, respectively.
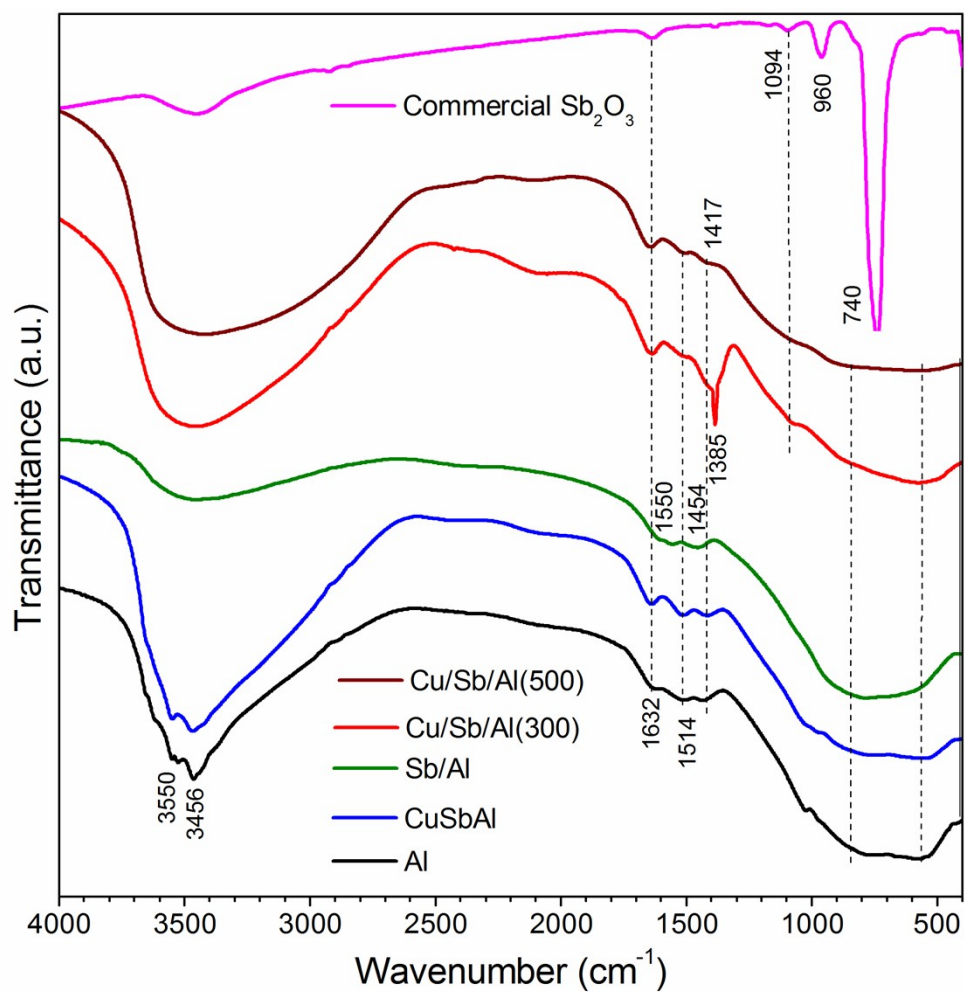
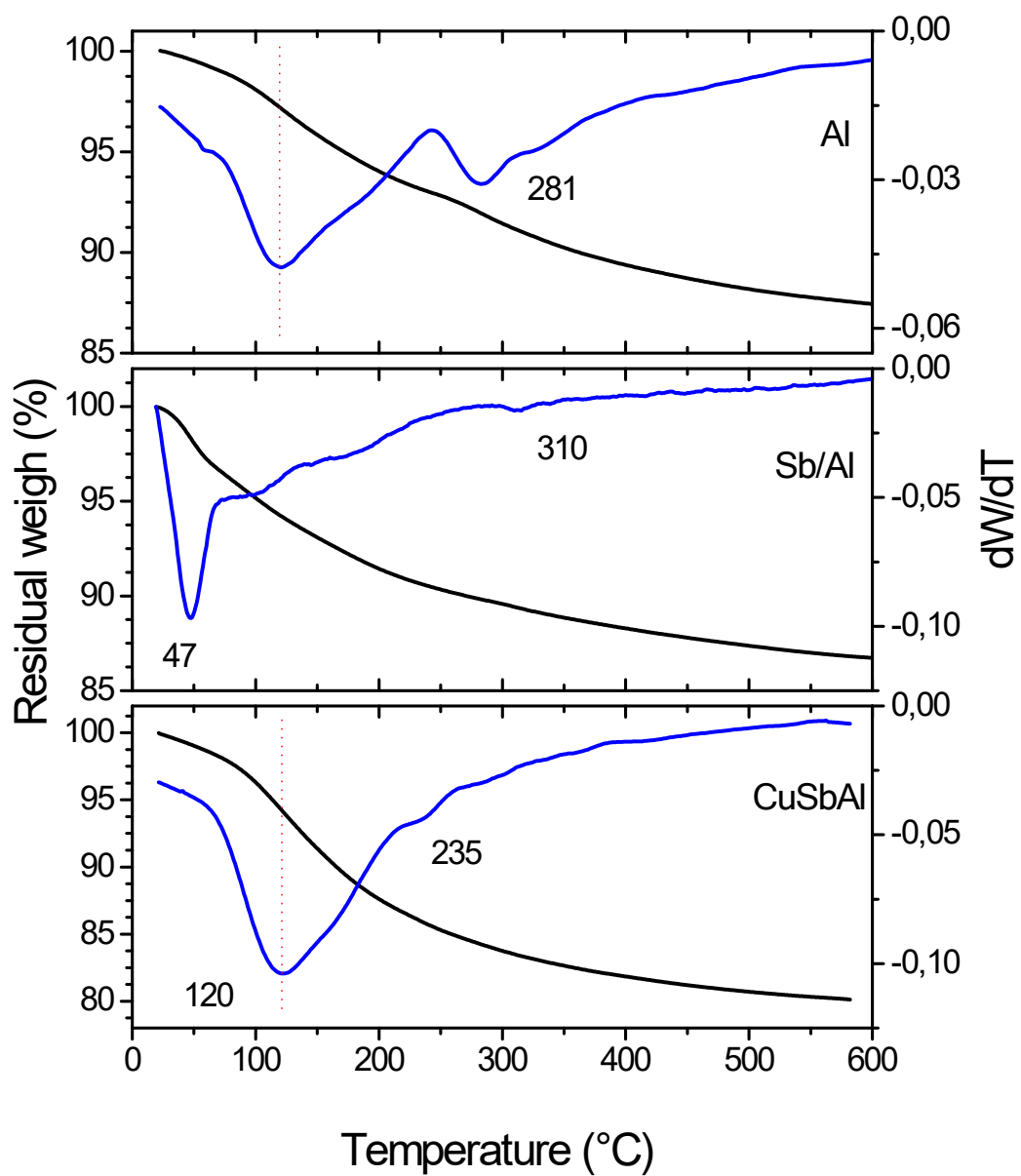**Fig. S2.** FT-IR spectra of the prepared samples and the commercial antimony oxide.

Fig. S3. TGA profiles and DTG curves obtained for Al, Sb/Al and CuSbAl samples after calcination at 500°C and exposure to the water vapour at room temperature.

Table S1. Calculated atomic charges originating from a Bader analysis for the surface atoms on the periodic models considered in this study.

Surfaces	Atomic Bader charges (e)					
	O(15)	O(38)	H(6)	Sb	Cu	Structure
Al – OH(001)	-1.39	-1.44	0.56			Fig.S1(b)
Sb/Al – OH(001)	-1.41	-	-0.39	0.99		Fig.S1(c)
Cu-Sb/Al – OH(001)	-1.46	-1.38	-0.37	0.87	0.10	Fig.S1(d)

\# Atom number correspondent position, see Figure. O(15) is the O atom bonded to the Sb atom. O(38) is the O atom bonded to the Cu atom. H(6) is the H atom bonded to the Sb atom.

Table S2. Atomic Bader charges for an isolated CO_2 molecule, Sb and Cu atoms, in the most stable CO_2 adsorption configurations on the different surfaces for comparison.

Structures	Atomic Bader charges (e)						
	C	O(a)	O(b)	Sb	Cu	Interaction site	Structure
CO_2/Al – OH(001)	2.20	-1.09	-1.10	-	-	O(b)···H(41)	Fig.9(a)
	2.16	-1.10	-1.09			O(b)···H(41)	Fig.9(d)
CO_2/Sb/Al – OH(001)	2.17	-1.11	-1.10	1.02	-	O(b)···H	Fig.9(b)
	2.20	-1.11	-1.12	1.01	-	O(b)···H(97)	Fig.9(e)
CO_2/Cu-Sb/Al – OH(001)	2.17	-1.10	-1.09	0.87	0.12	O(b) ···Cu-Sb	Fig.9(c)
	1.72	-1.05	-1.08	0.97	0.36	C –Cu-Sb	Fig.9(f)
CO_2 molecule	2.14	-1.07	-1.07	-	-		Fig.S1(f)

Table S3. Bader charges of the atoms (N, C4 and C5) for a pyridine molecule, Sb and Cu atoms, in the most stable pyridine adsorption configurations on the different surfaces. It also presents the pyridine molecule interaction type on the surface.

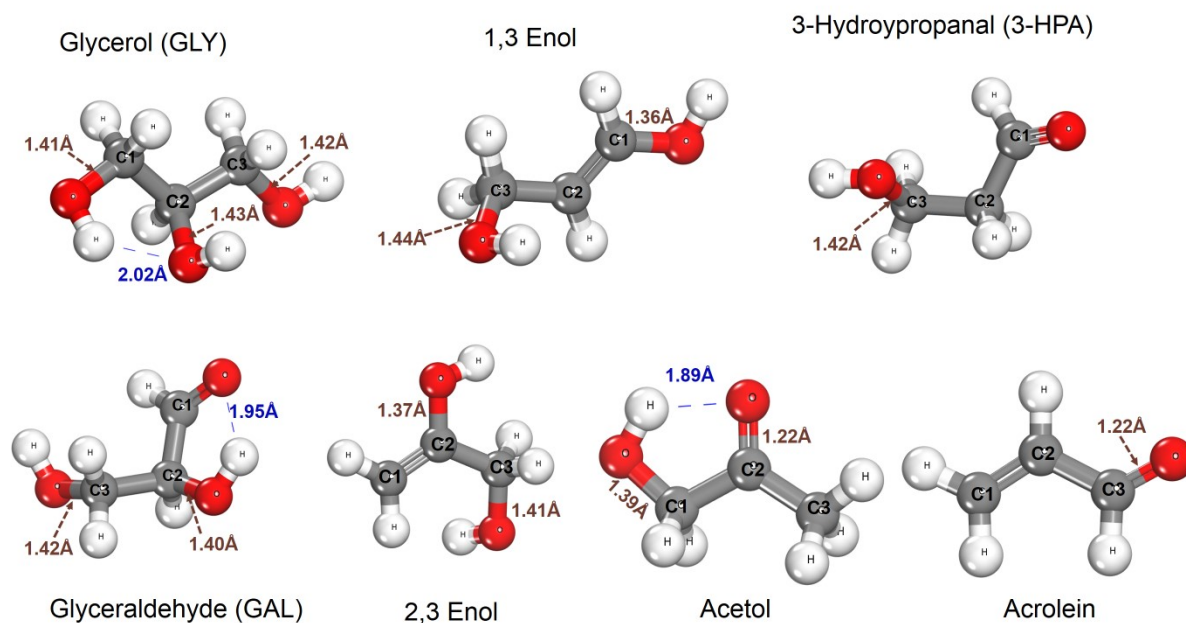| Structures	Atomic Bader charges (*e*)					Interaction site	Interaction type	Structure
	N	C(5)	C(4)	Sb	Cu			
Py/Al – OH(001)	-1.13	0.47	-0.05	-	-	N ···H(14)	Hydrogen	Fig.10(a)
	-1.20	0.49	-0.05	-	-	N ···H(14)	bond	Fig.10(d)
Py/Sb/Al – OH(001)	-1.28	0.30	-0.06	1.58	-	N –Sb	σ-bond	Fig.10(b)
	-1.14	0.47	-0.07	1.04	-			Fig.10(e)
Py/Cu-Sb/Al – OH(001)	-1.20	0.47	-0.03	0.76	0.26	N –Cu-Sb	σ-bond	Fig.10(c)
	-1.09	0.40	-0.13	0.75	0.31	C(i) –Cu-Sb	π-bond	Fig.10(f)
Pyridine molecule	-1.12	0.46	-0.03					Fig.S1(e)

Fig. S4. DFT optimized molecular geometries for glycerol, intermediates (1,3-enol, 3-hydroxypropanal, glyceraldehyde and 2,3-enol) and products (acetol and acrolein). The red, white and grey colours spheres represent O, H and C atoms, respectively.

Table S4. The DFT ground states energies (in eV and kJ/mol) for the molecular geometries shown in Figure S4.

Molecule isolated	E_{DFT} (eV)	E_{DFT} (kJ/mol)	*ΔE_{DFT} (eV)	*ΔE_{DFT} (kJ/mol)
Glycerol	-1877.66736	-181223.9	0.0000	0.0
1,3 -Enol	-1415.95727	-136661.8	461.7101	44562.2
3- Hidroxypropanal	-1416.16174	-136681.5	461.5056	44542.4
Glyceraldehyde	-1845.30572	-178100.5	32.3616	3123.4
2,3-Enol	-1415.90417	-136656.6	461.7632	44567.3
Acetol	-1416.65293	-136728.9	461.0144	44495.0
Acrolein	-954.288976	-92103.6	923.3784	89120.3

*ΔE_{DFT} = E –E_{GLY} means the relative DFT energy (in eV and kJ/mol) concerning the glycerol molecule.