

Electronic Supplementary information for:

Protodecarboxylation of carboxylic acids over heterogeneous silver catalysts

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1. X-ray diffractograms of 10 wt. % Ag on different supports
2. Nitrogen adsorption and desorption isotherms for Al₂O₃-supported Ag catalysts with 5 to 20 wt % loading. (Inset: pore size distribution curves).
3. Powder x-ray diffraction patterns of (a) calcined Al₂O₃ support (b) 5 (c) 10 (d) 15 and (e) 20 wt % Ag/Al₂O₃
4. TEM images of 5-20 wt. % Ag/Al₂O₃
5. XPS spectra of 5-20 wt. % Ag/Al₂O₃
6. Effect of the amount of K₂CO₃
7. Estimation of surface Ag atoms
8. Effect of silver loading on crystallite size and catalytic activity of Ag/Al₂O₃

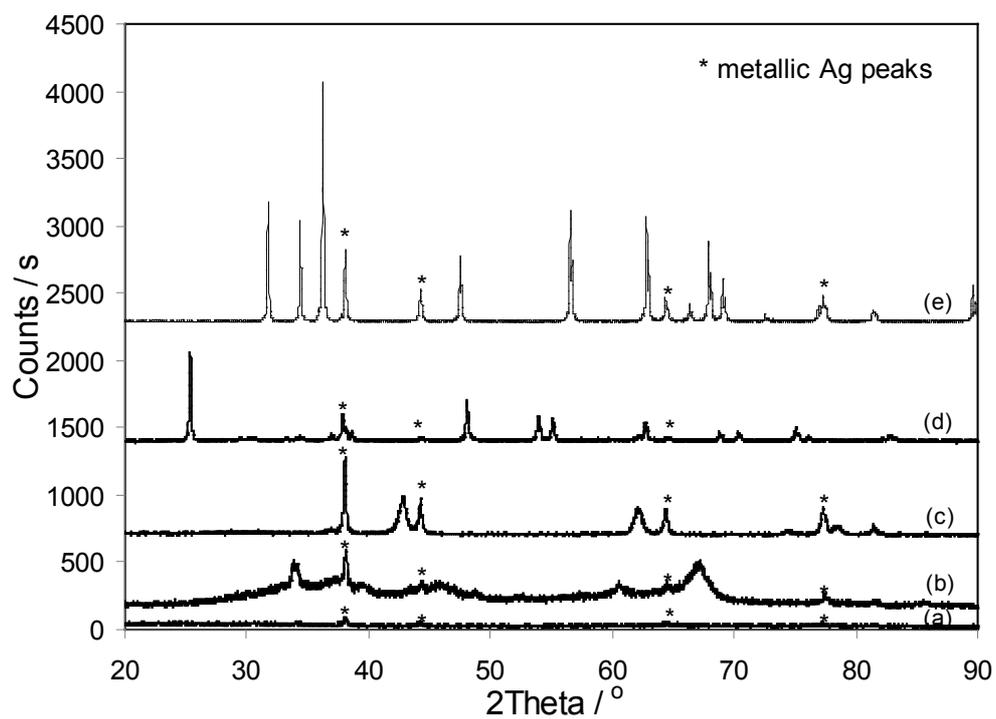


Fig. S1. X-ray diffractograms of 10 wt. % Ag supported on (a) SiO_2 (b) Al_2O_3 (c) MgO (d) TiO_2 and (e) ZnO .

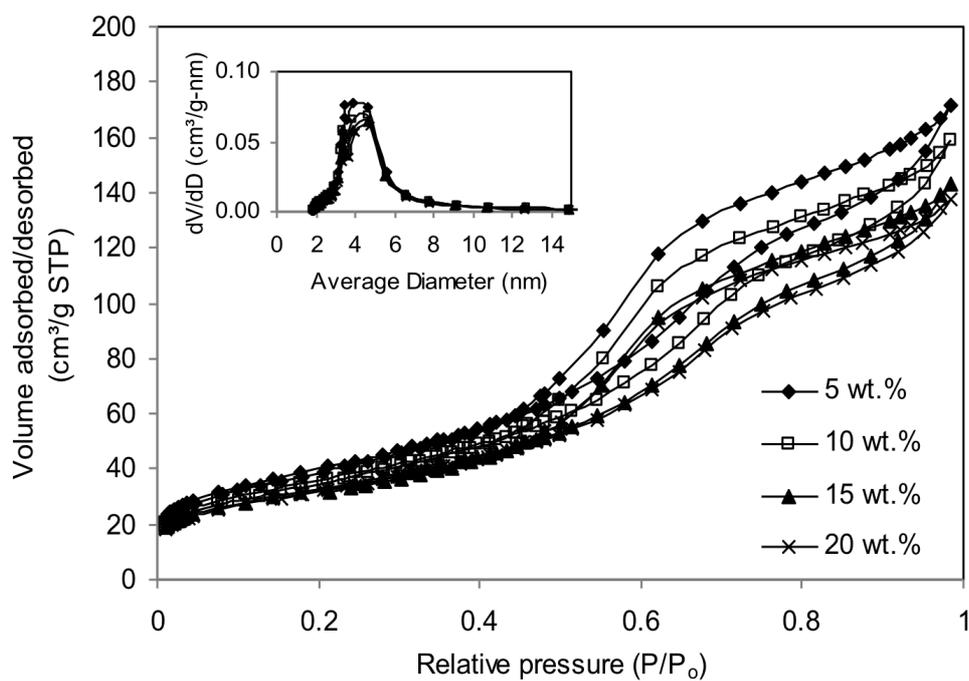


Fig. S2. Nitrogen adsorption and desorption isotherms for Al_2O_3 -supported Ag catalysts with 5 to 20 wt % loading. (Inset: pore size distribution curves).

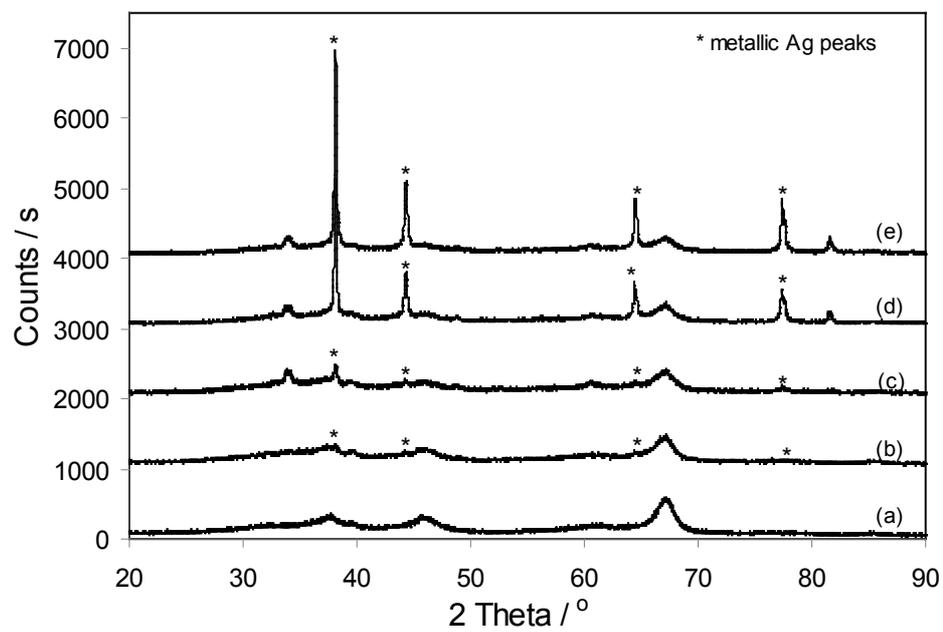


Fig. S3. Powder x-ray diffraction patterns of (a) calcined Al₂O₃ support (b) 5 (c) 10 (d) 15 and (e) 20 wt % Ag/Al₂O₃ (traces are offset by 1000 counts).

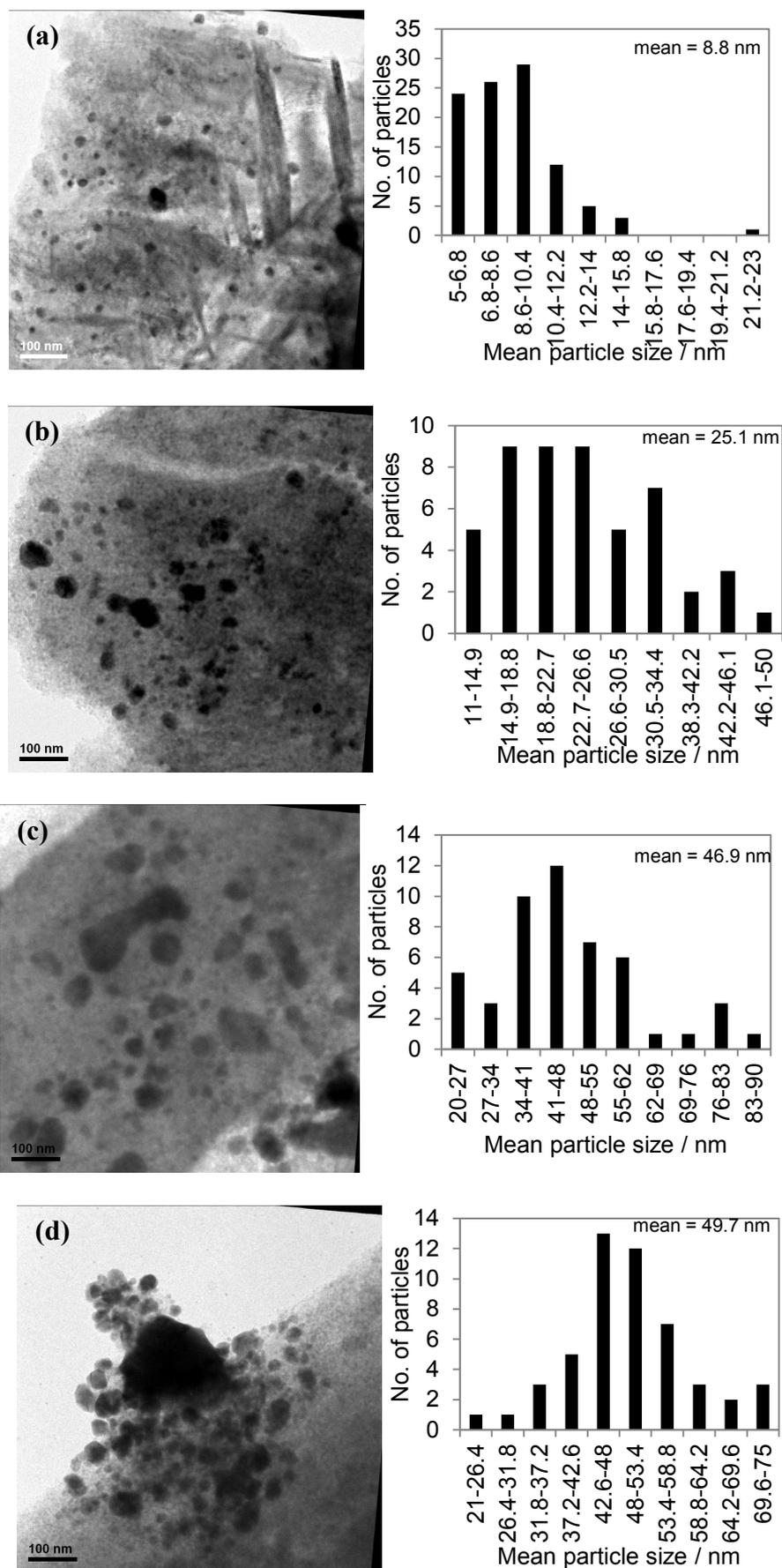


Fig. S4. TEM images of (a) 5 wt %, (b) 10 wt %, (c) 15 wt %, (d) 20 wt % Ag/Al₂O₃.

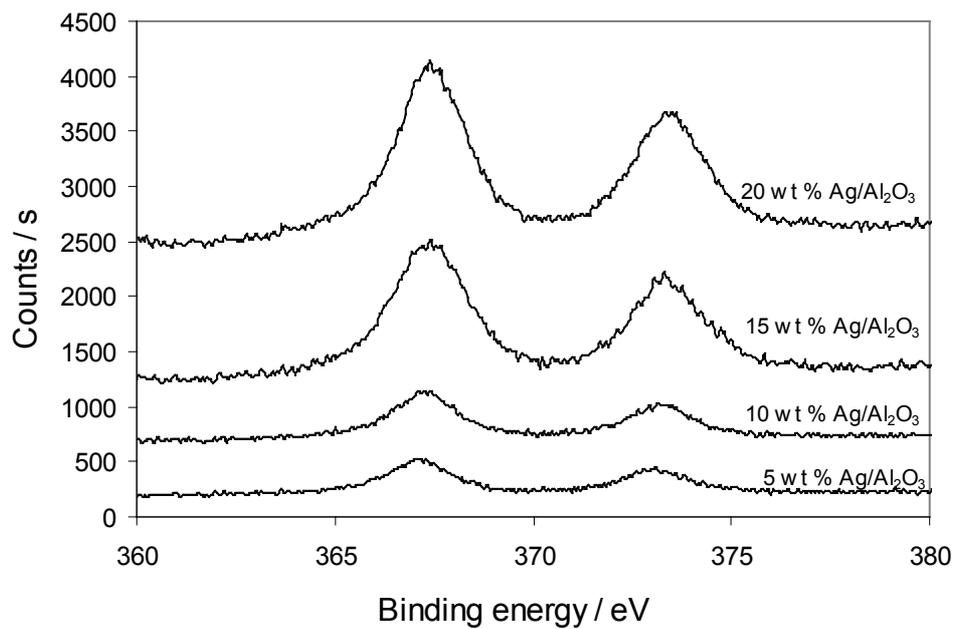


Fig. S5. Ag 3d_{5/2} photoelectron spectra for 5-15 wt % Ag/Al₂O₃.

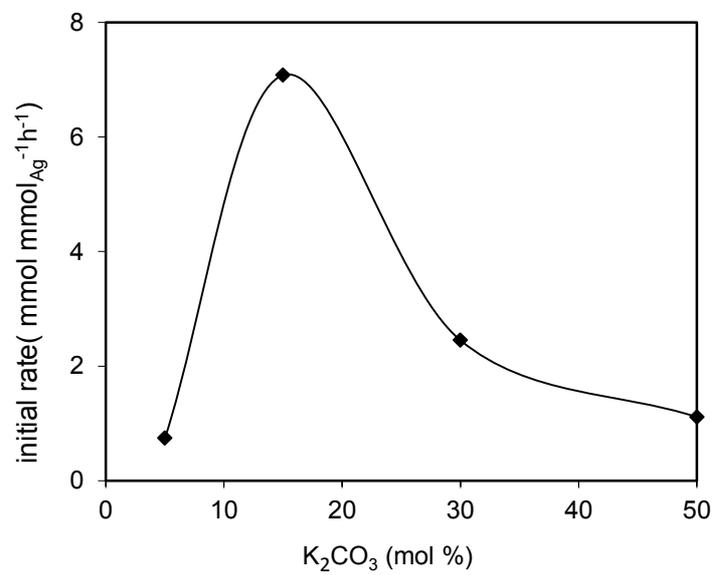


Fig. S6. Plot of initial rate versus mol % of K₂CO₃.

Estimation of surface Ag atoms

The supported Ag nanoparticles has a *fcc* crystal lattice structure and each atom is surrounded by twelve others, according to a full shell close packing model. The total number of Ag atoms (N_T) can be estimated according to equation (1), where $\langle d \rangle$ correspond to the mean diameter of Ag particles determined experimentally by Scherrer's equation using XRD data and d_{at} is the atomic diameter of Ag (0.289 nm). Number of shells, m , can be determined using equation (2) and used to estimate the total number of external atoms, N_s , according to equation (3).^{27,28}

$$\langle d \rangle = 1.105 \times d_{at} \times N_T^{1/3} \quad (1)$$

$$N_T = \frac{(10m^3 - 15m^2 + 11m - 3)}{3} \quad (2)$$

$$N_s = 10m^2 - 20m + 12 \quad (3)$$

Table S1. Effect of silver loading on crystallite size and catalytic activity of Ag/Al₂O₃

Ag loading (wt. %)	Crystallite size (nm)	N _s x10 ³ /particle	N _{s,rxn} x 10 ¹⁸	Initial rate (mmol.mmol _{Ag} ⁻¹ .h ⁻¹)	TOF ^a (h ⁻¹)
5	5	1	31	5.1	19.6
10	40	70	4.3	7.6	216
15	63	170	2.8	3.9	173
20	93	380	1.8	1.9	125
AgOAc	—	—	121	6.2	6.2
Ag ^b	2,200 ^d	350,000	0.06	0.047	90
Ag ^c	22,000 ^d	35,000,000	0.006	0.005	94
Ag ₂ O ^b	84	310	4.3	0.8	43
Ag ₂ O ^c	94	390	3.9	0.5	32

Reaction conditions: 2 mmol 2-nitrobenzoic acid, 0.2 mmol Ag, 15 mol % K₂CO₃, 4 mL DMA, 120 °C.

^awith respect to number of surface Ag atoms on the catalyst

^bex-Ag₂CO₃

^ccommercial source

^dcalculated from BET surface area