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Supported heterogeneous catalysts: What controls cobalt nanoparticle dispersion on alumina?

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Assemblage of 8 nm Cobalt particles onto alumina support

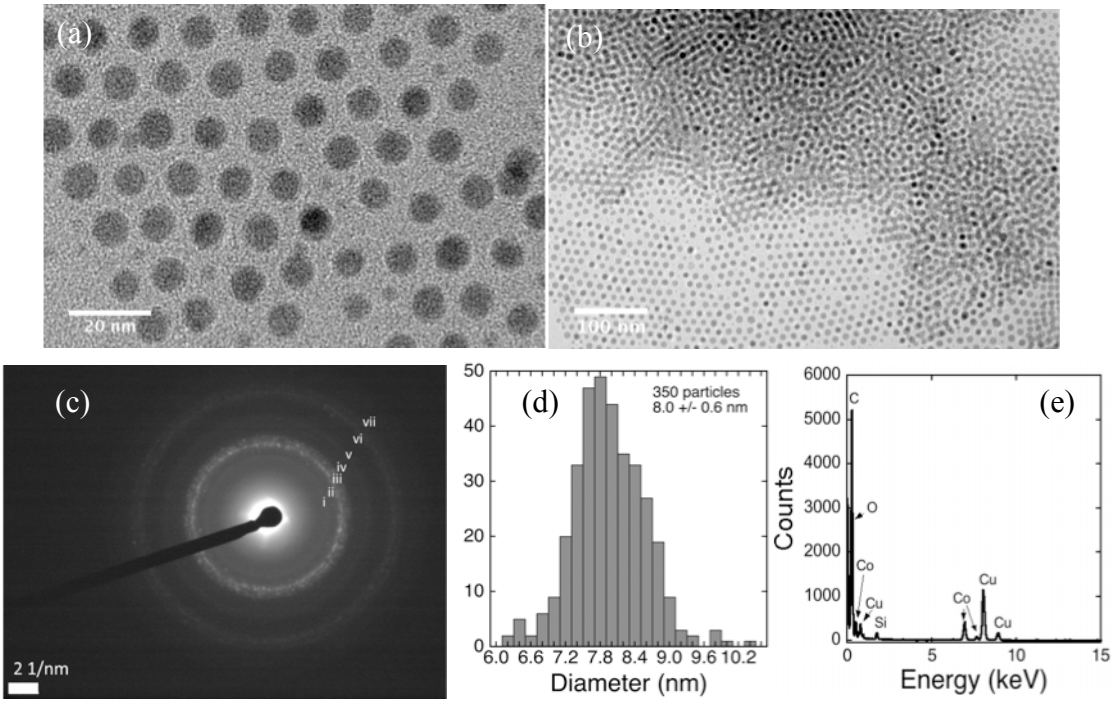

Fig. S1: *Bright field TEM images (a) (b) of 8.0 ± 0.6 nm Co nanoparticles used. (c) Selected area electron diffraction; labels correspond to the ε-Co phase ii (221) iii (310) iv (311) vi(510) vii(520) with some oxidation CoO i (111) v(220); (d) histogram of the 350 particles were used to determine the size. (e) Elemental analysis of the TEM confirms the presence of cobalt.*

Table S1: *SAED assignment of 8 nm particles.*

(hkl)	SAED d-spacings (nm)	SAED Figure S1c label	d-spacing ε-Co Angew. Chem. Int. Ed. 38 1788 (1999)	Relative intensity (%) ε-Co	d-spacing JCPDS 09-0402 CoO	Relative intensity (%)JCPDS 09-0402 CoO
(111)	0.253	i	-	-	0.246	74.7
(221)	0.205	ii	0.203	100	-	-
(310)	0.195	iii	0.193	58	-	-
(311)	0.188	iv	0.1838	25	-	-
(220)	0.150	v	-	-	0.150	49.8
(510)	0.121	vi	0.1195	21	-	-
(520)	0.114	Vii	0.103	19	-	-

It is noted that passive oxidation of the surface to CoO has occurred on exposure of the particles to air during characterization. Oxidation of the particles is likely to only occur at the surface of the particle < 2 nm. [1, 2]

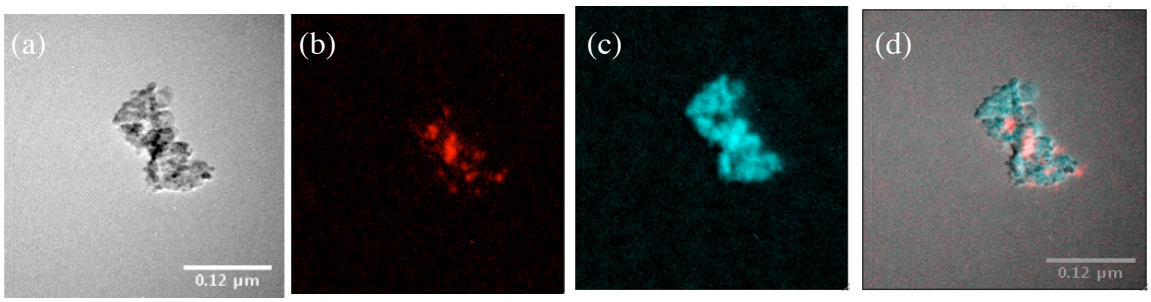

Fig. S2: *The distribution of the nanoparticles on the alumina support is difficult to see in the Bright field TEM images. EFTEM analysis is used (a-d) to highlight the cobalt particles. (a) Unfiltered image with all elemental energies shown; (b) a Co filtered map; (c) O filtered map and (d) is an overlay of (a), (b) and (c).*

Synthesis of large polycrystalline cobalt particles

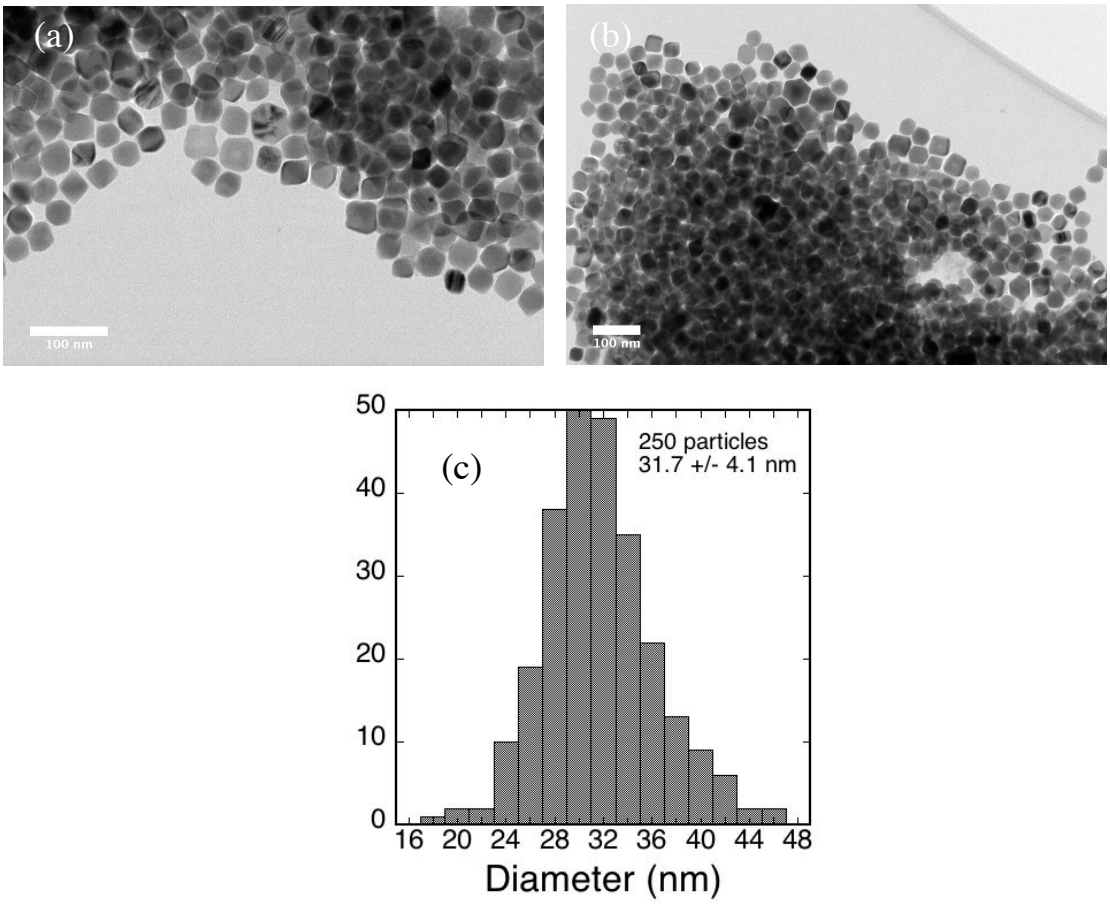

Fig. S3: *Bright field TEM images (a) (b) of 31 ± 4 nm Co nanoparticles used. (c) histogram of the 250 particles were used to determine the size.*

Assemblage of 8 nm Cobalt particles onto MCM-41 support

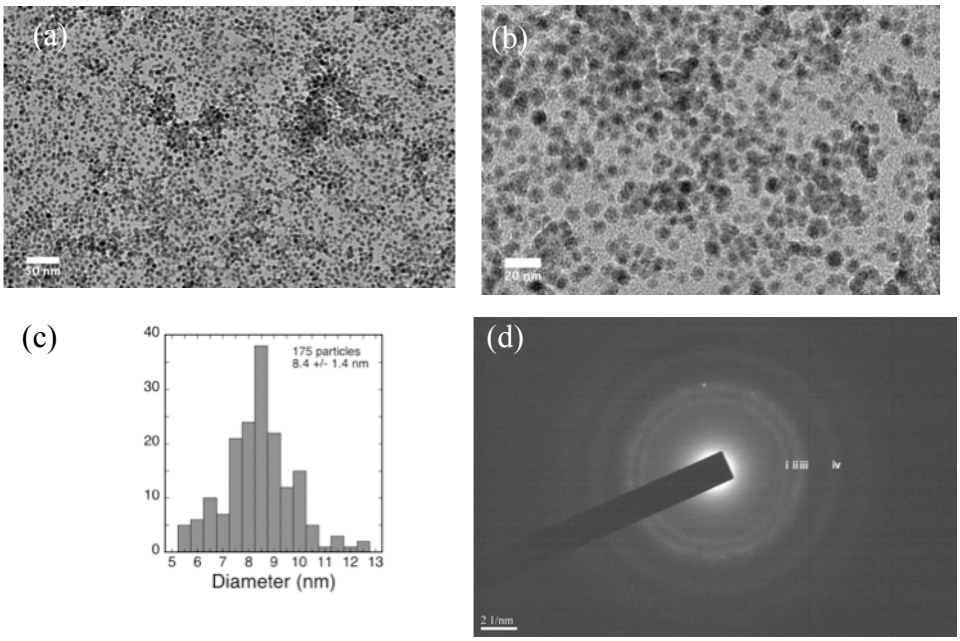

Fig. S4: *Characterisation of Co Nanoparticles assembled onto MCM-41 support. Bright field TEM images (a) (b) of 8.5 +/- 1.4 nm Co nanoparticles. (c) Histogram for the 175 particles used in the size analysis (d) SAED labels correspond to the i (211), ii (220), iii (221), and iv is broadened (311)/(510) ε-Co Angew. Chem. Int. Ed. 38 1788 (1999).*

Synthesis and characterisation of MCM-41

MCM-41 has been prepared using a literature method (Kumar, D.; Schumacher, K.; Hohenesche, C. d. F. v.; Grun, M.; Unger, K. K. *Colloids Surf. A,* **109,** 187-188, 2001.). Before use the support was heated at for 1 hour in N_2 then calcined overnight in air for 7 days at 550 ^{O}C (pore diameter 22 Å, BET surface area 1107 m^2/ g). Powder XRD of the material after calcination suggested hexagonal order with the observed 34.90, 20.13, and 17.45 Å d –spacings consistent with the (100) (110) and (200) of MCM-41 (JCPDS 49-712). A bright field TEM image of the calcined MCM material (Figure S5) highlights that the material is well ordered and highly porous.

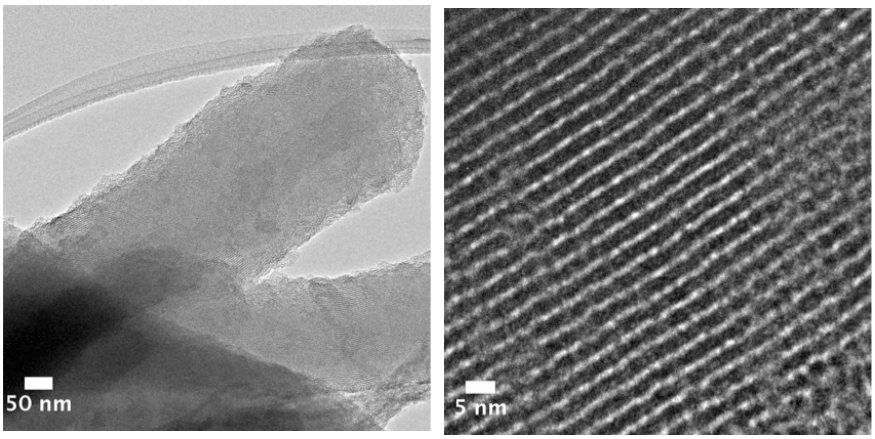

Fig. S5: *Bright field TEM images of MCM-41. (left) The material appears to be well order with a regular particles size and shaped. (right) The pores/channels viewed perpendicular to the pore axis result in alternate black and white lines.*

Treatment of alumina supports

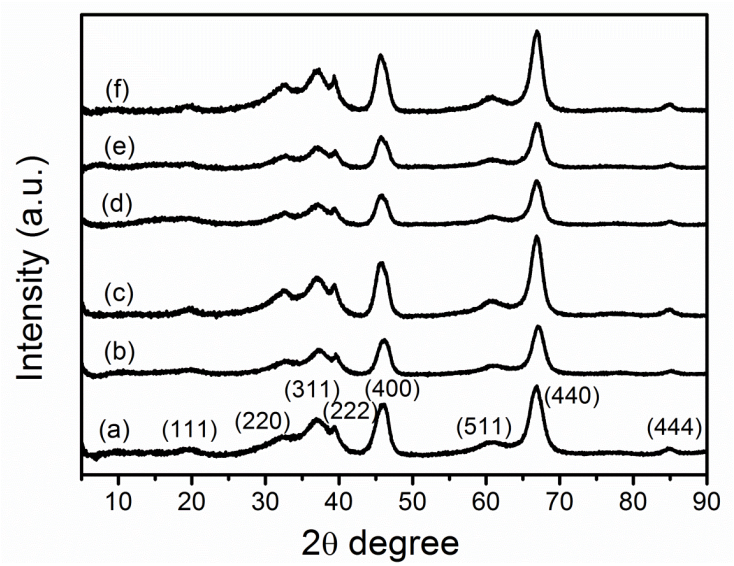

Fig. S6: *XRD spectra of the treated alumina supports. (a) commercial alumina (SASOL puralox SBa200 batch B27013 size < 90 micron) (b) calcined* (750 ^{o}C for 2.5 hrs) *alumina (c) calcined acid-alumina pH 2 treatment (d) calcined acid-alumina pH 4 treatment (e) calcined base-alumina pH 8 treatment (f) calcined base-alumina pH12 treatment. Assignment based on* γ*-*Al_2O_3 *JCDCS 50-0741.*

Table S2: *Textural properties of the chemically-treated alumina supports.*

Sample	BET Surface Area (m^2/g)	BJH Desorption pore diameter (Å)
Calcined Alumina	162	84
Calcined acid-Alumina pH2	160	89
Calcined acid-Alumina pH4	154	89
Calcined base – Alumina pH 8	151	89
Calcined base-Alumina pH 12	139	101

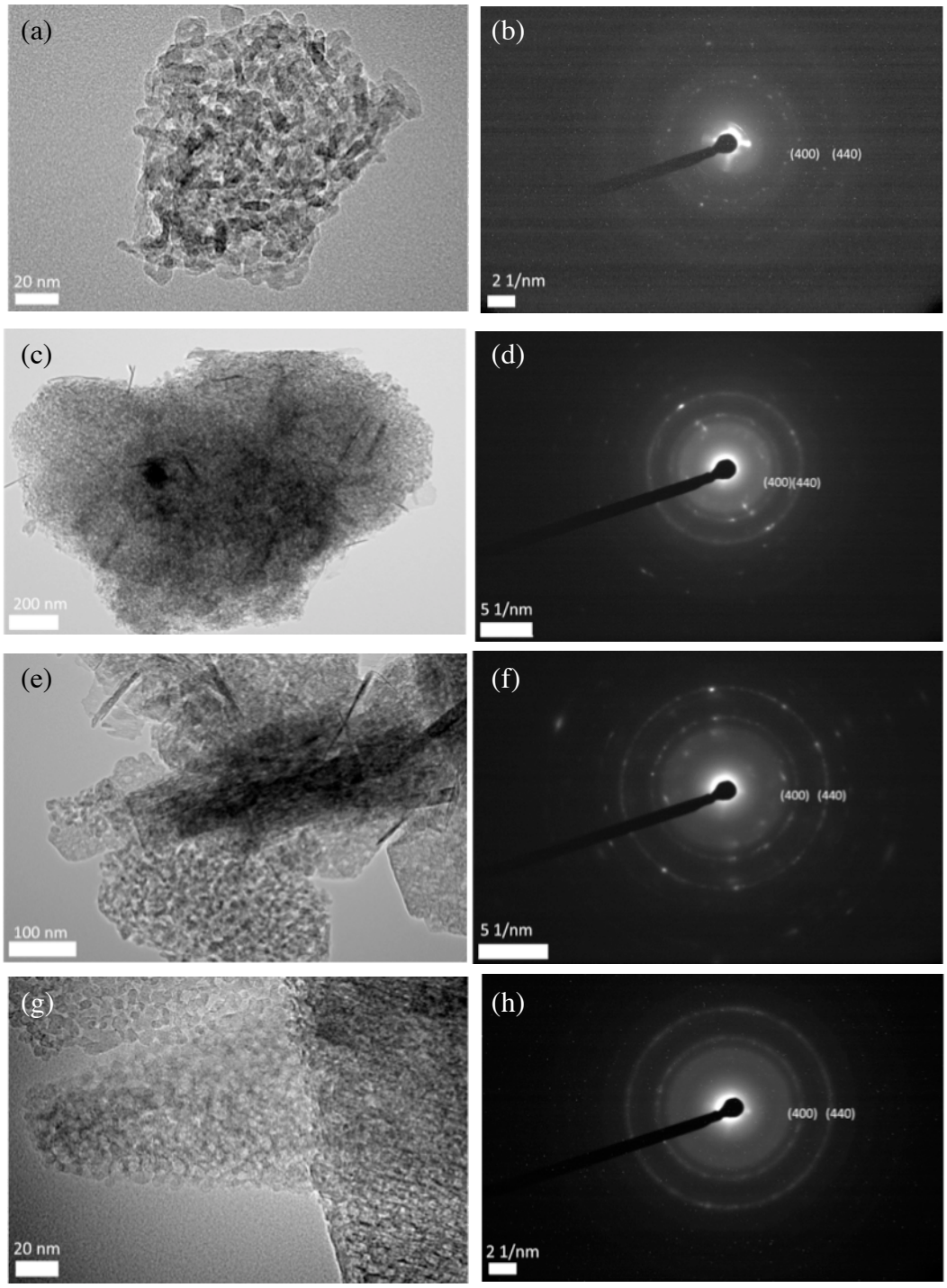

Fig. S7: *Bright field TEM images and SAED pattern (γ-Al_2O_3 JCDCS 50-0741 assignment) of chemically treated supports. (a,b) calcined acid-alumina pH 2 (c,d) calcined acid-alumina pH 4 (e,f) calcined base-alumina pH 8 (g,h) calcined base-alumina pH 12.*

Characterisation of Co nanoparticles assembled onto pH 2 and pH 12 treated supports

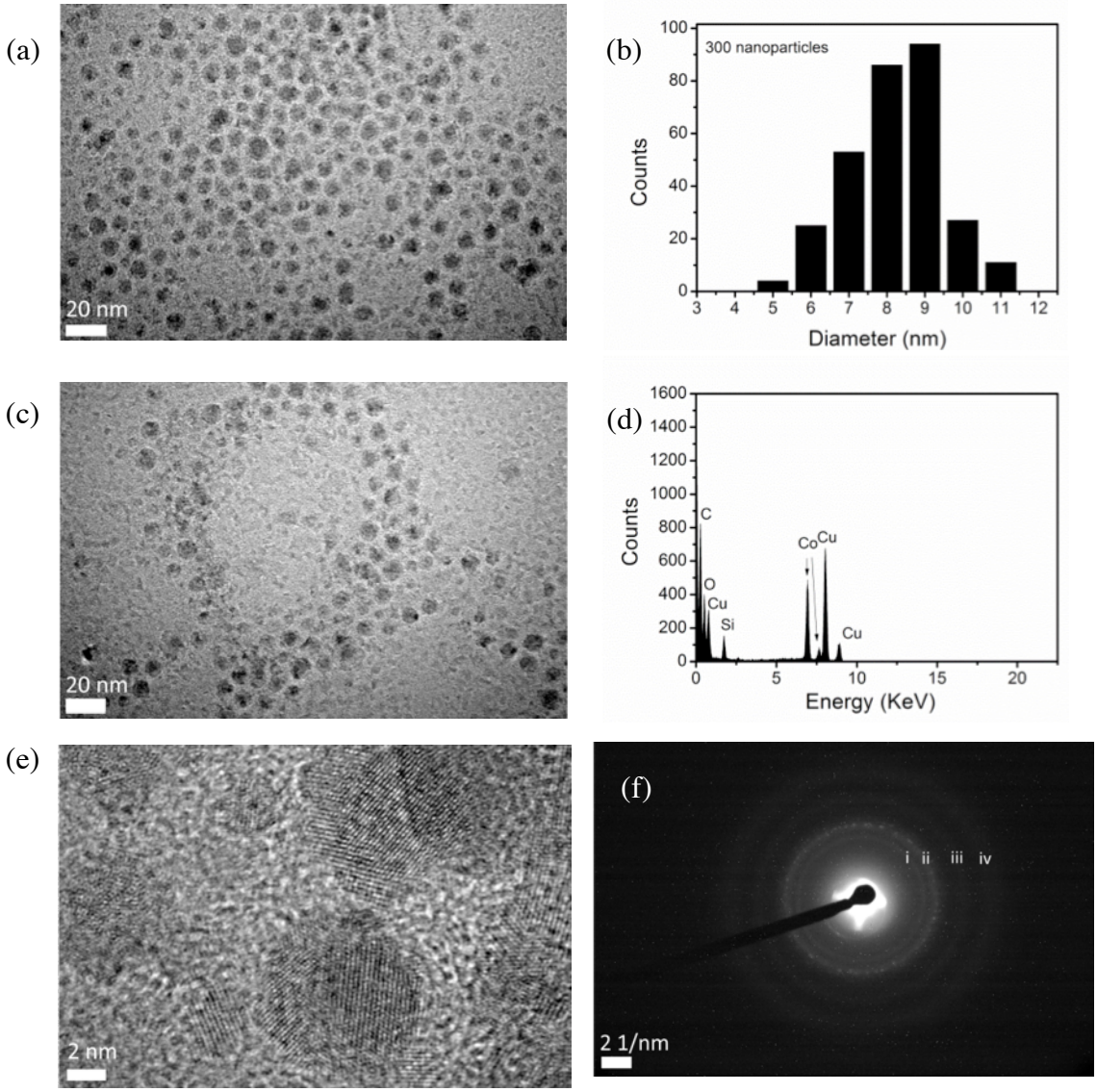

Fig. S8: *TEM characterisation of Co nanoparticle assembled onto acid (pH 2) and base (pH 12) treated supports (a) (c) Bright field TEM images of Co nanoparticles; (b) size distribution (7.6 ± 1.2 nm); (d) EDX spectrum; (e) HRTEM image; (f) SAED with assignment in Table S3.*

Table S3: *A comparison of d-spacing value with ε-Co Angew. Chem. Int. Ed. 38 1788 (1999) and CoO JCPDC 09-0402.*

Label SAED Figure S8(f)	(hkl)	Measured SAED d-spacings (nm)	d-spacing CoO JCPDC 09-0402	Relative intensity (%) CoO JCPDC 09-0402	d-spacing Angew. Chem. Int. Ed. 38 1788 (1999)	Relative intensity (%)
i	111	0.249	0.246	74.7	-	-
ii	221	0.205	-	-	0.203	100
iii	220	0.147	0.150	49.8	-	-
iv	510	0.121	-	-	0.012	21

Characterisation of Co nanoparticles assembled onto pH 4 and pH 8 treated supports

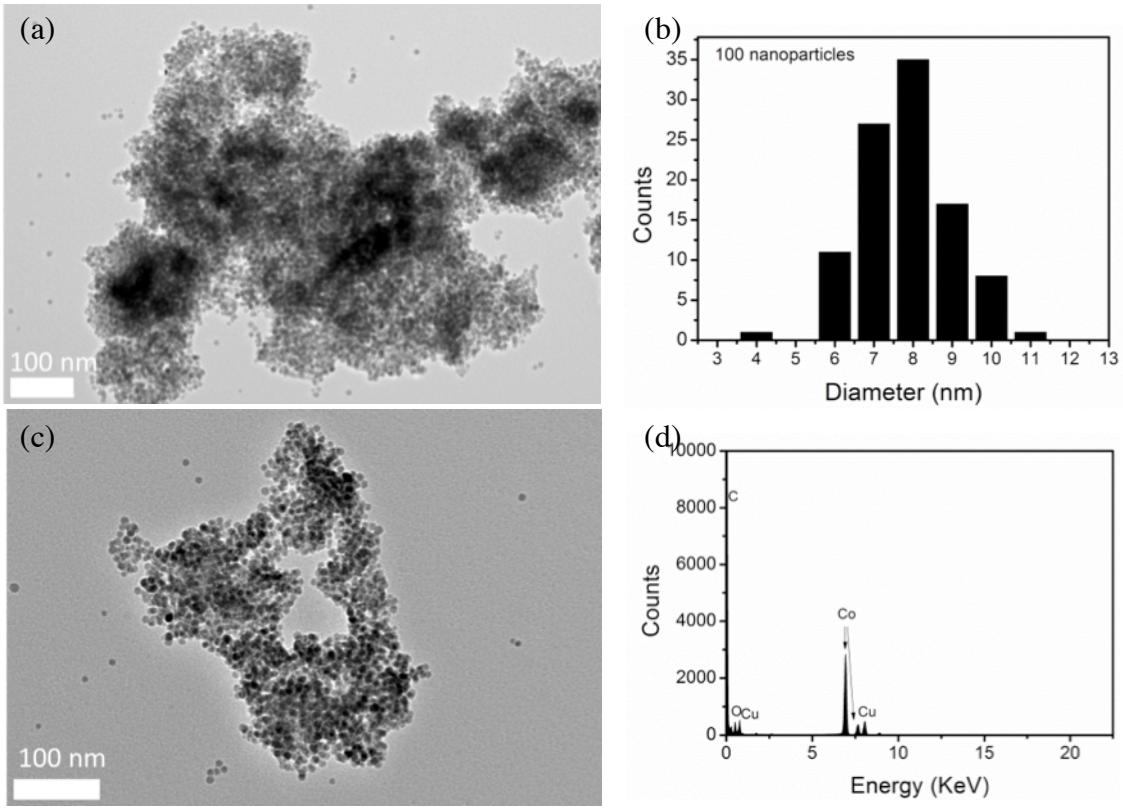

Fig. S9: *TEM characterisation of Co nanoparticle assembled onto acid (pH 4) and base (pH 8) treated supports (a)(c) Bright field TEM images of Co nanoparticles (b) size distribution (7.4 ± 1.2 nm) (d) EDX spectrum. Note TEM images have aggregations of monodisperse samples. Aggregation is a side effect of TEM sample preparation; solvent used has evaporated to rapidly leaving particles clustered on the grid.*

Characterisation of nanoparticles assembled on treated supports

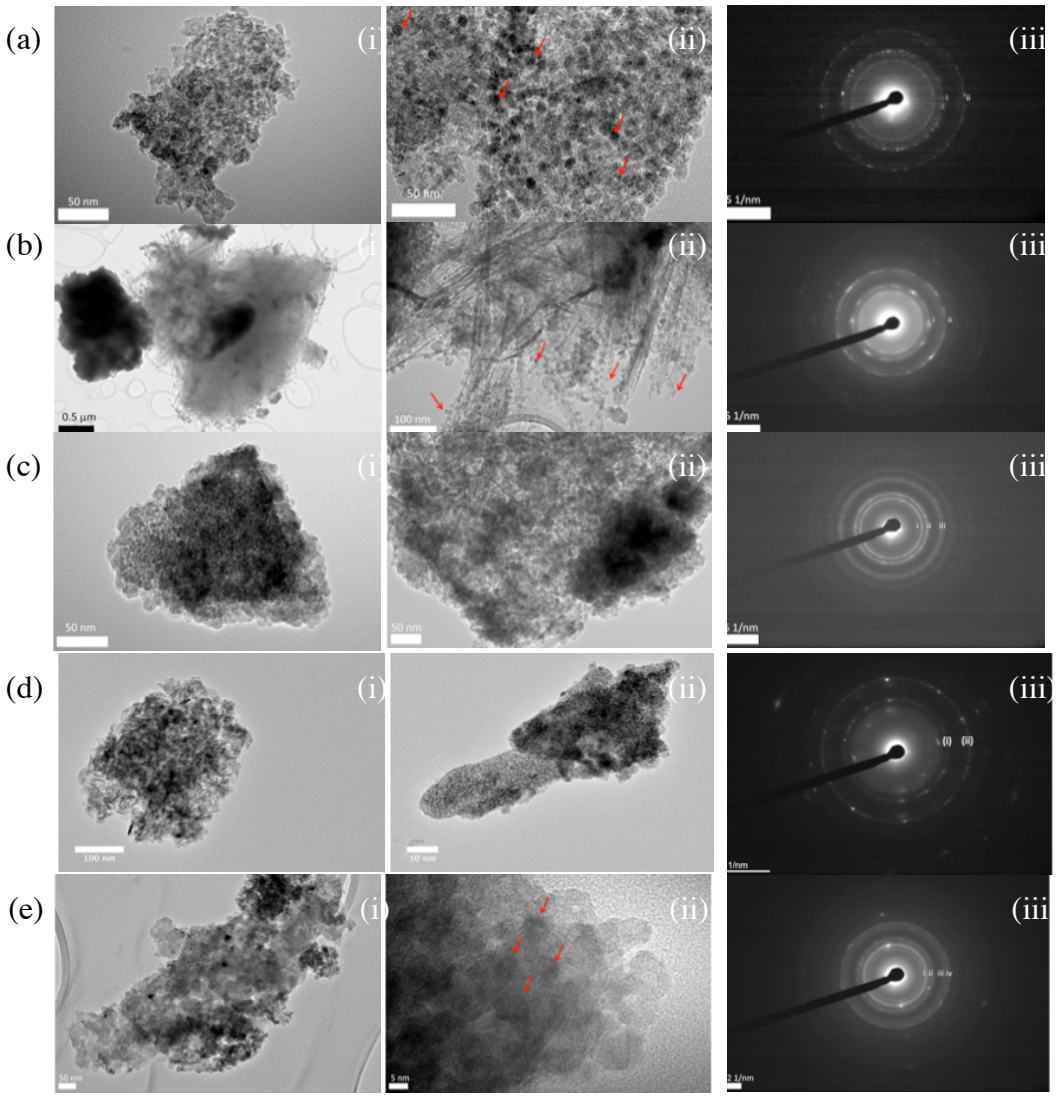

Fig. S10: *(i, ii) Bright Field TEM (iii SAED of nanocatalysts made by the assemblage of cobalt nanoparticles with (a) untreated alumina, (b) alumina pH 2 treatment, (c) alumina pH 4 treatment, (d) alumina pH 8 treatment and (e) alumina pH 12 treatment. SAED label assignment can be found in Table S4.*

SAED and XRD assignment confirms the occurrence of γ-Al_2O_3 (JCDCS 50-0741). Cobalt particles are not detected by these methods. XRF has been used to determine cobalt loadings. These along with the BET and BJH measurements are contained in Table J6. Surface area and pore size values are similar to the support material values before impregnation with nanoparticles.

Table S4: *d-spacing assignments for SAED in Figure S10a.*

SAED label	(hkl)	Measured SAED d-spacings (nm)
i	400	0.195
ii	440	0.135

Table S5: *d-spacing assignments for SAED in Figure S10b.*

SAED label	(hkl)	Measured SAED d-spacings (nm)
i	400	0.196
ii	440	0.135

Table S6: *d-spacing assignments for SAED in Figure S10c.*

SAED label	(hkl)	Measured SAED d-spacings (nm)
i	311	0.242
ii	400	0.204
iii	440	0.146

Table S7: *d-spacing assignments for SAED in Figure S10d.*

SAED label	(hkl)	Measured SAED d-spacings (nm)
i	400	0.195
ii	440	0.135

Table S8: *d-spacing assignments for SAED in Figure S10e.*

SAED label	(hkl)	Measured SAED d-spacings (nm)
i	311	0.244
ii	400	0.206
iii	511	0.152
iv	440	0.140

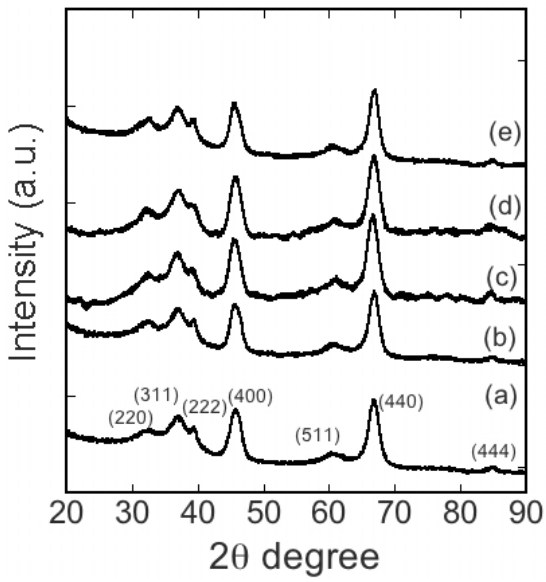

Fig. S11: *XRD spectrum of (a) Co nanoparticles on untreated alumina; (b) Co nanoparticles on pH 2 treated alumina; (c) Co nanoparticles on pH 4 treated alumina; (d) Co nanoparticles on pH 8 treated alumina; (e) Co nanoparticles on pH 12 treated alumina; Only the retention of the γ-Al_2O_3 (JCDCS 50-0741) structure is noted.*

Table S9: *Textural properties of the treated support nanocatalysts*

Nanocatalyst	BET Surface Area (m^2/g)	BJH Desorption pore diameter (Å)	Aluminium weight %	Cobalt weight %
pH 2	156	91	47.9	2.01
pH 4	142	88	46.5	4.55
pH 8	137	90	46.5	4.35
pH 12	140	101	48.7	1.38

Assemblage of particles using Chloroform

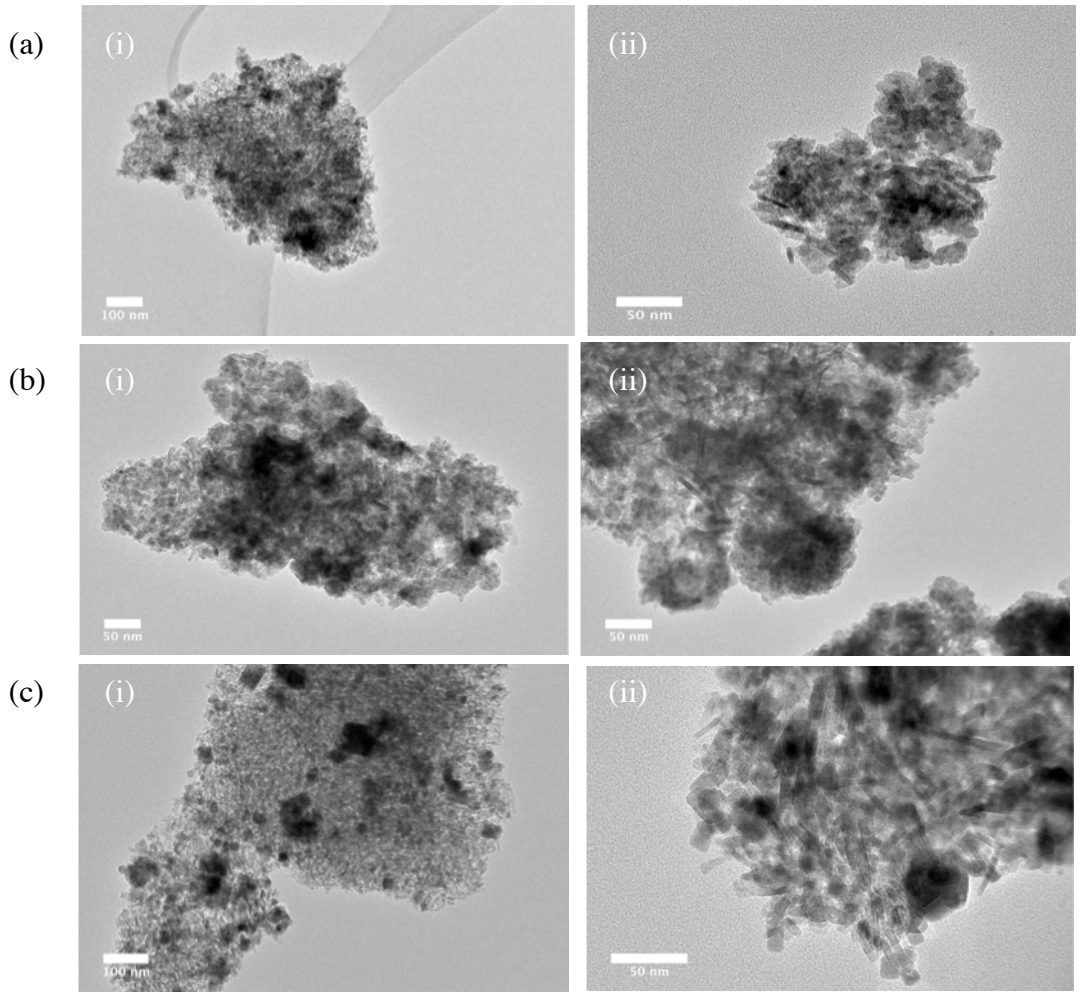

Fig. S12: *(i)(ii) Bright field TEM images of (a) uncalcined (b) calcined at 200 ^{o}C (b) calcined at 500 ^{o}C alumina supported* ε-Co *nanomaterials prepared in chloroform.*

1. Srikala, D.; Singh, V. N.; Banerjee, A.; Mehta, B. R.; Patnaik, S., Control of Magnetism in Cobalt Nanoparticles by Oxygen Passivation. *J. Phys. Chem. C* 2008, 112, (36), 13882-13885.
2. Verelst, M.; Ely, T. O.; Amiens, C.; Snoeck, E.; Lecante, P.; Mosset, A.; Respaud, M.; Broto, J. M.; Chaudret, B., Synthesis and Characterization of CoO, Co3O4, and Mixed Co/CoO Nanoparticules. *Chem. Mater.* 1999, 11, (10), 2702-2708.
3. Y. Wang; Zhang, X.; Liu, Y.; Jiang, Y.; Zhang, Y.; Wang, J.; Liu, Y.; Liu, H.; Sun, Y.; Beach, G. S. D.; Yang, J., Fabrication, structure and magnetic properties of CoPt3, CoPt and Co3Pt nanoparticles. *J. Phys. D: Appl. Phys.* 2012, 45.