Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Experimental and Catalytic Testing

Synthesis of Ag/Al_2O_3 catalysts

The alumina-supported Ag catalysts discussed were prepared with Ag loadings from 0.29 to 13 wt. % using the entrapped method. In a typical synthesis for a 2.4 wt. % Ag/Al_2O_3 sample, $AgNO_3$ (63 mg/0.37 mmol) and aluminium tri-*sec*-butoxide (8.32 ml/32.4 mmol) were dissolved in 2-butanol (1.98 ml). The resulting gel was stirred at 100 ^oC for 3 h to give a yellow suspension. At this point, 4.5 ml of deionized water were slowly added and the clear gel hydrolyzed instantly. Stirring was continued for another hour at 100 ^oC, before the suspension was allowed to cool to room temperature. The solid catalyst was filtered off, and the filter cake thoroughly washed with acetone, dried at 100 ^oC and calcined for 1 h at 600 ^oC (10 ^oC/min ramp). Prior to use, the catalyst was activated in flowing H_2 at 300 ^oC for 30 min. The same procedure was followed for preparing Cu/Al_2O_3 catalysts except that copper acetate was used. The metal content was determined by ICP-AES.

Procedure for N-alkylation of nitroarenes using alcohols

The catalytic N-alkylation of nitroarenes using alcohols was carried out under N_2 at 140 ^oC in a 25 ml round bottom flask equipped with a condenser. Typically, 1.0 mmol nitrobenzene and 6 mmol of benzyl alcohol were dissolved in 5 ml p-xylene; 0.100 g catalyst and 0.1 g base promoter were added. Aliquots were removed at regular time intervals and analyzed by gas chromatography. The products were identified by GC-MS.

Table S1 Effect of the ratio benzyl alcohol/nitrobenzene on the activity after 19 h

Ratio of benzyl alcohol/nitrobenzene	Conv.	Sel.(**3**)	Sel.(**4**)	Sel.(**5**)	Sel.(**6**)
3	100	8	13	60	19
6	100	98	2	0	0
8	100	92	7	1	0
12	100	96	4	0	0

Reaction condition: nitrobenzene 1 mmol,
Catalyst 100 mg metal 2.2 mol%, 100 mg Cs_2CO_3 100 mg 140 ^oC flowing N_2 19 h

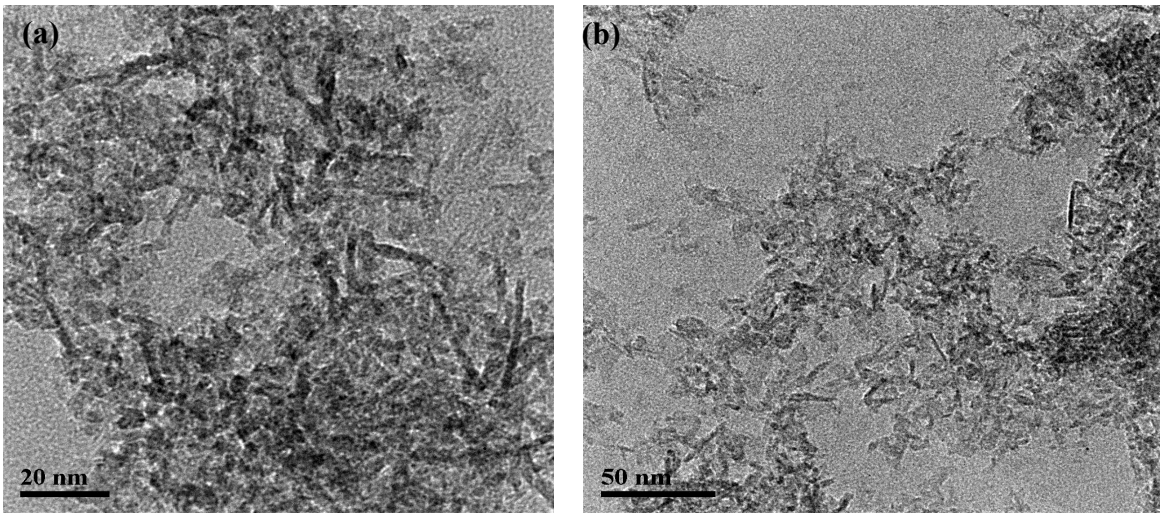

Figure S1. TEM image of the 2.4 wt% (a) before the reaction (b) after the reaction

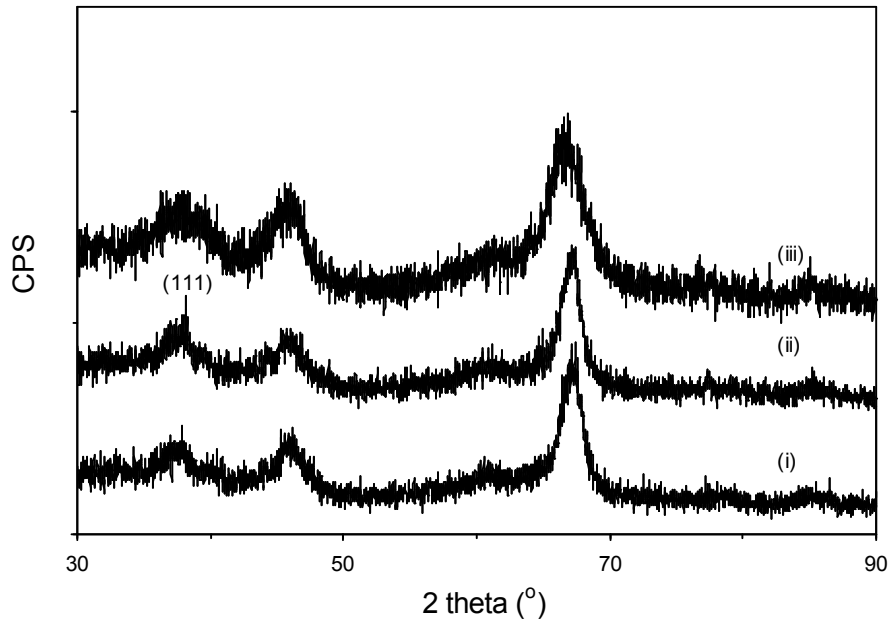

Figure S2. XRD diffractogram (i) commercial γ-Al_2O_3 (ii) 2.4 wt% Ag/ commercial γ-Al_2O_3 from wet impregnation method (crystalline size calculated to be 5.4 nm) (iii) 2.4 wt% Ag/ γ -Al_2O_3 from sol-gel method.

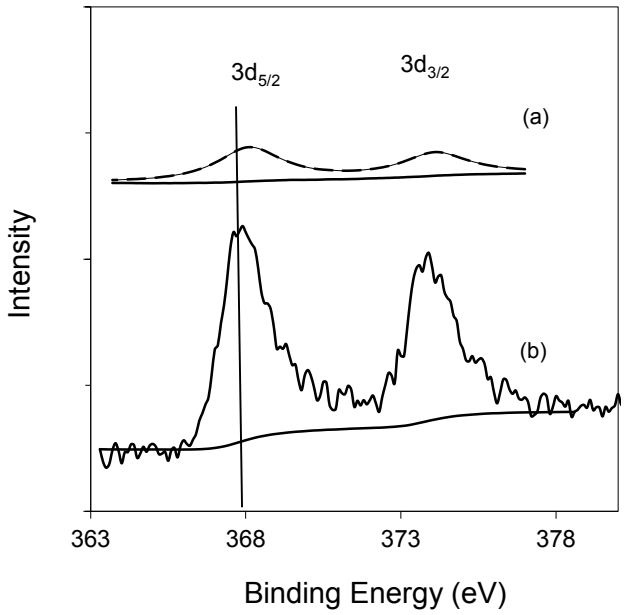

Fig S3 Ag XPS spectrum of (a) Ag/Al_2O_3 and (b) bulk Ag

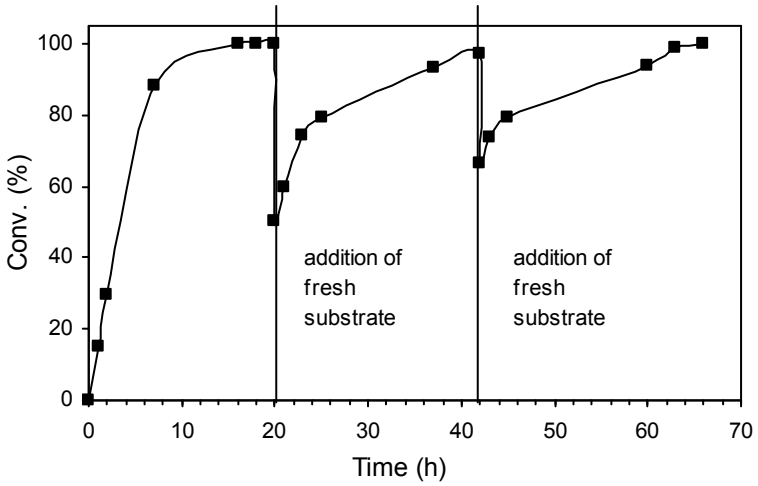

Figure S4. Recycling of Catalyst. Reaction condition: nitrobenzene 1 mmol, benzyl alcohol 6 mmol, basic additives 100mg, xylene 5 ml, Cat 2.2 mol%

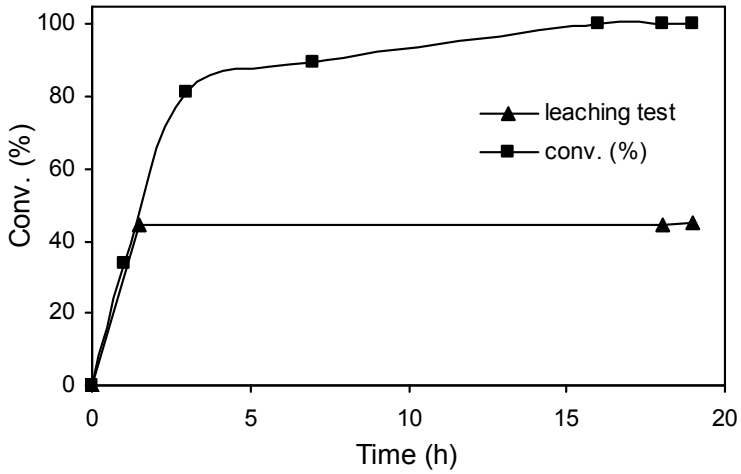

Figure S5. N-alkylation of nitrobenzene with benzyl alcohol in the presence (■) and absence (▲) of 2.4 wt % Ag/Al_2O_3 (catalyst was removed by filtration after 2 h).
Reaction conditions: nitrobenzene 1 mmol, benzyl alcohol 6 mmol, Catalyst 100 mg metal 2.2 mol%, 100 mg Cs_2CO_3 100 mg 140 ^oC flowing N_2 19 h