Electronic Supplementary Information (ESI)

Oxidation of ethylene by Cu/TiO_2: Reducibility of Cu^{2+} in TiO_2 as a possible descriptor of catalytic efficiency.

Rajendran Karuppusamy[a], Mandeep Sharma [a], Augustine Jaison [a], Menon Ankitha, Ankit. D. Tiwari [a], C. P. Vinod[c] and Dinesh Jagadeesan[a,b]*

[a]Department of Chemistry, Indian Institute of Technology Palakkad, Kerala, 678557, India

[b]Environmental Sciences and Sustainable Engineering Centre (ESSENCE), Indian Institute of Technology Palakkad, Kerala, 678557, India.

[c]Inorganic Chemistry and Catalysis Division, CSIR – National Chemical Laboratory, Pashan, Pune – 411 008, Maharashtra, India.

*Corresponding author: d.jagadeesan@iitpkd.ac.in

S.No	Catalyst	$CuSO_4.5H_2O$ (mg)	$Ti(OC_4H_9)_4$ (g)	Ethanol (mL)	ICP-OES (Cu wt.%)
1.	0.2% Cu/TiO_2	5.13	3.5	30	0.21
2.	1% Cu/TiO_2	25.66	3.5	30	1.06
3.	3% Cu/TiO_2	77.00	3.5	30	3.38
4.	4% Cu/TiO_2	102.67	3.5	30	4.03

Table S1 Data for the synthesis of Cu-doped TiO_2.

ICP-OES (Inductively coupled plasma - optical emission spectrometry)

Table S2 Volume-weighted average grain size (d) nm of TiO_2 and Cu doped TiO_2 calculated using Scherer equation

S. NO	Catalyst	volume-weighted average grain size 'd' (nm)
1.	TiO_2	10.3
2.	0.2% Cu/TiO_2	9.8
3.	1% Cu/TiO_2	9.7

4.	3% Cu/TiO_2	7.5
5.	4% Cu/TiO_2	7.4

Scherer equation: $d_{XRD} = K\lambda/W\cos\theta$

d_{XRD} = volume-weighted average grain size

K = Scherrer constant

λ = Wavelength

W = peak width

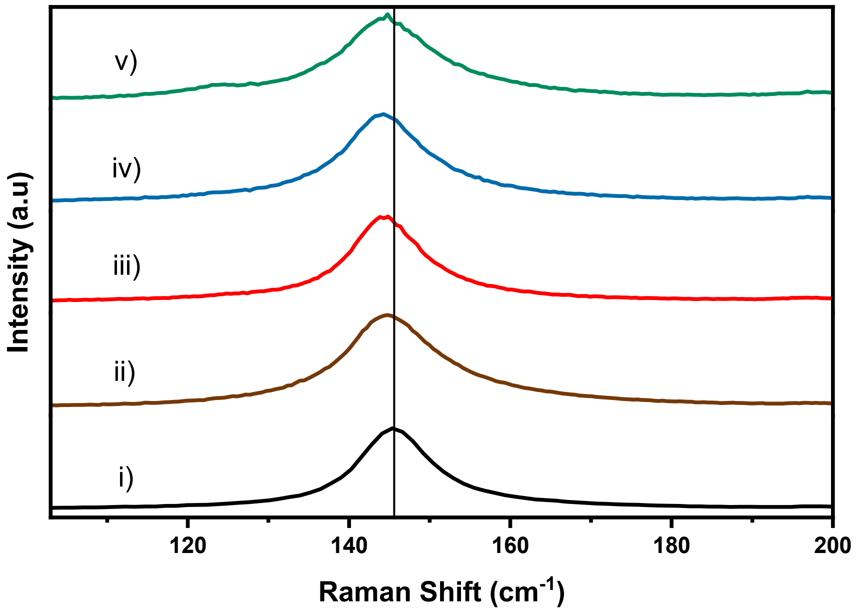

Fig. S1 Enlarged image of 144.9 cm^{-1} Raman shift i) TiO_2 (black) ii) 0.2% Cu/TiO_2 (brown) iii) 1% Cu/TiO_2 (red) iv) 3% Cu/TiO_2 (blue) v) 4% Cu/TiO_2 (green).

Table S3 Comparison of Temperature (K) of deconvoluted peaks in all the prepared catalyst

Catalyst	**Temperature (K)**			
	Cu^{2+} to Cu^{+}	**Cu^{+} to Cu^{0}**	**Ti^{4+}**	
TiO_2	–	–	770	880
0.2 Cu/TiO_2	–	–	715	825
1 Cu/TiO_2	577	615	729	729
3 Cu/TiO_2	540	583	656	841
4 Cu/TiO_2	538	611	680	874

Table S4 Comparison of H_2-consumption (micromole/gram) of deconvoluted peaks in all the prepared catalyst

Catalyst	**H_2-Consumption (µmol/gram)**					**Valence Ratio (Cu^{2+}/ Cu^{+}) approx.**
	Cu^{2+} to Cu^{+}	**Cu^{+} to Cu^{0}**	**Ti^{4+}**		**Total**	
0.2 Cu/TiO_2	–	–	311.4	990.8	1399.2	
1 Cu/TiO_2	1411.8	2520.7	1250.4		5182.9	0.5
3 Cu/TiO_2	582.8	1135.4	4408.9	5747.6	11874.1	0.5
4 Cu/TiO_2	782.9	1040.2	1425.7	3910.1	7158.9	0.7

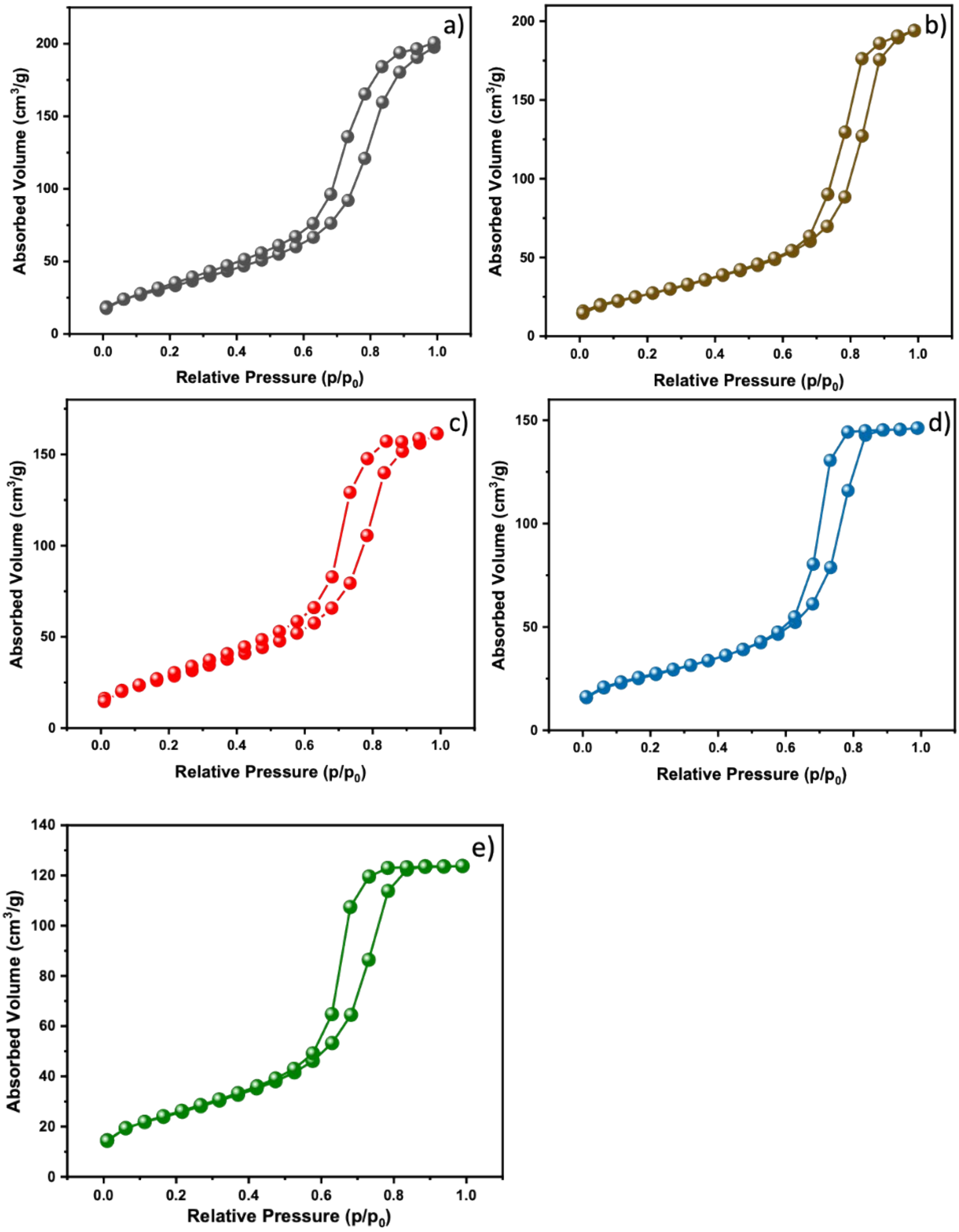

Fig. S2 N_2 adsorption-desorption isotherm at 77K a) TiO_2 b) 0.2% Cu/TiO_2 c) 1% Cu/TiO_2 d) 3% Cu/TiO_2 e) 4% Cu/TiO_2

Table S5 BET surface area, average pore size and total pore volume analysis of TiO_2 and Cu/ TiO_2 samples

S.No	Catalyst	BET Surface Area (m^2/g)	Average pore size (nm)	Total pore volume (cm^3/g)
1	TiO_2	119.9	5.0	0.30
2	0.2% Cu/TiO_2	97.4	6.1	0.30
3	1% Cu/TiO_2	103.4	4.8	0.24
4	3% Cu/TiO_2	94.3	4.7	0.22
5	4% Cu/TiO_2	91.0	4.2	0.19

BET and textual analysis

The N_2 adsorption and desorption isotherms (Fig. S2) of prepared materials was of type IV, which indicates mesoporous materials.[1] The surface area and other textural parameters of the samples are shown in the Table S2. BET surface area of the pure anatase TiO_2 was calculated to be 119.9 m^2/g, which was highest among all the materials. Increasing Cu concentration in TiO_2 lead to a slight decrease in surface area.[1] The average pore size of all the materials were around 4 - 6 nm which is in mesoporous range. Total pore volume and pore size also followed the same trend as BET surface area.

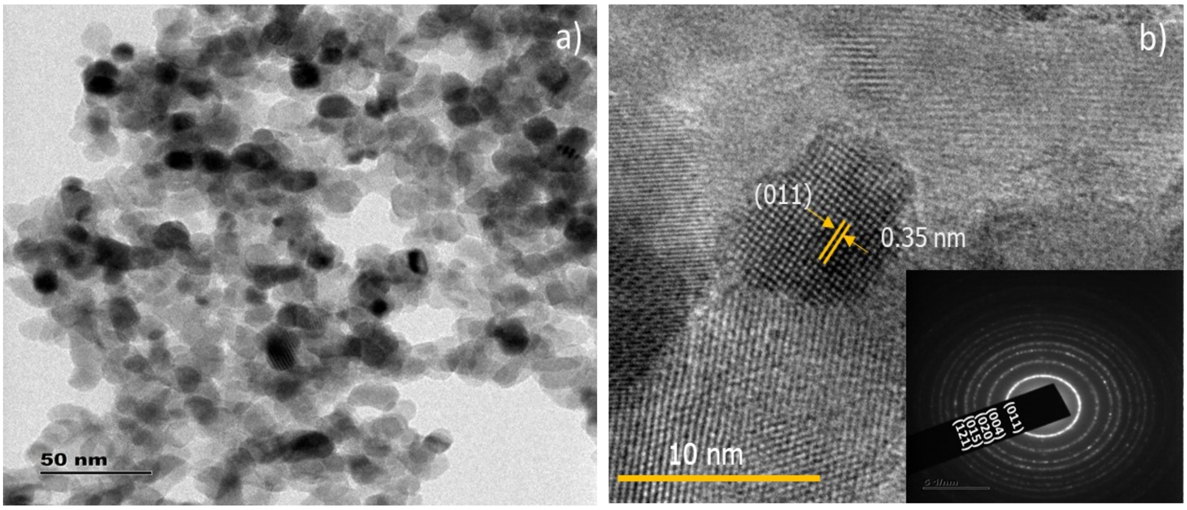

Fig. S3 a) TEM micrographs of 1% Cu/TiO_2 b) HR-TEM and SAED pattern (inset) of 1% Cu/TiO_2

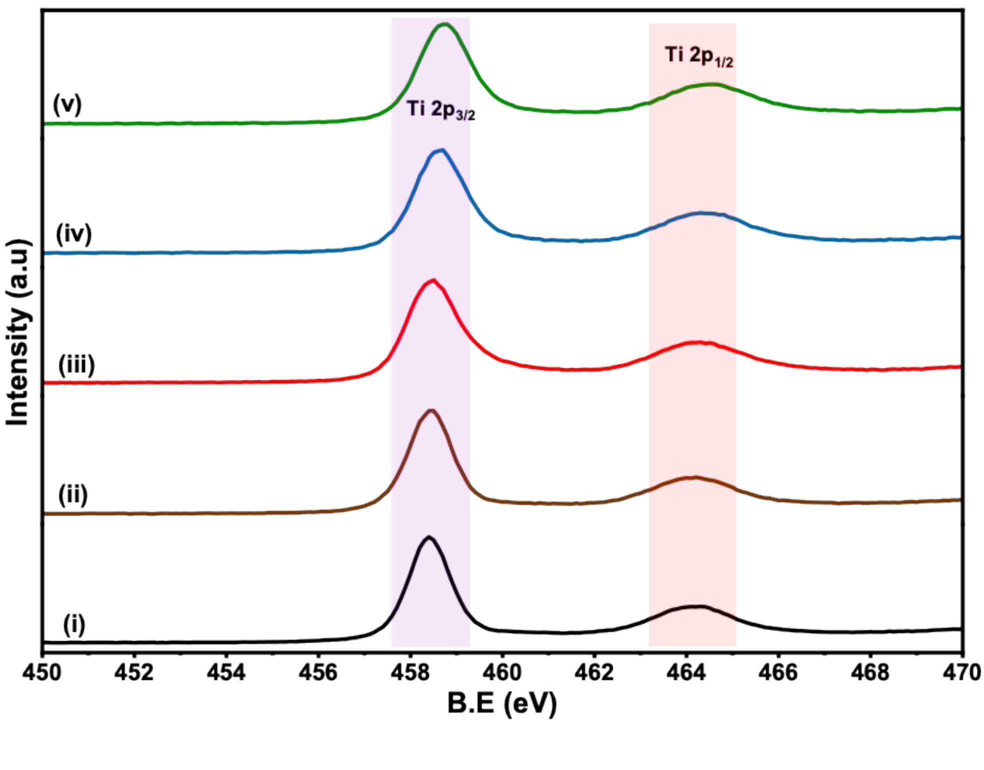

Fig. S4 X-ray photoelectron spectra of Ti 2p i) TiO_2 ii) 0.2% Cu/TiO_2 iii) 1% Cu/TiO_2 iv) 3% Cu/TiO_2 v) 4% Cu/TiO_2

Table S6 Valence ratio of Cu^{2+}/ Cu^{+} in all the prepared catalyst using X-ray photoelectron spectroscopy.

Catalyst	**Peak 1 (Cu^{+}) Area**	**Peak 2 (Cu^{2+}) Area**	**Valence Ratio(Cu^{2+}/ Cu^{+}) approx.**
0.2 Cu/TiO_2	6095	0	0
1 Cu/TiO_2	19872	4152	0.2
3 Cu/TiO_2	23347	10989	0.5
4 Cu/TiO_2	29701	26186	0.9

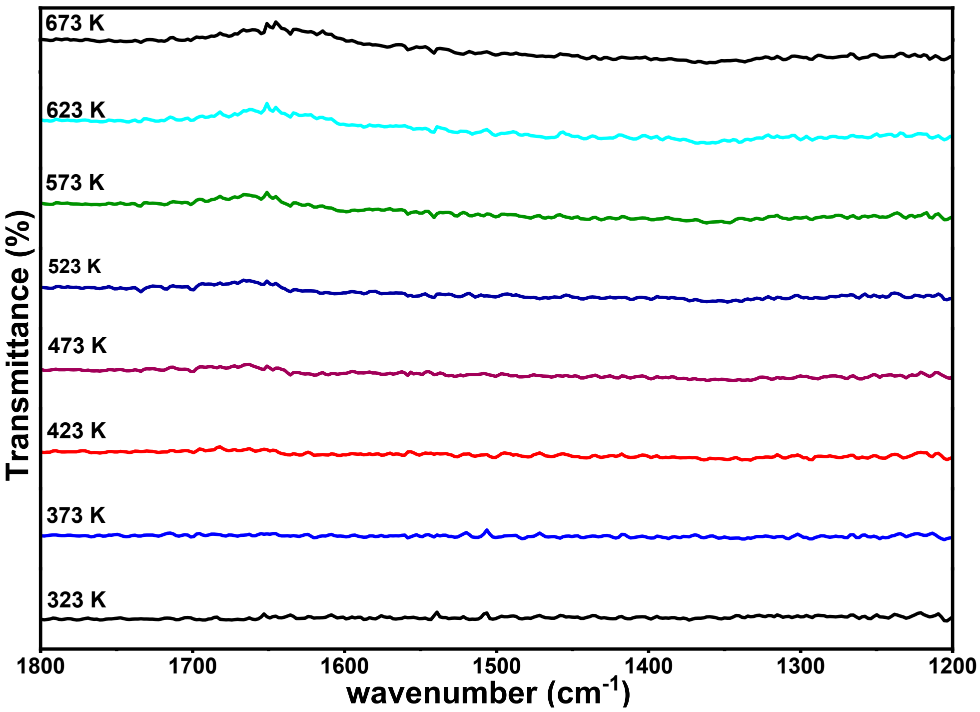

Fig. S5 CO_2 DRIFT of 1% Cu/TiO_2

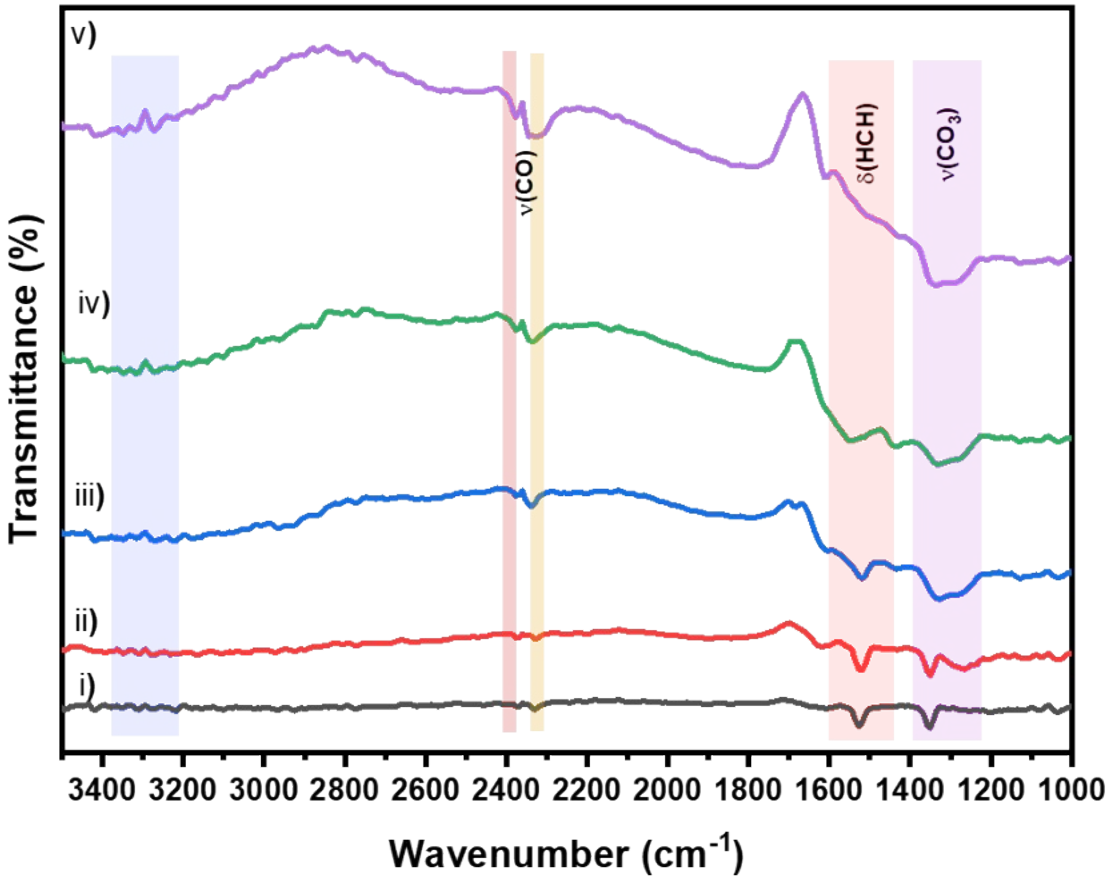

Fig. S6 DRIFTS measurement during oxidation of ethylene using 1% Cu/TiO_2 with the mixture of ethylene (1.5 vol %) and oxygen (5.9 vol %) at (i) 298 K; (ii) 373 K; (iii) 473 K; (iv) 573 K; (v) 673 K.

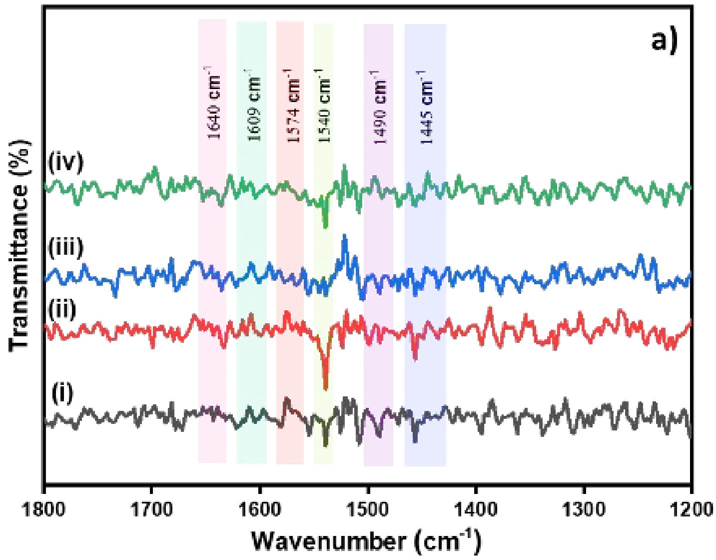

Fig. S7 a) Pyridine DRIFTS of TiO_2 i) 323 K ii) 373 K iii) 473 K iv) 573K

Reference

1. T. Sreethawong and S. Yoshikawa, *Catalysis Communications*, 2005, **6**, 661-668.