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Engineering active sites for enhancing synergy in heterogeneous catalytic oxidations

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Synthesis of the bimetallic Co^{III}Ti^{IV}AlPO-5 catalyst

Aluminum hydroxide (Al(OH)₃.xH₂O, Aldrich) and phosphoric acid (85wt% aqueous solution, Sigma Aldrich) were used as the initial synthesis precursors. Cobalt acetate tetrahydrate (Co(C₂H₃OO)₂.4H₂O, Aldrich) and titanium isopropoxide (Ti(OC₃H₇)₄, Aldrich) were used as the metal sources with N,N-dicyclohexylmethylamine (Aldrich) used as the structure directing agent (SDA). The composition of the gel was 0.96Al:1.5P:0.03Co:0.03Ti:0.8SDA:50H₂O.

0.0980 mols (9.601g, Aldrich) of H₃PO₄ was added to 10ml of deionised water and allowed to stir by magnetic stirrer in a PTFE beaker. 4.071g (0.0522mol, Aldrich) of Al(OH)₃ was added slowly and was left stirring for 10minutes with the addition of a further 10ml of water.

Cobalt acetate tetrahydrate (0.415g, 1.667mmol, Aldrich) was dissolved in 10ml of deionised water while 1.667mmol (0.474g, Aldrich) of titanium isopropoxide was measured out and simultaneously these two solutions were added slowly to the main reaction mixture. The reaction mixture was left stirring for 20minutes to homogenize.

N-methyldicyclohexylamine (0.044mol, 8.682g, Aldrich) was added slowly with the remaining 18ml of water. This gel was left stirring for 30 minutes (1200rpm) to obtain a fully homogeneous mixture.

The reaction mixture was transferred to a Teflon-lined autoclave (capacity 40ml), sealed and put in the oven for 2 hours at 180°C. After 2 hours, the autoclaves were removed and immediately quenched in cold water, the product was filtered and washed with water and dried in the oven (50-90°C).

Calcination was carried out at 550°C for a minimum of 8 hours in a tube furnace with a gentle flow of air throughout; the temperature ramp was 5 degrees per minute. The resulting sample was stored in a desiccator to minimise the reduction of the active sites through water adsorption

The monometallic catalysts Co^{III}AlPO-5, Ti^{IV}AlPO-5, TS-1 and TiMCM-41 were synthesized using reliable procedures that have been reported in the literature, as well as by following protocols documented in the International Zeolite Association web site.

Characterization. XRD patterns were obtained on a Siemens D5000 diffractometer using Cu K_{α1} radiation, $\lambda=1.54056\text{\AA}$. Volumetric analysis (N₂ adsorption/desorption at 77K) were carried out on a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. Diffuse Reflectance (DR) UV-Vis experiments were performed using a Cary 5000 instrument equipped with an integrated sphere, coated with BaSO₄. The reflectance spectra were then elaborated by using Kubelka Munk function. All the spectra are recorded at 298K in vacuo after the thermal treatments. Scanning electron microscopy was carried out using a JSM5910 microscope with carbon coating during sample preparation. BET was carried out using Micromeritics Gemini 2360 Surface area analyser with N₂ adsorption/desorption at 77K.

Catalysis. All epoxidation reactions were carried out using a stirred (500 rpm) glass-lined reactor at atmospheric pressure. 0.313mols of dichloromethane (Aldrich) was used as a solvent and triethylene glycol dimethyl ether (triglyme, 8.98mmol, Aldrich) used as the internal standard. In each reaction, 5.75g of acetylperoxyborate (3.9%PAA) was dissolved in 20ml of H₂O before being added to ca 9.25mmol of

cyclohexene ($\geq 99.5\%$ pure, Aldrich) with *ca* 0.25-0.30 g of fresh catalyst. Reactions were run at 65°C for 3 hours with samples removed for analysis at 30 minute intervals. Analysis was carried out using a Varian Star 3400CX gas chromatograph with flame ionization detector (FID) and HP1 cross linked methylsiloxane column (30m x 0.32mm x $1\mu\text{m}$ film thickness).

The identities of the products were first confirmed using authenticated standards and their individual response factors were determined using a suitable internal standard (triglyme) by the calibration method. The overall yields were normalized with respect to the (GC) response factors obtained as above and the conversions and selectivities were determined by the following equations:

$$\text{Conv. \%} = [(\text{moles of initial substrate} - \text{moles of residual substrate}) / (\text{moles of initial substrate})] \times 100$$

$$\text{Sel. \%} = [(\text{moles of individual product}) / (\text{moles of total products})] \times 100$$

For the internal standard GC method, the response factor (RF) and mol % of individual products were calculated using the following equations:

$$\text{RF} = (\text{mol Product/mol Standard}) \times (\text{Area Standard/Area Product})$$

$$\text{Mol \% Product} = \text{RF} \times \text{Mol Standard} \times (\text{Area Product/Area Standard}) \times 100/\text{Mol Sample}$$

The catalysts have been re-used at least four times without appreciable loss in catalytic activity or selectivity. Further, experiments analogous those reported earlier [1, 2], were carried out to rule out the possibility of leaching.

Refinement Results

Initial values : (Refinement keys on 2nd line)

Zero Lambda a b c alpha beta gamma volume
0.000 1.54180 13.7336 13.7336 8.4463 90.00 90.00 120.00 1379.64
0 0 1 0 1 0 0 0

H	K	L	2Th(obs)	2Th_obs-shift	2Th(Calc)	diff.
0	1	0	7.4200	7.4200	7.4326	-0.0126
1	1	0	12.8800	12.8800	12.8918	-0.0118
0	2	0	14.8800	14.8800	14.8967	-0.0167
1	2	0	19.7200	19.7200	19.7486	-0.0286
0	0	2	21.1400	21.1400	21.0357	0.1043
1	2	1	22.4000	22.4000	22.4034	-0.0034
1	1	2	24.8600	24.8600	24.7490	0.1110
0	2	2	25.9000	25.9000	25.8750	0.0250
1	3	1	29.0400	29.0400	29.0602	-0.0202
0	4	0	30.0000	30.0000	30.0528	-0.0528
2	2	2	33.7000	33.7000	33.6405	0.0595
1	3	2	34.5000	34.5000	34.4998	0.0002
0	4	2	37.0400	37.0400	36.9728	0.0672
0	5	0	37.8000	37.8000	37.8198	-0.0198
1	4	2	40.9600	40.9600	40.8075	0.1525
2	4	1	41.6600	41.6600	41.5760	0.0840
1	5	0	42.3600	42.3600	42.3086	0.0514
1	5	1	43.8600	43.8600	43.7081	0.1519
3	3	2	45.2400	45.2400	45.0494	0.1906
0	6	0	45.9000	45.9000	45.7717	0.1283
2	5	0	47.7800	47.7800	47.7542	0.0258

Sqrt(Sum(2Th O-C)**2)/(Nref-Npar) : 0.0878

Sqrt(Sum(2Th O-C)**2)/Nref : 0.0835

Final values : (Standard errors on 2nd line)

Zero Lambda a b c alpha beta gamma volume
0.000 1.54180 13.7116 13.7116 8.4161 90.00 90.00 120.00 1370.31
0.0000 0.00000 0.0301 0.0000 0.0044 0.000 0.000 0.000 3.091

H	K	L	2Th(obs)	2Th_obs-shift	2Th(Calc)	diff.
0	1	0	7.4200	7.4200	7.4445	-0.0245
1	1	0	12.8800	12.8800	12.9126	-0.0326
0	2	0	14.8800	14.8800	14.9207	-0.0407
1	2	0	19.7200	19.7200	19.7806	-0.0606
0	0	2	21.1400	21.1400	21.1120	0.0280
1	2	1	22.4000	22.4000	22.4498	-0.0498
1	1	2	24.8600	24.8600	24.8255	0.0345

0	2	2	25.9000	25.9000	25.9520	-0.0520
1	3	1	29.0400	29.0400	29.1157	-0.0757
0	4	0	30.0000	30.0000	30.1022	-0.1022
2	2	2	33.7000	33.7000	33.7234	-0.0234
1	3	2	34.5000	34.5000	34.5837	-0.0837
0	4	2	37.0400	37.0400	37.0595	-0.0195
0	5	0	37.8000	37.8000	37.8828	-0.0828
1	4	2	40.9600	40.9600	40.8991	0.0609
2	4	1	41.6600	41.6600	41.6516	0.0084
1	5	0	42.3600	42.3600	42.3798	-0.0198
1	5	1	43.8600	43.8600	43.7874	0.0726
3	3	2	45.2400	45.2400	45.1472	0.0928
0	6	0	45.9000	45.9000	45.8494	0.0506
2	5	0	47.7800	47.7800	47.8357	-0.0557

$\text{Sqrt}(\text{Sum}(2\text{Th O-C})^{**2}/(\text{Nref-Npar})) : 0.0602$

$\text{Sqrt}(\text{Sum}(2\text{Th O-C})^{**2}/\text{Nref}) : 0.0573$

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