Immobilisation of BINOL on Magnetic Iron Oxide Particle as Recyclable Organocatalyst for Asymmetric Aldol Reaction

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Introduction

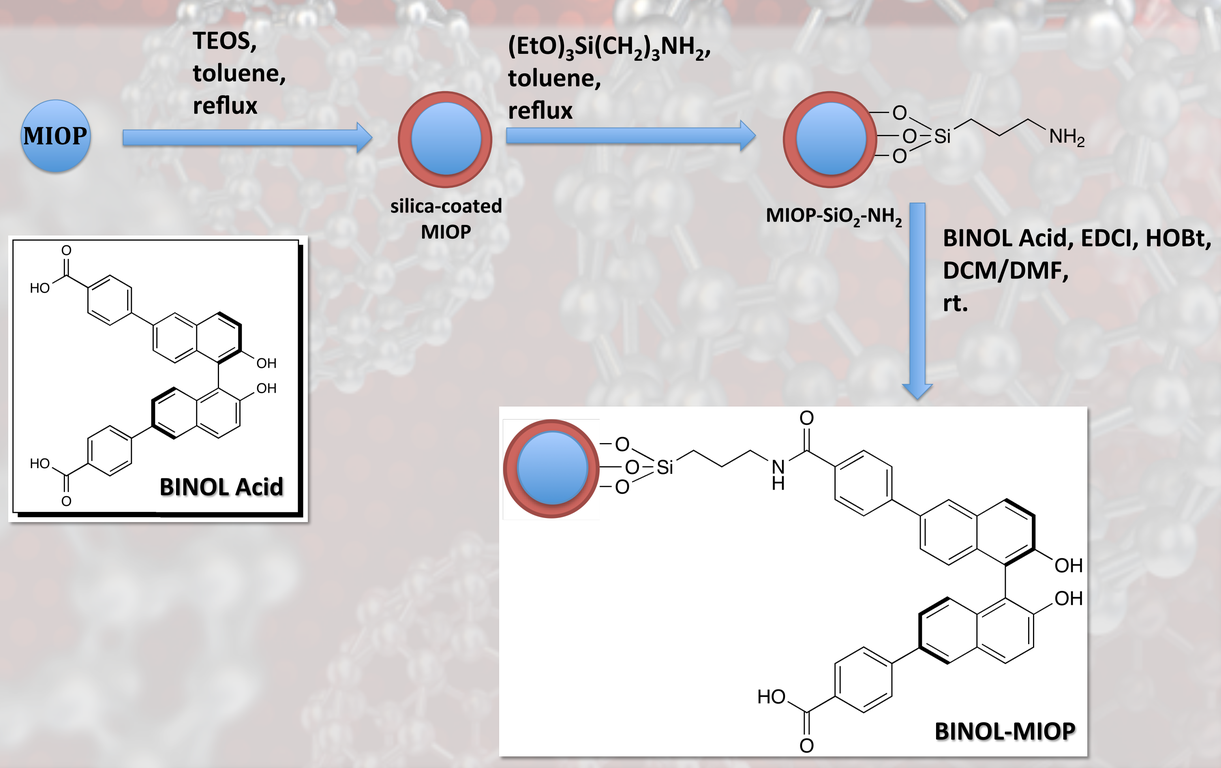
Organocatalyst has emerged as one of the powerful tools for asymmetric organic reactions[1]. Among the various type of reported organocatalyst, 1,1'-bi-2-naphthol (BINOL) and its derivatives are among the attractive and powerful catalysts for wide range of the asymmetric organic reactions[1, 3], such as hydrocyanations[4], aldol[5], Mannich[6], Friedel-Crafts[7], Diels-Alder reactions[8] and etc. Numerous BINOL derivatives are expensive; where in most cases they are not commercially available. The desirable BINOL derivatives are only made available by going through a tedious multi-step reactions and purifications[9]. Thus, catalysts recycling are required to recover these precious organocatalysts. Efforts to make heterogeneous BINOL organocatalyst were revealed by immobilising BINOL onto different heterogeneous material, such as polystyrene[10], polyethylene glycol[11], micelle-derived polymer[12], polysaccharide-based chiral stationary phase[13], aminated silica[14], mesoporous silica[15] and microporous silica[2].

To the date, magnetic iron oxide particle (MIOP) have emerged as a new supporting material in the purpose of catalyst recovery[16]. The success of MIOPs as solid support to immobilize transition metals, organic ligands, organocatalysts, and biocatalysts were exemplified through absorption or formation of covalent bonds[17]. The MIOP-modified catalyst can be easily separated from the solubilised reactants and products mixture by applying an external magnetic field, followed by decantation for further purification workup. MIOP was selected as solid support in this study due to its easy-separation ability from reaction mixture and the facile surface modification[17]. Although there are reports concerning the immobilisation of organocatalyst onto MIOP[17], the BINOL immobilisation onto MIOP has not been reported.

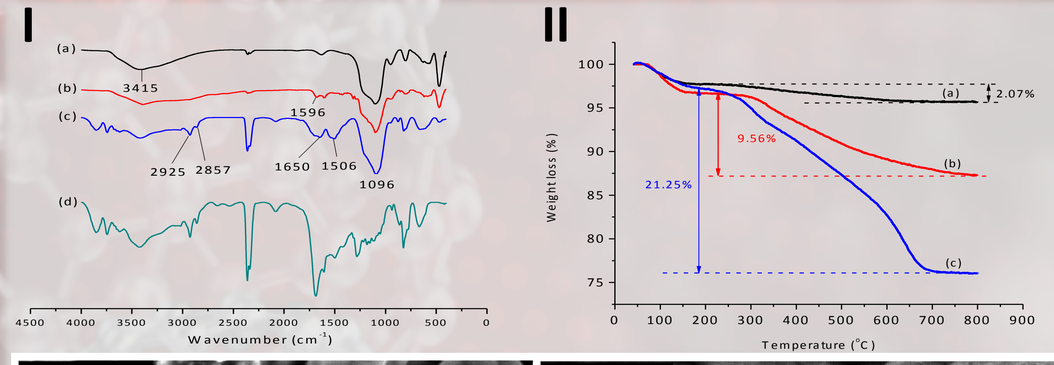
Objectives

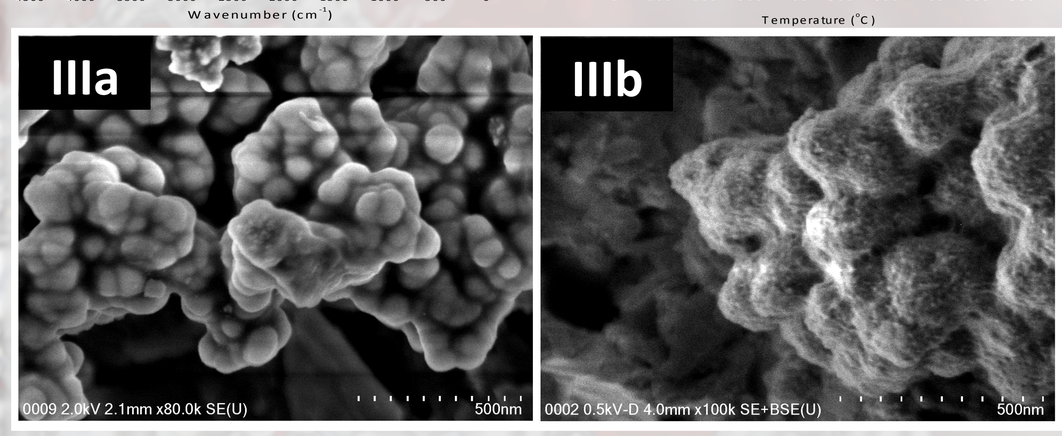
1. To develop a general method to immobilise a BINOL-derived catalyst onto MIOP for the preparation of recyclable BINOL catalyst (BINOL-MIOP)
2. To characterise the BINOL-MIOP
3. To evaluate the performance of the BINOL-MIOP via asymmetric aldol reactions
4. To assess of the reusabilities of the BINOL-MIOP

Synthesis of BINOL-MIOP



Characterisation of BINOL-MIOP

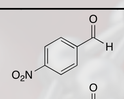
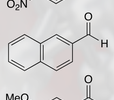
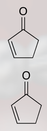
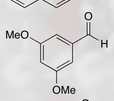
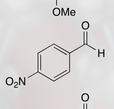
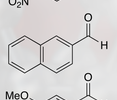
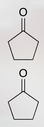
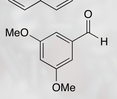




I: IR spectrum of (a) silica-coated MIOP, (b) MIOP-SiO_2-NH_2, (c) BINOL-MIOP, and (d) BINOL-Acid.
II: TGA curves of (a) silica-coated MIOP, (b) MIOP-SiO_2-NH_2, and (c) BINOL-MIOP. Commercially available aminopropyl silica gel had 9.2% weight loss corresponded to 1 mmol of NH_2 per gram of solid[14]. Therefore, 7.49% weight loss was corresponded to 0.81 mmol of NH_2 per gram of MIOP-SiO_2-NH_2. BINOL-MIOP had additional 11.69% weight loss as compared to MIOP-SiO_2-NH_2. Considering the weight loss that is attributed to dehydroxylation of silanol groups, decomposition of propyl amine groups and BINOL-acid groups from MIOPs, the estimated loading of BINOL was 0.23 mmol per gram.
III: SEM image of (IIIa) MIOP-SiO_2-NH_2 and (IIIb) BINOL-MIOP.

Catalytic Evaluation of BINOL-MIOP

1. Aldol reaction between benzaldehydes and pentanone/pentenone

Entry	Aldehyde	Ketone	Time, hour	% conversions	Syn:Anti	% ee (Syn, Anti)
1			14 (16[a], 21[b])	98 (96[a], >99[b])	79:21 (76:24)[a], (70:30)[b]	0.6, 35.0 (0, 50)[a]
2			72	45	77:23	0.3, 3.3
3			72	93	72:28	0, 35.0
4			14	99	73:27	2.7, 1.1
5			72	57	70:30	0.2, 1.2
6			72	94	71:29	2.2, 0.2

* Aldol reactions were carried out in THF: $NaHCO_3$ (1M) = 0.5: 2 at room temperature
a: results obtained from homogeneous 20% BINOL-catalysed reaction
b: results obtained from homogeneous reaction without BINOL

2. BINOL-MIOP reusability experiment for aldol reaction between 4-nitrobenzaldehydes and pentenone

Attempt	% conversions	Syn:Anti	% ee (Syn, Anti)
1	98	79:21	0.6, 35.0
2	95	81:19	1.0, 36.0
3	95	78:22	5.0, 34.0
4	96	76:24	6.0, 38.0
5	95	84:16	0.8, 40.0
10	98	81:19	0.4, 38.0

Acknowledgements

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