

Adamantyl-BINOL-based chiral porous polymers for heterogeneous catalysis

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We report the synthesis of adamantyl-BINOL-based chiral porous aromatic polymers (Ad-BINOL-PAFs) for heterogeneous catalysis.

Introduction

Porous organic polymers (POPs) as covalent organic frameworks (COFs), hypercross-linked polymers (HCPs), conjugated microporous polymers (CMPs), polymers of intrinsic microporosity (PIMs), have been prepared from different building blocks and have been applied for gas storage, catalysis, sensors and organic optoelectronics [1]. The “bottom-up” approach is a more effective strategy to heterogenize molecular catalysts in comparison with the classical supported catalysts and the resulting porous polymers catalysts possess the catalytic centers more accessible and homogeneously distributed.

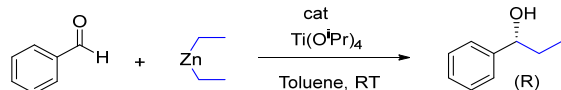
Results and discussion

The synthesis of chiral polymer Ad-BINOL-OH-PAFs and their soluble counterpart Ad-BINOL-OH is outlined in Scheme 1. The precursor (B) was easily done from commercially available (*R*)-BINOL and 1-adamantanol. Robust BINOL-frameworks (BINOL-PAFs) were prepared via palladium-catalyzed Suzuki or Sonogashira cross-coupling reaction (under microwave heating) of (*R*)-4,4'-dibromo-2,2'-diethoxy-6,6'-adamantyl (B) with a boronic acid or an alkyne structural building block and deprotection with BBr₃. The solid materials were characterized by FTIR, ¹³C CP/MAS NMR and the porous properties measured by nitrogen adsorption/desorption isotherms at 77 K indicated that Ad-BINOL-OH-PAFs are porous with BET surface area of 365.5 - 455 m².g⁻¹.

Ad-BINOL-OH-PAFs were used as heterogenized BINOL ligand for the formation of chiral catalysts by treating with excess Ti(OiPr)₄. Resulting Ti-catalysts were applied

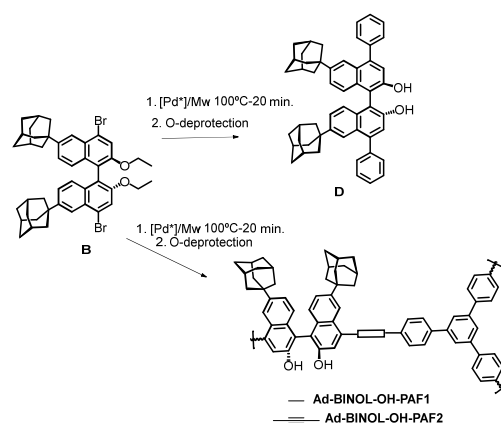
for the addition of diethylzinc to benzaldehyde and compared with that obtained from the corresponding soluble D-[Ti]-catalyst (Table 1).

Table 1. Asymmetric ethylation of benzaldehyde-



Entry	Catalyst	Conv (%) ^b (h)	ee (%) ^{c,d}
1	D-[Ti] ^a	91 (1)	87.0
2	Ad-BINOL-O[Ti]-PAF1 ^b	100 (3)	88.0
3	Ad-BINOL-O[Ti]-PAF2 ^b	100 (3)	78.0
5	7run	90 (3)	50.0

^aD/[Ti]/Aldehyde/[Zn] (0.1/1/1.0/3.0), 1h; ^bcat./Aldehyde/[Zn] (20mg/10/7.0/ 20), 3h; ^{c,d}GC using (CP-Chirasil-Dex).



Scheme 1. Preparation of BINOL-PAF.

When soluble and heterogenized Ad-BINOLs were treated with Ti(OiPr)₄ are a highly active catalytic system in the addition of diethylzinc to benzaldehyde to afford (*R*)-1-phenylpropan-1-ol. The reactions are quantitative and selective for the secondary alcohol. The enantiomeric excess for the heterogenized catalyst was 88% (from at least three batch) similar to that obtained with the corresponding soluble D-[Ti].

The recovered catalyst (after washing) was able to perform diethylzinc addition to benzaldehyde for seven cycles without loss of conversion although the enantioselectivity decreases due to the rest of zinc oxides or unreactive titanium compounds

Conclusions

We have incorporated chiral adamantyl-BINOLs into porous polymeric frameworks giving solid recyclable catalysts for ethylation of aldehydes.

References

[1] A. I. Cooper, Adv. Mater., 2009, 21, 1291.

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