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Oxidative coupling of 2-naphthols catalysed by clays-supported iron catalysts

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Iron pillared clays (Fe-PILC) were compared to Fe-exchanged K10 (Fe-K10) for the oxidative coupling of 2-naphthols to the corresponding binaphthols. Fe-K10 appeared as the most efficient heterogeneous catalyst giving nearly quantitative yields with many naphthols. The highest activity displayed by Fe-K10 is attributed to the easier accessibility of catalytic sites of the clay. The catalyst can be recycled several times with success.

Keywords: oxidative coupling, 2-naphthols, iron pillared clay, binaphthols, recycling

1. Introduction

The synthesis of binaphthols by oxidative coupling of 2-naphthols has been of great synthetic interest, since binaphthols and their derivatives, for example, 1,1′-bi-2-naphthol (BINOL) [1] and 2′-bis(diaryl phosphino)-1,1′-binaphthol (BINAP) [2] have wide applicability as chiral auxiliaries and ligands in organic chemistry. Earlier, the oxidative coupling of 2-naphthols has been carried out as stoichiometric reactions using $FeCl_3$ [3], $K_3Fe(CN)_6$ [4], $Mn(acac)_3$ [5], and Cu(II) amine complexes [6] and $FeCl_3$ under microwave irradiation [7] without solvent. Apart from the disadvantage of being stoichiometric, these methods suffer from difficulties in separation of organic and inorganic products, low yields of the desired products and eventually requirement of microwave irradiation.

A clear improvement has been the introduction of heterogeneous catalysis using oxidation by air or oxygen. Hence alumina-supported copper(II) sulfate [8] and Cu-exchanged montmorillonite [9] catalysts were used for the oxidative coupling of 2-naphthols. Pillared clays [10] are materials of increasing potential interest because of their properties as catalysts for alcohol dehydration, alkylation, hydrocarbon cracking and other acid-promoted reactions. Pillared clays are prepared by the intercalation of metal hydroxyoxy oligomers between the silicate layers of smectite type clays. Recently, we have reported [11] that iron pillared clays were the most efficient catalysts for Friedel–Crafts alkylation of aromatic hydrocarbons. We report in this article the results of the oxidative coupling of 2-naphthols by iron supported either on a pure montmorillonite clay (Fe-PILC) or an acid-treated mesoporous clay. Fe catalysts give a significantly higher activity, with a final yield increasing from the 50% observed for Cu to 95%. Such a high yield greatly simplifies the procedure of separation of the product, therefore since the catalysts appear to be easily recycled, this process could be of practical use.

2. Experimental

2.1. Preparation of catalysts

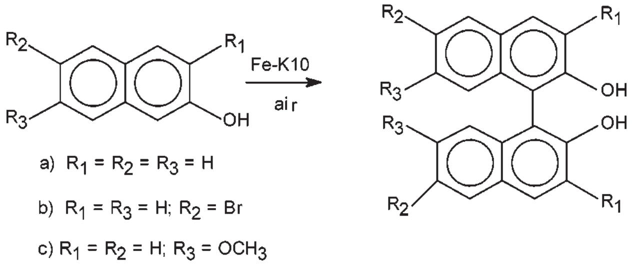
K10, an acid-treated montmorillonite purchased from Fluka chemicals, which shows essentially mesopores of about 3 nm, and Kunipia clay obtained from Japan were used as such. Iron pillared clays were prepared in accordance with an earlier procedure reported by Yamanaka and Hattori [12]. Iron catalysts were obtained from mesoporous K10 using the procedure of ion exchange described in [13].

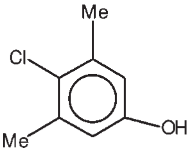
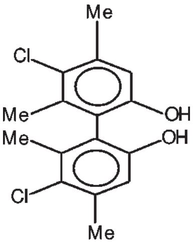
2.2. Characterization

The Fe^{3+} content analysis of the catalysts was carried out as reported by Vogel [14]. X-ray diffraction patterns were determined on a Philips instrument, using Ni-filtered Cu-Kα radiation.

The products of the reaction were characterized by comparison of their NMR, IR and mass spectra with those of products prepared in accordance with literature procedures. Proton nuclear magnetic resonance (^{1}H NMR) spectra were taken on a Gemini Varian (200 MHz) NMR spectrometer, using TMS as an internal standard. IR spectra were recorded on a Nicolet DX-5 spectrometer. Mass spectroscopic analyses were performed with a Micromass VG7070H spectrometer.

Table 1
Oxidative coupling of 2-naphthols catalysed by Fe-K10.



Entry	2-naphthols	Binaphthols	Time (h)	Isolated yields* (%)
1	1a	2a	2	88 (86**)
2	1b	2b	2	95 (93**)
3	1c	2c	2	90 (87**)
4			2	40 (40**)

* The products were characterized by NMR, IR and mass spectrometry.
** With recovered catalyst.

3. Catalytic reactions

3.1. Typical procedure

In a three-necked round bottom flask, 0.14 g (1 mmol) of 2-naphthol and 0.10 g of iron pillared clay in 10 ml chlorobenzene were stirred vigorously at 140 °C for 2 h with continuous bubbling of air through the mixture. The reaction was followed by thin layer chromatography (TLC). After completion of the reaction, the mixture was filtered and the catalyst washed with dichloromethane (2 × 10 ml) and acetone (2 × 10 ml). The combined filtrate was evaporated under reduced pressure to afford the crude product. Purification by column chromatography on silica gel (hexane : acetone, 4 : 1) gave the desired binaphthol with a yield of 0.126 g (88 wt%).

3.2. Results and discussion

Results of the oxidative coupling of 2-naphthols carried out with Fe/K10 are reported in table 1. Both Fe clays gave high yields. The data in table 2 show that the reaction is faster and gives quantitative yields with Fe-K10, whereas the control reaction with K10 montmorillonite is slow. Iron pillared catalysts prepared from pure montmorillonite (Kunipia clay), which can be intercalated to yield a microporous solid (12) showed moderate activity as is evident in table 2. In a control reaction with Kunipia clay, poor yields were obtained.

Two factors have thus an influence: the % Fe and accessibility to the internal surface. The higher activity of Fe/K10 clay, an acid-treated one over the Fe-PILC obtained from Kunipia clay can be ascribed to the more open porosity. K10 has disturbed layers caused by acid treatment and mesopores were developed during this treatment. Therefore, Fe catalysts are very efficient for this reaction, but the easier accessibility of catalytic sites of the mesoporous clay material induces a much higher activity than with a pillared clay.

Table 2
Oxidative coupling of 6-bromo-2-naphthol.

S. No.	Catalyst	Fe_2O_3 (%)	Time (h)	Conversion (%)
1	K10 mont.	4.62	24	90
2	Kunipia clay	3.91	24	30
3	Fe-K10	20.40	2	95
4	Kunipia Fe-PILC	23.41	12	95

This new methodology offers many advantages over previous methods: (1) montmorillonite is cheaper and abundantly available in nature; (2) the catalytic reaction affords binaphthols in good yield; (3) filtration facilitates a simple and easy work-up; (4) the recovered catalyst can be recycled without loss of catalytic properties.

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