Catalysis Letters Vol. 112, Nos. 1–2, November 2006 (© 2006)
DOI: 10.1007/s10562-006-0162-3

An efficient oxidative coupling of naphthols catalyzed by Fe impregnated pillared montmorillonite K10

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Received 11 April 2006; accepted 29 June 2006

Montmorillonite K10 was modified with pillaring solutions of Fe. The catalyst was activated at different temperatures. The resultant heterogeneous catalyst was used for coupling of 2-naphthol and derivatives under mild operating conditions. The activity of catalyst was compared with Fe pillared bentonite, Fe-exchanged montmorillonite K10 and bentonite catalysts. Amongst them, K10-FePLS120 showed better activity and selectivity. The catalyst can be recycled without loss of activity.

KEY WORDS: binol; Fe impregnated pillared; montmorillonite K10; oxidative coupling.

1. Introduction

Binol (1,1′-Bi-2-naphthol) has gained considerable interest as an important chiral auxiliary for asymmetric synthesis [1]. Therefore much attention has been paid to the development of binol derivatives, which are versatile sources of the various 1,1′-binaphthalene skeleton. A convenient and economic way for obtaining the enantiomers is the resolution of racemic 1,1′-binaphthalene-2,2′-diol [2]. Various synthetic approaches to this compound have been developed. The typical method of preparation involves transition metals, which acts as a catalyst and/or oxidant. Frequently employed transition metals are Fe(III) and Cu(II); though use of Mn(III), Ti(IV), V(V), Ru(III) have also been reported [3]. This methodology suffers through disadvantages like catalyst/product separation, also demanding for sophisticated techniques such as high-pressure reactors to carry out the reaction when O_2/air is used as an oxidant. In the laboratory scale synthesis as well as for the manufacture of large volume chemicals, "greener" catalytic ones with clean, safe and inexpensive oxidant should replace the environmentally unacceptable processes. In this regards few heterogeneous catalysts have been reported, which offers some advantages with regard to ease of isolation of products, however typically high volumes of organic solvents have been used for reaction (15–20 ml of either xylene or chlorobenzene per mmol of 2-naphtol). Solid phase oxidation with $FeCl_3$ and Cu(II)-amine complexes, also various other metal complexes have been immobilized on solid supports for the same reaction [4]. For e.g. $FeCl_3$ adsorbed on alumina, silica gel; $CuSO_4$ on alumina, Fe(III) and Cu(II) exchanged zeolites, clays have also been used [5, 6]. Non-conventional techniques such as microwave [7] and ultrasound [6a] have been reported for the coupling of naphthols. Recently, treatment of sodium-2-naphthoxide with bromine, molecular O_2 as oxidant in presence of $VO(acac)_2$ and $Ru(OH)x$ has been reported [8].

The review of literature suggests, modifying montmorillonite K10 by impregnating it with the pillaring solutions of Fe. The procedure used, lead to impregnation of Fe ion with different metal ions present on the surface of K10. This approach offers several advantages over pillared clays (PILCs); (1) the time required for the preparation of the catalyst is less as compared to the time required for preparation of PILCs; (2) drastic reduction in the metal ion/ clay ratio and (3) less amount of water to be handled during catalyst preparation. Pillared clays have already been used for various organic reactions such as Friedel Crafts alkylations, Dehydrogenation but not yet for oxidative coupling reactions [9]. The pillaring species impregnated catalysts (K10FePLS) and Fe-exchanged catalysts (K10-FeA) activated at different temperature were compared for coupling of 2-naphthol using TBHP as an oxidant for this probe reaction.

2. Experimental

2.1. *Preparation of catalysts*

Montmorillonite K10 was obtained from M/s Aldrich (manufactured by Sud-Chemie AG). The chemical composition (wt%) of the clay main elements was Al_2O_3: 14.6; SiO_2: 67.6; Fe_2O_3: 2.9; MgO: 1.8. The BET surface area was 220 ± 20 m^2/g and the micropore volume was 0.1 m^3/g. Bentonite was obtained from M/s Aldrich. The chemical composition (wt%) of the

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bentonite clay (main elements) was Al_2O_3: 20.10; SiO_2: 70.9; Fe_2O_3: 3.38; MgO: 2.5;CaO: 1.27. The BET surface area was 26.6 m^2/g. Tertbutylhydropeoxide (TBHP) was obtained from Lancaster as a 70% aq. solution. Fe pillared clay catalysts were prepared as reported in the literature [10].

2.1.1. FePLS catalysts

Pillaring solutions (500 ml) of Fe were prepared. Montmorillonite K10/Bentonite (10 g) was added to it over a period of 10 min. The resultant slurry was stirred at room temperature for 5 h. The clay was filtered, washed with deionized water till free from Cl^- ions, dried in an oven at 80 °C and crushed to a fine powder.

2.1.2. FeA catalysts

To an anhydrous $FeCl_3$ (15 g), dissolved in deionized water (60 ml), montmorillonite K10/Bentonite (10 g) was added over a period of 10 min. The resultant slurry was stirred at room temperature for 5 h. The clay was filtered, washed with deionized water till free from Cl^- ions, dried in an oven at 80 °C, and crushed to a fine powder. Each catalyst was activated at 120 and 550 °C. The catalysts were then preserved in desiccators.

2.2. Characterization

Powder X-ray diffraction patterns of pillared bentonite and montmorillonite K10 catalysts (figure 1) were recorded on a JEOL JDX-8030 X-ray diffractometer using Cu K P radiation. Figure 1(A) confirms the pillaring and shows the basal spacing in the range of 18–20 Å. Figure 1(B) shows no pillaring effect, and confirms the impregnation of the pillaring species on the surface of montmorillonite K10.

2.3. Reactions

All the reactions were carried out in a two neck round bottom flask (25 ml) equipped with reflux condenser, containing 10 ml of water, to which preactivated catalyst (100 mg), 2-naphthol (144 mg; 1 mmol) and TBHP (3–4 drops ~0.1 ml) was added. The reaction mixture was heated in thermo stated oil bath, preset at 80 °C. The progress of the reaction was monitored using HPLC [Jasco LC-900 series with uv/vis detector (jasco-975) at 280 nm and Acetonitrile:water (60:40) as a mobile phase]. After the completion, the reaction mass was filtered through sintered glass funnel (G4), catalyst was washed with acetonitrile. The combined extract was evaporated in vaccuo and the product was isolated by column chromatography using ethyl acetate:hexane (5:95) as a eluent (figure 2).

3. Results and discussion

The Fe pillaring solutions impregnated montmorillonite K10 catalyst was compared with other catalysts such as ion-exchanged montmorillonite K10, bentonite and pillared bentonite catalysts for their performance in oxidative coupling of 2-naphthol with TBHP at 80 °C. The results obtained are shown in table 1.

The Fe pillaring solution impregnated montmorillonite K10 was found to be superior than other catalysts providing 94% yield of product within 3 h, whereas K10-FeA120 gave 54% yield in 7 h. When reaction was

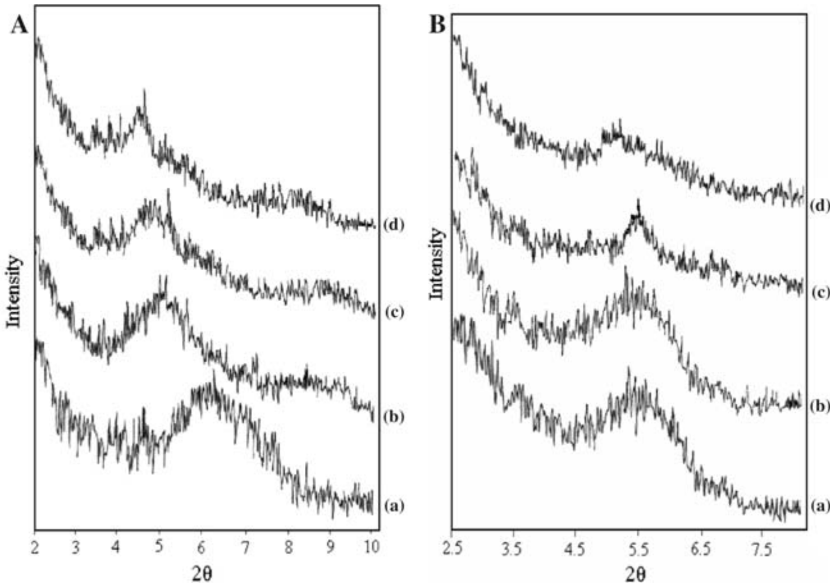


Figure 1. XRD pattern of catalysts. (A) X-ray diffraction pattern of (a) Bentonite, (b) Ben-FePLS550, (c) Ben-FeA120, (d) Ben-FePLS120. (B) X-ray diffraction pattern of (a) Mont. K10 (b) K10-FePLS550 (c) K10-FeA120 (d) K10-FePLS120.

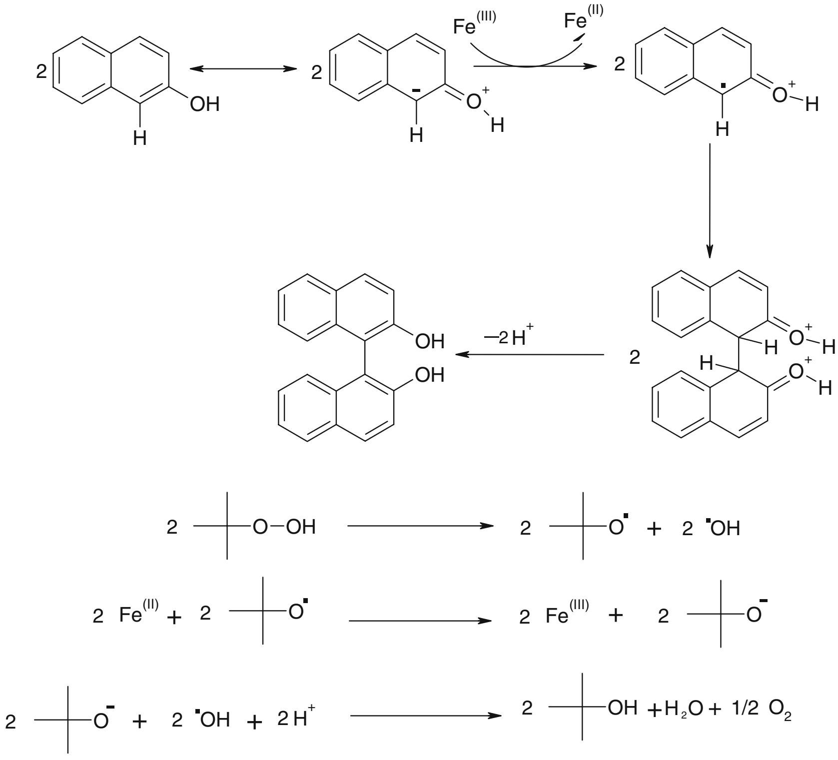
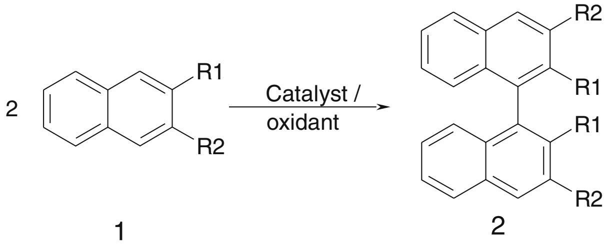


Figure 2. Mechanism.

performed without TBHP, lower yields were observed indicating the importance of catalyst/TBHP combination (entry 1 and 7).

3.1. *Effect of activation on catalysts*

The effect of thermal treatment was reported by purnell et al. [11] on the nature of acidity and catalytic properties of metal exchanged clays. The decrease in the Bronsted acidity is more pronounced than in the Lewis acidity. When Clay is calcined at 500 °C and above, it shows only Lewis acidity. Figueras et al. [12] showed that K10 undergoes major structural changes on heat treatment at high temperatures. This behavior indicates that the exchangeable cations present in the interstitial spaces of the clay may get incorporated into the structural framework and are not accessible to the reactants resulting in poor catalysis. Thus all the catalysts were calcined at 550 °C, to find effect of calcinations on the activity. Calcination at 550 °C leads to deactivation of K10-FePLS whereas K10-FeA found to give comparatively good yields than others (entry 9–12).



Scheme 1. Symmetrical coupling of naphthalenes.

3.2. *Effect of Fe^{+3} content*

Fe^{+3} content of the catalysts was determined as reported by Cheng et al. [13]. The result of Fe^{+3} variation is compared in table 2. It can be seen that Fe content in K10-FeA120 is less than the K10-FePLS120. Low reduction potential of Fe^{+3} (+ 0.771 eV) also

Table 1

Effect of various catalysts on coupling of 2-naphthol[a]

Entry	Catalyst	Time (h)	Conversion[c] (%)	Yield[c] (%)
1	- - - - - -	10	10	5
2	Mont.K10	10	25	10
3	Bentonite	10	20	8
4	K10-FeA120	7	98	54
5	Ben-FeA120	8	98	52
6	K10-FePLS120	3	99	94
7[b]	K10-FePLS120	10	6	3
8	Ben-FePLS120	8	98	86
9	K10-FeA550	8	98	77
10	Ben-FeA550	8	69	38
11	K10-FePLS550	10	98	43
12	Ben-FePLS550	10	75	35

[a]Reaction conditions: 2-naphthol (144 mg, 1 mmol), catalyst (100 mg), TBHP(0.1 ml), water (10 ml). [b]TBHP was not added. [c]Conversion and yield was determined by HPLC.

Table 2
Fe content in catalysts[a]

Catalyst	Fe (%)	Time (h)	Conversion[b] (%)	Yield[b] (%)
K10-FeA120	1.12	7	98	54
K10-FePLS120	4.8	3	99	94

[a]Reaction conditions: 2-naphthol (144 mg, 1 mmol), catalyst (100 mg), TBHP (0.1 ml), water (10 ml). [b]Conversion and yield was determined by HPLC.

facilitates the reaction. With increase in the Fe^{+3} content the accessibility of polyoxocations of Fe on the surface of montmorillonite K10 increases, which leads to increase in the acidity of the catalyst [9a]. This increase in the acidity leads to enhancement in the catalytic activity.

3.3. *Effect of catalyst loading*

The effect of loading of K10-FePLS120 on the coupling reaction of 2-naphthol is shown in table 3. It can be seen that reaction can also be performed using lower quantities of catalyst but considering the time and yield factors, 8.5 mol% of Fe (100 mg) of catalyst was used for the entire study.

3.4. *Effect of temperature on coupling of 2-naphthol*

Temperature effect on coupling reaction is shown in table 4, which shows that the reaction can also be performed at room temperature with very good yields. However, considering the time factor reactions were carried out at 80 °C. This indicates that catalyst is also highly active even at room temperature.

Table 3
Effect of catalyst loading on coupling of 2-naphthol[a]

Entry	Fe mol% (qty, in mg)[c]	Time (h)	Conversion[b] (%)	Yield[b] (%)
1	1.00 (15)	24	97	59
2	2.00 (30)	9	98	64
3	4.25 (50)	5	98	71
4	8.50 (100)	3	99	94
5	10.00 (115)	3	99	93

[a]Reaction conditions: 2-naphthol (144 mg, 1 mmol), TBHP (0.1 ml), water (10 ml). [b]Conversion and yield was determined by HPLC. [c]Fe^{+3} content of catalyst is 4.8%.

Table 4
Effect of temperature on coupling of 2-naphthol[a]

Entry	Temperature (°C)	Time (h)	Conversion[b] (%)	Yield[b] (%)
1	Room temperature (30)	10	98	94
2	55	6	99	94
3	80	3	99	94
4	100	3	99	94

[a]Reaction conditions: 2-naphthol (144 mg, 1 mmol), catalyst (100 mg), TBHP (0.1 ml), water (10 ml). [b]Conversion and yield was determined by HPLC.

Table 5
Effect of solvents on coupling of 2-naphthol[a]

Entry	Solvent	Time (h)	Conversion[b] (%)	Yield [b] (%)
1	Dichloroethane	6	97	90
2	Ethyl acetate	12	85	78
3	Toluene	8	92	80
4	Water	3	99	94
5	DMF	16	35	26
6	THF	18	25	15

[a]Reaction conditions: 2-naphthol (144 mg, 1 mmol), catalyst (100 mg), TBHP (0.1 ml), solvent (10 ml). [b]Conversion and yield was determined by HPLC.

3.5. *Effect of solvents on coupling of 2-naphthol*

Various solvents were screened as summarized in table 5. The reaction needs longer time in dichloroethane, toluene, ethyl acetate for complete conversion while in case of polar solvents like DMF, THF lower yields were obtained. This can be attributed to the solubilization of reactants in organic solvents and their accessibility on the surface of heterogeneous catalyst gets minimized. Recently, Matsushita et al. [8b] have reported coupling of naphthols in water. Thus, when water was used for the present reaction, it gave best results completing the reaction within 3 h with 94% yield.

3.6. *Effect of oxidants on coupling of 2-naphthol*

Effect of oxidants for coupling is shown in table 6. Hydrogen peroxide, air, molecular oxygen was found to give lower yields, whereas TBHP gave better results. When O_2 and air is used as an oxidant, demands for high-pressure reactors and relatively high pressures of oxidants. These oxidants were not effective in oxidizing Fe^{+2} to Fe^{+3} as compared to TBHP.

3.7. *Recyclability*

Recyclability of catalyst was studied up to five cycles

Table 6
Effect of oxidants on coupling of 2-naphthol[a]

Entry	Oxidant	Time (h)	Conversion[b] (%)	Yield[b] (%)
1	TBHP	3	99	94
2	H_2O_2	8	23	17
3	H_2O_2[c]	8	6	3
4	Air[d]	8	6	3
5	O_2[d]	8	15	9

[a]Reaction conditions: 2-naphthol (144 mg, 1 mmol), catalyst (100 mg), water (10 ml). [b]Conversion and yield was determined by HPLC. [c]Carried out under solvent free conditions. [d]Air and O_2 was purged into the solution.

using K10-FePLS120 at 80 °C. The catalyst after each cycle was recovered by filtration through sintered funnel (G4) and used for next cycle after activation at 120°C. K10Fe-PLS120 showed good conversion after each cycle without loss of activity (table 7).

Thus the optimized conditions were applied to substituted naphthalene derivatives and were found to give good results (table 8).

The isolated products were characterized by means of spectroscopic tools such as IR, NMR.

1,1′-binaphthalene-2,2′-diol (2a):- ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 7.95 (d, 2H), δ 7.87 (d, 2H), δ 7.4–7.1 (m, 8H), δ 5.03 (s, 2H). IR (KBr) 3493 (OH), 3417, 1591,1509, 1490, 1384, 1317, 1177 cm^{-1}.

1,1′-binaphthyl-2,2′-diamine (2b):- ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 7.8 (d, 2H), δ 7.78 (d, 2H), δ 7.4–7.1 (m, 8H), δ 3.38 (s, 2H). IR (KBr) 3316(NH_2), 3206, 1620,1509, 1379, 1325 cm^{-1}.

3,3′-Bis(methoxycarbonyl)-1,1′-binaphthalene-2,2′-diol (2c):- ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 8.69 (s, 2H), δ 7.9 (s, 2H), δ 7.4–7.1 (m, 8H), δ 4.065 (s, 6H). IR (KBr) 3350, 2933, 1694, 1505, 1450, 1338, 1233, 1152 cm^{-1}.

Similar conditions can also be applied for unsymmetrical coupling of 2-naphthol with 2-naphthyl amine providing higher selectivity and good yield.

2-Amino-2′-hydroxy-1,1′-binaphthyl (2e):- ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.90 (dd, 2H), δ 7.81 (dd, 2H), δ 7.4–7.0 (m, 8H), δ 2.5 (s, 1H), δ 2.4 (s, 2H). IR (KBr) 3489 (OH), 3412 (NH_2), 1625, 1514, 1470, 1389, 1182, 1149 cm^{-1}.

Table 7
Recyclability of K10-FePLS120 catalyst[a]

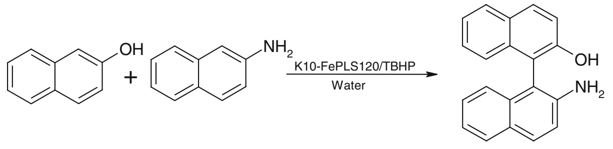
Cycle	Conversion[b] (%)	Yield[b] (%)
1	99	94
2	99	93
3	98	91
4	97	90
5	95	87

[a]Reaction conditions: 2-naphthol (144 mg, 1 mmol), catalyst (100 mg), TBHP (0.1 ml), water (10 ml). [b]Conversion and yield was determined by HPLC.

Table 8
Symmetrical coupling of naphthalenes[a] (as per Scheme 1)

Entry	R1	R2	Time (h)	Isolated yield (%)	M.P. (°C)
a	OH	H	3	92	217
b	NH_2	H	5	84	191
c	OH	$COOCH_3$	4	86	277
d	OH	$COOC_2H_5$	4	88	- - - -

[a]Reaction conditions: Substrate(1 mmol), catalyst (100 mg), TBHP (0.1 ml), water (10 ml).



1a 1b 2e

Time,hrs	Isolated yield, (%)	M.P. (^{0}C)
7	68	240

Scheme 2. Unsymmetrical coupling[a]. *a*Reaction conditions: 2-naphtol and 2-naphthylamine (1 mmol each), catalyst (100 mg), TBHP (0.1 ml), water (10 ml).

3.8. Mechanism

Toda *et al.* suggested radical mechanism for coupling of 2-naphthol [6a] in which Fe^{+3} gets reduced to Fe^{+2} and 1-naphthyl radical formed undergoes coupling, thus leading to the formation of product.

Plillared clays are also known to follow radical type mechanism [9] where reduced Fe^{+2} gets oxidized to Fe^{+3} by means of tertbutylhydroperoxide during the reaction. Thus, Fe^{+3} is again available for coupling reaction. This resembles that Fe requires in catalytic amount for the reaction.

4. Conclusion

Pillaring Fe impregnated, K10-FePLS120 was found to be the best catalyst at 80 °C, using TBHP as an oxidant and environmentally benign water as a solvent for coupling reaction of 2-naphthol. Various substituted naphthalene's can also be coupled selectively with good yields. K10-FePLS120 is highly active even at room temperature and can be recyclable without any loss in activity.

Acknowledgments

Authors would like to thank to TIFR, Mumbai for XRD facility and IIT, Mumbai for ^{1}H-NMR facilities. Financial assistance from DAE/BRNS for this work is acknowledged.

References

[1] (a) C. Rosini, L. Frnzini, A. Raffaelli and P. Salvadori, Synthesis (1992) 503 (b) Y. Chen, S. Yekta and A.K. Yudin, Chem. Rev. 103 (2003) 3155.

[2] (a) J.-M. Brunel and G. Buono, J. Org. Chem. 58 (1993) 7313 (b) L. Pu, Chem. Rev. 98 (1998) 2405 (c) M. Sridhar, S.K. Vadivel and U.T. Bhalerao, Tet. Lett. 38 (1997) 5695 (d) Y. Wang, J. Sun and K. Ding, Tetrahedron 56 (2000) 4447.

[3] (a) M.J.S. Dewar and T. Nakaya, J. Am. Chem. Soc. 90 (1968) 7134 (b) J. Doussot, A. Guy and C. Ferroud, Tet. Lett. 41 (2000) 2545 (c) D.R. Hwang, C.P. Chen and B.J. Uang, Chem. Comm. (1999) 1207.

[4] (a) H.J. Deussen, P. Fredriksen, T. Bijornhoim and K. Bechgaard, Org. Prep. Proceed. Int. 28 (1996) 484 (b) M. Noji, M. Nakjima and K. Koga, Tet. Lett. 35 (1994) 7983 (c) M. Smcrina, J. Polakova, S. Vyskocil and P. Kocovsky, J. Org. Chem. 58 (1993) 4534 (d) M. Nakajima, I. Miyoshi, K. Kanayama, S. Hashimoto, M. Noji and K. Koga, J. Org. Chem. 64 (1999) 2264.

[5] (a) T. Sakamoto, H. Yonehara, C. Pac, J. Org. Chem. 59 (1994) 6859 (b) T. Sakamoto, H. Yonehara and C. Pac, J. Org. Chem. 62 (1997) 3194 (c) T.S. Li, H.Y. Duan, B.Z. Li, B. Tewari and S.H. Li, J.C.S. Per. Trans. 1 (1999) 291 (d) E. Armengol, A. Corma, H. Garcia and J. Primo, Eur. J. Org. Chem. (1999) 1915.

[6] (a) F. Toda, K. Tanaka and S. Iwata, J. Org. Chem. 54 (1989) 3007 (b) B.E. Love and R.A. Bills, Synth. Comm. 32 (2002) 2067 (c) M. Nakajima, S. Hashimoto, M. Noji and K. Koga, Chem. Pharm. Bull. 46 (1998) 1814.

[7] (a) D. Villmin and F. Sauvaget, Synlett (1994) 435 (b) S.-J. Ji, J. Lu, X. Zhu, J. Yang, J.-P. Lang and L. Wu, Synth. Comm. 32 (2002) 3069.

[8] (a) P. Holy, M. Belohradsky and J. Zavada, Synth. Comm. 26 (1996) 2597 (b) M. Matsushita, K. Kamata, K. Yamaguchi and N. Mizuno, J. Am. Chem. Soc. 127 (2005) 6632.

[9] (a) B.M. Choudary, M.L. Kantam, M. Sateesh, K.K. Rao and P.L. Sunthi, Appl. Catal. A: Gen. 149 (1997) 257 (b) D.U. Singh and S.D. Samant, J. Mol. Catal. A. 223 (2004) 111 (c) L.M. Gandia, A. Gil, M.A. Vicente and C. Belver, Cat. Lett. 100 (2005) 229.

[10] H.G. Rightor, M.S. Tzou and T.J. Pinnavaia, J. Catal. 130 (1991) 29.

[11] J.H. Purnell, J.M. Thomas, P.A. Diddams, J.A. Bullantine and W. Jones, Catal. Lett. 2 (1989) 125.

[12] F. Figueras, C. Cativicla, J.M. Fraile, J.I. Graeia, J.A. Mayoral, L.C. Menorval and E. Pires, Stud. Surf. Sci. Catal. 83 (1994) 391.

[13] K.L. Cheng, R.H. Kurtz and R.H. Brag, Anal. Chem. 24 (1952) 1640.