

The effect of counter cations in zeolites on the efficient preparation of the binaphthol–titanium complex

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Abstract

Na-zeolites, among zeolites with a variety of counter cations, are found to provide the active binaphthol–titanium catalyst for an asymmetric carbonyl-ene reaction. A sufficient content of Na cations in zeolites is the key for the efficient formation of the active catalyst. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

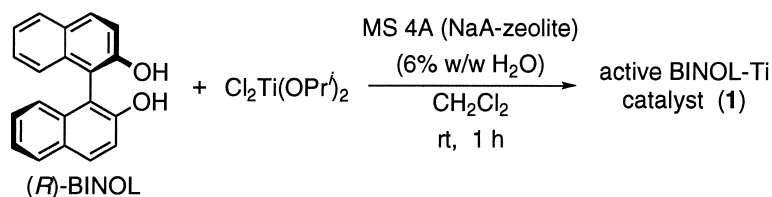
Zeolites have been extensively used as heterogeneous catalysts not only for industrial petrochemical processes but also for fine chemical transformations [1–7]. The combination of acid/base character, shape selectivity due to the nature and content of counter cations as well as the pore size of the zeolites are important factors that determine their catalytic abilities. We have reported that hydrated zeolites, molecular sieves (MS) 4A (NaA-zeolite) [8–13], catalyze the ligand-exchange reaction of $\text{Cl}_2\text{Ti}(\text{OPr}^i)_2$ with optically pure binaphthol (BINOL) into an active BINOL–Ti catalyst (**1**) (Scheme 1) [14–17]. The chiral BINOL–Ti catalyst (**1**) thus obtained serves as an efficient catalyst for asymmetric carbon–carbon bond forming reactions [18–20] such as the carbonyl-ene reaction

[21–24]. We here report that the catalytic activity of the binaphthol-derived titanium complexes is significantly dependent on the counter cations in zeolites employed in the catalyst preparation step.

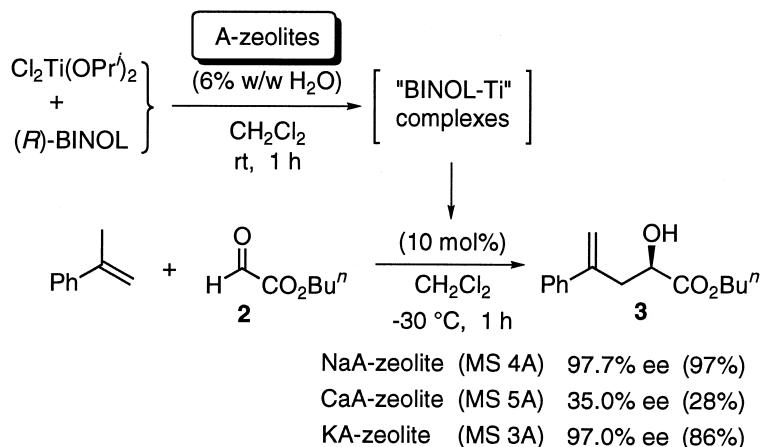
2. Results and discussion

In our continuous study on the asymmetric catalysis by the BINOL–Ti catalyst (**1**), the hydrated MS 4A (NaA-zeolite) has been found to act not only as H_2O donor but also as a base to trap HCl eventually providing the active BINOL–Ti catalyst (**1**) [25]. In order to investigate the effect caused by counter cations in zeolites, we examined isomorphous A-zeolites with different counter cations. The carbonyl-ene reaction of glyoxylate (**2**) was carried out at -30°C for 1 h by using 10 mol% of a titanium complex which was prepared in situ by stirring a mixture of $\text{Cl}_2\text{Ti}(\text{OPr}^i)_2$ and optically pure BINOL for 1

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Scheme 1.



Scheme 2.

h in the presence of A-zeolite (6% w/w H₂O, 5 g/1 mmol of Ti) with varying counter cations (Scheme 2) ¹.

¹ Typical procedure for carbonyl-ene reaction: To a solution of dried (R)-(+)-binaphthol (28.6 mg, 0.10 mmol) in CH₂Cl₂ (1 ml) was added Cl₂Ti(OPrⁱ)₂ (23.7 mg, 0.10 mmol) at room temperature under an argon atmosphere. The resulting mixture was added to a suspension of zeolite (0.5 g; 6% w/w H₂O) in CH₂Cl₂ (3 ml). After stirring for 1 h at that temperature, the reddish brown suspension was cooled to -30°C. α-Methylstyrene (118 mg, 1.00 mmol) and a solution of freshly-distilled n-butyl glyoxylate (156 mg, 1.20 mmol) in CH₂Cl₂ (0.4 ml) were added in this order to the suspension. After stirring for 1 h at -30°C, the reaction mixture was quenched with a solution of triethylamine (0.1 ml) in hexane (10 ml). The zeolite was filtered off through a pad of Celite and the filtrate was concentrated under vacuum. The crude material was purified by silica gel chromatography (hexane:ethyl acetate = 20:1) to give n-butyl 2-hydroxy-4-phenyl-4-pentenoate. The enantiomeric purity was determined by HPLC analysis using CHIRALPAK-AS as a chiral stationary phase column; hexane/PrⁱOH = 3:1, 0.5 ml/min, t_R of (R)-isomer: 9.5 min and (S)-isomer: 12.6 min.

As shown in Scheme 2, the catalytic activity of the titanium complexes is strongly affected by the counter cation in the A-zeolite. The titanium complex prepared in the presence of CaA-zeolite (MS 5A) is found to give the ene product (3) in quite a low yield along with low enantioselectivity. This is in contrast to the ordinary NaA-zeolite (MS 4A). Here the ene reaction proceeds almost quantitatively with extremely high enantioselectivity. In the presence of KA-zeolite (MS 3A), the ene product (3) is obtained with high enantioselectivity but in slightly decreased chemical yield. It is obvious that sodium is the most effective counter cation in A-zeolites in order to obtain the highly active BINOL-Ti catalyst.

To gain an insight into the significant differences of catalytic activity (chemical yield and enantioselectivity) observed, we next conducted an NMR analysis of the titanium complexes

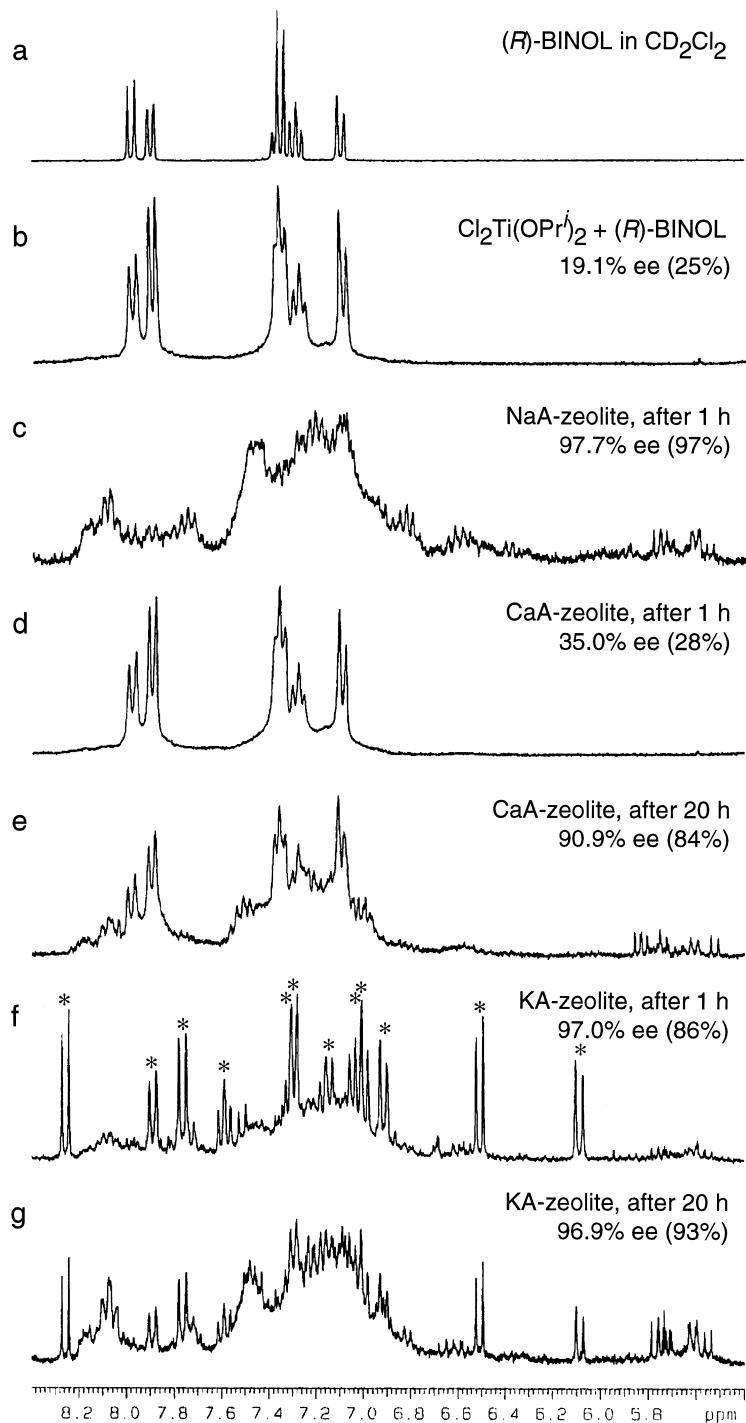


Fig. 1. NMR spectra of the titanium complexes prepared in the presence of A-zeolite.

prepared in the presence of A-zeolite (Fig. 1)².

In the absence of zeolites, the chemical shifts of the BINOL signals in the presence of $\text{Cl}_2\text{Ti}(\text{OPr}^i)_2$ (chart b) in CD_2Cl_2 were the same as those of the free BINOL ligand (chart a) except for considerable line broadening. However, upon addition of NaA-zeolite, the broadened signals changed into a complex pattern of NMR peaks (chart c) and the active BINOL–Ti catalyst (**1**) was formed within 1 h (Scheme 2). In the presence of CaA-zeolite, however, no change was observed (chart d) resulting in the same NMR as observed in the absence of zeolite (chart b). Low chemical yield and low enantioselectivity observed with CaA-zeolite is inferred from a quite slow transformation into the active BINOL–Ti catalyst (**1**). In fact, the ene reaction catalyzed by the titanium complex prepared in the absence of zeolite (chart b) exhibited similarly low chemical yield and enantioselectivity. Even after prolonged stirring (20 h) (chart e), a considerable amount of the free BINOL ligand remained unchanged, whilst showing an increased amount of **1** as could be concluded from the observation of the complex NMR pattern. It was identical to the one found in chart c (MS 4A, 1 h) and the ene reaction led to a significant increase not only in chemical yield (28 → 84%) but also in enantioselectivity (35.0 → 90.9% ee). Interestingly enough, in the presence of KA-zeolite (chart f), spectroscopically distinguishable peaks of a new titanium complex (**4**) appeared in the complex NMR pattern similar to those observed with NaA-

Table 1
BINOL–Ti complex prepared with various Na-zeolites

Run	Na-zeolite ^a	Pore size (Å)	Na ^b (wt%)	Ee (%)	Yield (%)
1	NaA (MS 4A)	4.2	16.2	97.7	97
2	NaX	7.4	14.8	96.8	99
3	NaY	7.4	10.1	95.0	88
4	Na–mordenite	6.7 × 7.0	6.0	75.3	55

^aNa-zeolite contain 6% w/w H₂O.

^bBased on dry Na-zeolites.

zeolite. This new complex (**4**) is assumed to be composed of 2 sets of naphthyl rings on the basis of a COSY experiment³. Prolonged preparation time (chart g) led to a decrease in these peaks and in turn an increase in the complex peaks observed with NaA-zeolite (chart c) for complex **1**. The higher chemical yield (86 → 93%) following the longer preparation time (1 → 20 h) also suggests that the titanium complex (**4**) is gradually transformed into the active BINOL–Ti catalyst (**1**). It should be emphasized here that the use of sodium as counter cation (Na-zeolite) is critical to provide the active BINOL–Ti catalyst (**1**) efficiently and quickly.

Finally, we examined the effect of different pore sizes and of varying sodium content in Na-zeolite (6% w/w H₂O) (Table 1). It is of particular interest that the catalytic activity is strongly dependent on the sodium content in zeolites regardless of the pore size. By the use of NaX-zeolite bearing a larger pore size than NaA-zeolite, the ene product (**3**) was obtained in an equally high chemical yield and enantioselectivity as with NaA-zeolite (run 1 versus 2). On the other hand the chemical yield and enan-

² NMR experiments: Titanium complexes were prepared in a similar manner as described above. To a solution of dried (*R*)-(+)-binaphthol (14.3 mg, 0.05 mmol) in CD_2Cl_2 (0.5 ml) was added $\text{Cl}_2\text{Ti}(\text{OPr}^i)_2$ (11.8 mg, 0.05 mmol) at room temperature under an argon atmosphere. The resulting mixture was added to a suspension of zeolite (0.25 g; 6% w/w H₂O) in CD_2Cl_2 (1.5 ml). After stirring for 1 h at that temperature, the reddish brown suspension was centrifuged and the zeolite was sedimented. The supernatant solution (0.6 ml) was transferred to an NMR tube by a syringe under an argon atmosphere. Prolonged stirring samples were prepared likewise.

³ In contrast to the active BINOL–Ti catalyst (**1**) (Cl: 0.6%; Ti: 11.4%) [25], elemental analysis of titanium complex (**4**) showed the presence of a significant amount of Cl (Cl: 7.14%; Ti: 10.2%) with the ratio of Cl/Ti reaching almost 1. Furthermore ¹⁷O NMR analysis of the titanium complex (**4**) which was prepared in the presence of MS 3A doped with H₂¹⁷O (10 atom % enriched) exhibited a peak at 519 ppm with significant broadening ($W_{1/2} = 1220$ Hz). Thus the titanium complex (**4**) is composed of μ_3 -oxo (450–650 ppm) titanium chloride species. See Ref. [26–28].

tioselectivity were significantly decreased with decreasing sodium content in zeolite (run 2 \rightarrow 3 \rightarrow 4).

In summary, we have demonstrated that Na-zeolite is the most effective additive for this type of ligand exchange reaction. The high content of sodium in the zeolites is crucial to the transformation of BINOL and $\text{Cl}_2\text{Ti}(\text{OPr}^i)_2$ into the active BINOL–Ti catalyst (**1**).

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