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Improved method for immobilization of a chiral complex on PTA/alumina for asymmetric hydrogenation of a β -ketoester

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ABSTRACT

Ru-BINAP was immobilized on alumina using the well-known Augustine method with heteropoly acid (HPA) as the anchoring agent ("Augustine catalyst"). The supported catalyst was tested in a high-pressure reaction such as asymmetric hydrogenation of methyl acetoacetate (MAA). Since the activity of the supported catalyst was significantly lower than that of the homogeneous catalyst, the solvent used in preparing PTA/Al₂O₃ was changed from ethanol to a solution of HCl. The modified supported catalyst ("modified Augustine catalyst") exhibited higher conversion, better selectivity, and improved enantiose-lectivity compared with the catalyst prepared by the Augustine method. The modified Augustine catalyst also produced β -hydroxyesters with good yield and enantioselectivity in asymmetric hydrogenation of various β -ketoester derivatives. The modified Augustine catalyst was examined by FT-IR, XRD, NH₃-TPD, and ICP-AES, which revealed the existence of strong acid sites formed by HPA with a Keggin structure. These results were attributed to the effect of enhanced acidity on the modified Augustine catalyst.

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1. Introduction

Chiral catalysts have received a great deal of attention due to the importance of obtaining pure enantiomers in the production of fine chemicals and pharmaceuticals. Among these processes, enantioselective hydrogenation with homogeneous catalysts is the most widely used approach, and there have been many attempts to develop such catalysts [1,2]. However, the use of these catalysts is limited due to recovery and recycling issues, which detract from their practical application. To overcome the disadvantages of homogeneous catalysts, a number of approaches have been taken to develop effective methods for the heterogenization of homogeneous catalysts [3–5]; however, in most cases, the activity and enantioselectivity of the supported catalysts has been significantly lower than that of the homogenous catalysts.

Augustine et al. reported a very dependable and widely applicable method [6–12] to avoid these problems. Specifically, they immobilized chiral or achiral metal complexes on supports modified with heteropoly acids as anchoring agents (herein referred to as the 'Augustine method'), and the resulting catalysts (herein referred to as 'Augustine catalysts') exhibited good performances in many reactions, including asymmetric hydrogenation of compounds with C=C bonds at moderate pressure [6–9]. Similarly, Ru-BINAP/PTA/alumina catalysts prepared by our group using the Augustine method exhibited good activity and enantioselectivity in asymmetric hydrogenation of DMIT [13]. However, there have been no reports to date on the application of Augustine catalysts in slower, high-pressure reactions, such as hydrogenation of compounds like β -ketoesters. The catalytic hydrogenation of methyl acetoacetate (MAA), a representative β -ketoester, is useful in preparing optically active β -hydroxy esters, which are important chiral building blocks for production of fine chemicals and pharmaceuticals [1].

In the present study, we attempted to apply Ru-BINAP/PTA/alumina prepared by the Augustine method to the hydrogenation of MAA. We also modified the step of supporting PTA in the Augustine method by using an acidic solvent instead of ethanol in an effort to enhance the activity of the Augustine catalyst. The catalytic performance of the newly prepared catalyst ('modified Augustine catalyst') was evaluated for the asymmetric hydrogenation of MAA and various β -ketoester derivatives. Catalysts were characterized by FT-IR, XRD, NH₃-TPD, and ICP-AES to examine the changes in the physical properties of the catalysts according to the immobilization method. The enhancement in the performance of the modified Augustine catalysts was evaluated in relation to the acid sites of the catalysts.

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2. Experimental

2.1. Materials

Prior to its use, γ -Al₂O₃ (activated, neutral, Brockmann I, 150 mesh, Aldrich), which was used as the support, was washed with ethanol to remove fine particles. Phosphotungstic acid (PTA), phosphomolybdic acid (PMA), silicotungstic acid (STA), and silicomolybdic acid (SMA), which were used as anchoring agents, were purchased from Aldrich and dehydrated at 110 °C prior to use. Ru-BINAP [RuCl₂((R)-BINAP)] was purchased from Strem Chemicals and used as received. Methyl acetoacetate (MAA) was obtained from Aldrich, and ethyl acetoacetate (EAA), methyl 3-oxovalerate (MOV), and *tert*-butyl acetoacetate (TBAA) were purchased from TCI; chemicals were degassed at reduced pressure with an aspirator for 1–2 h before use. EtOH (99%) was obtained from Merck and degassed at reduced pressure before use, and 0.5 M HCl was purchased from Riedel-de Haen and used without further purification.

2.2. Preparation of immobilized Ru-BINAP catalysts

2.2.1. Augustine method

All reactions used for catalyst preparation were performed using standard Schlenk techniques under an inert atmosphere. Nitrogen and hydrogen were purified by passing through columns packed with a molecular sieve (4Å) and Ridox copper. All solvents were degassed with an aspirator prior to use.

A 250 mL glass reactor was charged with 4.5 g of pre-washed Al₂O₃, which was evacuated and refilled with dried nitrogen several times to remove air from the pores of the solid. Next, 40 mL of ethanol was added to the reactor using a cannula under positive nitrogen pressure. A phosphotungstic acid (PTA) solution (0.96 g in 30 mL of EtOH) was then added dropwise into the suspension of Al₂O₃ with stirring for 30 min. After completion of the addition, the mixture was stirred at room temperature for 4h. The reaction mixture was then filtered and the resulting solid was washed five times with 20 mL of ethanol. The PTA/Al₂O₃ solid residue was subsequently dried at room temperature overnight under vacuum. Next, 3.5 g of the prepared PTA/Al₂O₃ was charged in a glass reactor and 40 mL of ethanol was added, followed by the slow dropwise addition of 0.1526 g (0.192 mmol) of Ru-BINAP dissolved in 40 mL of deoxygenated ethanol into the PTA/Al₂O₃ slurry with vigorous stirring. The resulting mixture was stirred at room temperature for 24 h, after which the reaction liquid was filtered and the remaining solid was washed with ethanol until no color was observed in the filtrate. Lastly, the obtained yellow solid was dried at room temperature overnight under vacuum to give the Ru-BINAP/PTA/Al₂O₃ catalyst, which was referred to as the Augustine catalyst.

2.2.2. Modified Augustine method

Preparation of PTA/Al₂O₃ was carried out under ambient atmosphere, which is different from that of the Augustine method described above. First, 0.875 g of PTA was charged in a 100 mL glass reactor. Next, 41 mL of 0.5 M HCl was added to the reactor to dissolve the PTA, followed by 4.5 g of Al₂O₃ after complete dissolution of PTA. The mixture was then stirred at room temperature for 4 h, and the reaction liquid was removed by heating at 80 °C under reduced pressure. Next, the remaining solid was dried at 110 °C overnight. The resulting PTA/Al₂O₃ solid residue was calcined at 400 °C for 4 h, and immobilization of Ru-BINAP was performed by the Augustine method as described previously. The immobilized Ru-BINAP catalyst that was prepared in this way was referred to as the modified Augustine catalyst.

2.3. Characterization

The metal contents of the immobilized Ru-BINAP catalysts were determined using an ICP-AES instrument (SPECTRO FLAME). The acid sites of the supports and supported catalysts were investigated by NH₃ TPD (Autochem 2920, Micromeritics, USA). Briefly, after pretreatment in He (500 °C, 50 mL/min, 2 h), 100 mg samples were exposed to 15% NH₃/He at 100 °C for 2 h and purged with helium. Next, the temperature was increased at a rate of 10 °C/min from 100 °C to 980 °C with He (30 mL/min), and the desorption of ammonia was monitored with a TCD detector.

FT-IR spectra of Al_2O_3 and PTA/Al_2O_3 were obtained with a Varian spectrophotometer in the range of $400-4000 \text{ cm}^{-1}$ using KBr pellets. XRD patterns of Al_2O_3 , PTA, and PTA/Al_2O_3 were also obtained using a Rigaku D/Max-2500 with Cu K α radiation at 40 kV and 20 mA. A 2θ range from 2° to 50° was scanned at 2° min⁻¹.

2.4. Catalytic hydrogenation

Catalytic hydrogenation reactions were carried out in a 50 mL autoclave equipped with a magnetic bar. The reaction temperature was controlled by an electric heater and maintained at a set temperature. All reaction temperatures were 60 °C, and the hydrogen pressure was set at 40 bar. Prior to use, all substrates and solvents were degassed at reduced pressure with an aspirator. Under inert atmosphere conditions, catalyst, degassed solvent, and substrate were introduced sequentially into the reactor. The reactor was connected to a hydrogenation apparatus and purged with hydrogen (3 bar) five times before stirring was initiated. The reaction was initiated by introducing hydrogen at a pressure of 40 bar. Samples were obtained at predetermined time intervals from the reaction mixture to determine the reaction rate and enantioselectivity. The products were analyzed by gas chromatography (HP 6890) using a Rtx-1701 column. Enantiomeric excess was determined by GC using a Chiraldex G-TA column.

3. Results and discussion

3.1. Catalytic properties of the modified Augustine catalysts

The loading of active components on the support was analyzed by ICP-AES. Table 1 shows the result of ICP-AES analysis for Ru-BINAP/PTA/Al₂O₃. Ru and W were well deposited on alumina by both methods and the Ru loading and PTA content of the modified Augustine catalysts were slightly lower than those of the Augustine catalyst. ICP-AES analysis indicated that immobilization efficiency with the Augustine method was higher.

The properties of the prepared catalysts were tested by asymmetric hydrogenation of MAA. The main product from the asymmetric hydrogenation of MAA with Ru-BINAP/PTA/Al₂O₃ was methyl (R)-3-hydroxybutylate (MHB), while small amounts of methyl-3,3-diethoxybutanoate (ketal) and ethyl hydroxyl butylate (EHB) were obtained as well. Fig. 1 shows the changes in product distribution with time. It is notable that a ketal was formed in the initial stage, but disappeared in later stages.

Table 2 shows that the reaction catalyzed by Ru-BINAP/PTA/Al₂O₃ prepared by the Augustine method exhibited a much lower activity (28% conversion in 6 h), selectivity to MHB (52.5%), and enantioselectivity (80.8%) compared to the homogeneous Ru-BINAP catalyst (100% conversion in 6 h, 98% selectivity, and 99% enantioselectivity). This result was disappointing in the context of the superior performances of the Augustine catalyst for low-pressure hydrogenation of C=C bonds in previous reports [9,13]. Thus, it would appear that diffusion of the substrate within

Table 1

ICP-AES results of Ru-BINAP catalysts prepared by different immobilization methods.^a

Catalyst	Preparation method	Ru (wt.%)	W (wt.%)	Ru (µmol/g cat.)	PTA (µmol/g cat.)
Ru-BINAP/PTA/Al ₂ O ₃	Modified Augustine	0.27	2.85	27	12
Ru-BINAP/PTA/Al ₂ O ₃	Augustine	0.32	3.35	32	15

^a Reagent amounts used in the preparation: 0.53 wt.% Ru (52 µmol Ru/g cat.), 13.64 wt.% W (62 µmol PTA/g cat.).

Table 2

Catalytic activities of Ru-BINAP catalysts prepared by the modified Augustine method and the Augustine method for asymmetric hydrogenation of MAA.^a

Catalyst	Conversion (%)	Selectivity ^d (%)	Yield _{MHB} (%)	$TOF_{60}^{e}(h^{-1})$	ee ^f (%)
Homogeneous Ru-BINAP	100	98.0	98.0	810	99.1
Ru-BINAP/PTA/Al ₂ O ₃ ^b	28	52.5	14.5	60	80.8
Ru-BINAP/PTA/Al ₂ O ₃ c	100	95.0	95.0	587	98.3
Ru-BINAP/STA/Al ₂ O ₃ ^b	30	51.7	15.3	90	80.5
Ru-BINAP/STA/Al ₂ O ₃ c	72	75.8	54.9	316	96.0
Ru-BINAP/PMA/Al ₂ O ₃ ^b	10	75.8	7.5	45	81.0
Ru-BINAP/PMA/Al ₂ O ₃ ^c	58	96.0	55.6	351	95.0

^a Reaction conditions: 60 °C, 40 bar H₂, 25 mL ethanol, 0.68 mL MAA, S/C 1000, 6 h.

^b Immobilized Ru-BINAP catalysts were prepared by the Augustine method.

^c Immobilized Ru-BINAP catalysts were prepared by the modified Augustine method.

^d Percentage of R and S-MHB from the converted substrate with the corresponding ketal as the other product.

^e TOF (mol_{substrate converted}/mol_{cat.}/h) calculated at the indicated time.

 $^{\rm f}$ The (R) enantiomer ((R)-methyl hydroxybutylate, (R)-MHB) formed preferentially.

the supported catalyst limited the reaction rate significantly in a high-pressure MAA hydrogenation reaction.

In an effort to improve the performance of the supported catalyst, PTA/Al_2O_3 was prepared in an acidic solvent instead of ethanol and Ru-BINAP was immobilized on the support to generate the modified Augustine catalyst. The modified Augustine catalyst exhibited a much higher activity (100% conversion in 6 h), selectivity (95%), and enantioselectivity (98.3%) compared with the Augustine catalyst. Indeed, the performance of the modified Augustine catalyst was almost similar to that of the homogeneous catalyst.

Modified Augustine catalysts with other types of heteropoly acid (HPA), including PMA and STA, also showed better performances than the Augustine catalysts with the other types of HPA (Table 1). The reaction rates, selectivities, and ee values for the modified Augustine catalysts were much higher. The performances of the modified Augustine catalysts were different according to the type of HPA. Specifically, the catalytic activity was in the order of PTA > STA > PMA, while selectivity was in the order of PMA = PTA > STA.

In order to confirm the efficiency of the modified Augustine method shown above, the modified Augustine catalyst was tested



Fig. 1. Reaction profile for MAA hydrogenation over an immobilized Ru-BINAP catalyst.

for asymmetric hydrogenation of other β -ketoesters. The hydrogenation of four β -ketoesters with different alkyl substituents was evaluated, and the results are shown in Table 3. All substrates were converted with similarly high yields (95–99%) and enantioselectivities (96.5–98.6%). These results show that the Ru-BINAP/PTA/Al_2O_3 catalyst prepared by the modified Augustine method was efficient for the asymmetric hydrogenation of β -ketoesters, which needs to be performed at high pressure.

The scalability of the modified Augustine catalyst was also tested in reactions at higher substrate to catalyst ratios (S/C ratio), the results of which are shown in Table 4. As the S/C ratio increased from 1000 to 5000, the TOF increased by 5-fold. However, when the S/C ratio increased from 1000 to 10,000, TOF increased 4.6fold. Selectivity and enantioselectivity did not change significantly with different S/C ratios. Together, these results indicated that the modified Augustine catalyst performed well in reactions at higher S/C ratios.

3.2. Acidic properties of the modified Augustine catalyst

The above results demonstrated that the modified Augustine catalyst was more efficient than the Augustine catalyst with respect to hydrogenation of MAA. Furthermore, the results of ICP-AES analysis indicated that the Ru loading and PTA content of the modified Augustine catalysts were slightly lower than those of the Augustine catalyst and that the amount of Ru loading was not the reason for the improved performance of the modified Augustine catalyst.

Since the primary difference between the two methods was the change of the impregnation solvent from ethanol to a hydrochloric acid solution, the acidic properties of the modified Augustine catalyst may have changed, which subsequently may have caused an enhancement of catalytic activities in MAA hydrogenation. There are several relevant studies regarding the effects of acid on reactivity in asymmetric hydrogenation. Wolfson et al. [14] found that reaction rates are improved by the addition of acid into the reaction mixture during the asymmetric hydrogenation of MAA over a Ru-BINAP catalyst, which they attributed to the acid providing additional routes for hydride transfer by protonating the carbonyl bond of MAA. King et al. [15] also reported that the severe reaction conditions of asymmetric hydrogenation of β -ketoester derivatives over [RuCl₂(BINAP)]₂·NEt₃ catalysts could be reduced by the addition of small amounts of a strong acid.





980

^a Reaction conditions: 60 °C, 40 bar H₂, 25 mL ethanol, 6.3 mmol substrate, S/C 1000, 6 h.

^b TOF (mol_{substrate converted}/mol_{cat.}/h) calculated at the indicated time.

 $C(CH_3)_3$

^c Percentage of R and S-product esters from the converted substrate with the corresponding ketal as the other product.

^d Yield was determined by GC analysis on a Rtx-1701 column.

^e ee was analyzed by GC on a Chiraldex G-TA column.

Table 4

1d

CH₃

Effect of S/C ratio on the catalytic activities of Ru-BINAP catalyst prepared by the modified Augustine method in asymmetric hydrogenation of MAA.^a

S/C	Time (h)	Conversion (%)	$TOF^{b}(h^{-1})$	Selectivity ^c (%)	ee ^d (%)
1000	6	100	587	95.0	98.3
5000	10	100	2950	95.0	97.3
10,000	26	100	2735	94.0	97.6

^a Reaction conditions: 60 °C, 40 bar H₂, 25 mL ethanol, 0.68-6.8 mL MAA.

TOF (mol_{substrate converted}/mol_{cat.}/h) calculated at the indicated time.

^c Percentage of R and S-MHB from the converted substrate with a corresponding ketal as the other product.

^d The (R) enantiomer ((R)-methyl hydroxybutylate, (R)-MHB) was preferentially formed.

For these reasons, we investigated the acidic properties of the supported catalysts in our study. First, changes in the acid sites on the support and supported catalysts modified by impregnation with solvent were examined by NH₃-TPD. The NH₃-TPD profile for PTA/Al₂O₃ (Fig. 2) showed high temperature peaks (strong acid sites) and low temperature peaks (weak acid sites). Based on the NH₃-TPD profiles, it was determined that the support prepared by the modified Augustine method had a larger number of stronger acid sites than the support prepared by the Augustine method. These trends were also observed with the supported catalysts (Fig. 3). Together, these results suggested that additional acid sites of higher adsorption strength were formed after impregnation of PTA by the modified Augustine method, and that these



Fig. 2. NH₃-TPD profiles of PTA/Al₂O₃ supports prepared by different methods.



99.0

Config.

R

R

R

R

Fig. 3. NH₃-TPD profiles of immobilized Ru-BINAP/PTA/Al₂O₃ catalysts prepared by different methods.

additional acid sites persisted even after deposition of the metal complex.

The nature of the additional acid sites on the modified Augustine catalyst was examined by FT-IR. Fig. 4 shows FT-IR spectra of alumina treated with PTA and pure Al₂O₃. In the spectrum of PTA/Al₂O₃ prepared by the modified Augustine method, the characteristic peaks of Keggin anions of PTA (P–O (1080 cm⁻¹),



Fig. 4. (a-c) FT-IR spectra of pure Al₂O₃ and PTA/Al₂O₃ supports prepared by different methods



Fig. 5. XRD patterns of (a) pure Al_2O_3 , (b) PTA/ Al_2O_3 prepared by Augustine method, (c) PTA/ Al_2O_3 prepared by modified Augustine method, and (d) PTA.

W=O_t (983 cm⁻¹), W–O_c–W (898 cm⁻¹), W–O_e–W (797 cm⁻¹)) are clearly identifiable in addition to the alumina peak (1650 cm⁻¹). On the other hand, absorption peak at 1080 cm⁻¹ was only observed in the spectrum of PTA/Al₂O₃ prepared by Augustine method, while the other peaks were broad. These observations were in agreement with a previous report [16] showing that Keggin structures are preserved by impregnation of PTA on alumina in a 0.5 M HCl aqueous solution, whereas they are degraded by impregnation in EtOH.

Differences in the properties of the PTA immobilized supports were also evaluated using XRD patterns. Fig. 5 shows the XRD patterns of modified Al_2O_3 and pure Al_2O_3 . The XRD pattern of the PTA/ Al_2O_3 prepared by Augustine method (b) was similar to that of alumina (a) except for a broad peak at $3-7^\circ$, whereas in the case of the PTA/ Al_2O_3 prepared by modified Augustine method (c), sharp XRD peaks corresponding to crystalline PTA were observed at $6-9^\circ$.

It was apparent that the Keggin structure was better maintained during impregnation of PTA in 0.5 M HCl (modified Augustine method) than in EtOH (Augustine method). It is well known that PTA with a Keggin structure behaves as a strong Bröensted acid [18]. Therefore, the additional acidities of the modified Augustine catalyst appeared to be related to PTA with well-preserved Keggin structure.

3.3. Evaluation of enhanced performance of modified Augustine catalysts

Based on the results shown above, the improved activity and selectivity of the modified Augustine catalysts was considered to be due to the strong acid sites of PTA. Specifically, acid sites on the surface of the modified Augustine catalyst were thought to be formed as follows. In preparing the modified Augustine catalyst, PTA dissolved in HCl solution was impregnated on alumina and the recovered PTA/alumina powder was subsequently impregnated with Ru-BINAP in EtOH. Therefore, various kinds of acid sites could have been formed including adsorbed PTA and HCl on the support of the modified Augustine catalyst. PTA is known to adsorb on Al₂O₃ very strongly due to electrostatic interactions between acidic proton-Keggin polyanions and pairs of basic-Lewis acid sites on Al₂O₃ as suggested by Rao et al. [17]. Thus, PTA could have remained intact on the surface even after metal deposition, to form acid sites on alumina. HCl was also thought to weakly adsorb on alumina, but was likely washed out by EtOH during the washing step following deposition of the metal complex.

During the adsorption step in HCl solution, strong acid sites of PTA with definite Keggin structure may have formed on the modified Augustine catalyst. These strong acid sites on the modified Augustine catalyst appeared to correspond with the high temperature peak of its associated NH_3 TPD diagram (Fig. 3). On the other hand, no strong acid sites formed from PTA on the Augustine catalyst due to degradation of Keggin structure of PTA during its adsorption in ethanol solvent.

Of these strong PTA acid sites, the sites uncovered by the Ru complex might have behaved as additional sites for MAA hydrogenation as the acid was added to the reaction mixture, as described previously by Wolfson[14], who demonstrated the enhanced rate and enantioselectivity of asymmetric hydrogenation of MAA. The formation of EHB from the reaction (3% yield) also supported this conclusion. It was previously reported [15] that EHB is produced by transesterification during the hydrogenation of β -ketoesters with added acid. Therefore, the acid sites on the catalysts prepared by the modified Augustine method likely produced the transesterification product EHB.

It may also be possible that the electronic state of the Ru metal adsorbed over strongly acidic PTA might have been changed due to the higher electron withdrawing power of PTA, which could have led to the increased activity and selectivity of the modified Augustine catalyst. In support of this possibility, Augustine reported that there is direct interaction between HPA and the metal atoms of organometallic complexes, which results in an enhancement of catalytic reactivity [9].

4. Conclusions

In this work, we attempted to prepare Ru-BINAP catalysts by the well-known Augustine method of immobilization using PTA as the anchoring agent. The catalyst was then applied to high-pressure reactions of B-ketoester hydrogenation. We also developed a modified Augustine method employing HCl as the impregnating solvent instead of ethanol. With respect to asymmetric hydrogenation of β-ketoesters, the overall catalytic activities of the modified Augustine catalysts were superior to those of the Augustine catalysts and were similar to those of the homogeneous catalyst. NH₃-TPD analvsis of the modified Augustine catalyst revealed the presence of a significant number of strong acid sites when compared to the Augustine catalyst. The FT-IR spectra of the PTA/alumina of the modified Augustine catalyst showed that the Keggin structure of PTA remained intact during impregnation, which was also confirmed by XRD. The strong acid sites formed by HPA with Keggin structure on the modified Augustine catalyst appeared to enhance the rate and enantioselectivity of asymmetric hydrogenation of β -ketoesters through formation of additional active sites or an electronic effect on Ru metal. Furthermore, these results showed that the modified Augustine method was efficient for preparing active supported metal catalysts for high-pressure reaction of asymmetric hydrogenation of β-ketoesters.

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