

Cu(CH₃CN)₄PF₆ immobilized on halloysite as efficient heterogeneous catalyst for oxidation of allylic C–H bonds in olefins under mild reaction condition

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Abstract

Considering the importance of oxidation of allylic C-H bonds in olefins and the unresolved challenging issues, such as long reaction time and the large quantity of catalyst required, and encouraged by the excellent performance of halloysite as a catalyst support, a novel catalytic system was developed to promote this reaction efficiently. To prepare the catalyst, halloysite was first functionalized with ionic liquid then reacted with 2-aminopyrimidine to afford a potential support, Hal-P. The latter was then used for in situ immobilization of Cu(CH₃CN)₄PF₆ and applied to promote the reaction of cycloolefin and tert-butyl p-nitrobenzoperoxoate under mild reaction condition. The results showed that the nature of copper could play an important role in the catalytic activity. Moreover, the presence of ionic liquid and 2-aminopyrimidine in the structure could improve the activity of the final catalyst. Notably, low amounts of catalyst could catalyze the reaction to afford corresponding allylic esters in good yield. It was also found that the reaction was size selective and that cyclic olefins with lower strain could undergo this reaction more effectively. Study of the recyclability of the catalyst confirmed that it was recyclable and could be recovered and recycled for five consecutive reaction runs.

Keywords Halloysite \cdot Allylic C–H bond oxidation \cdot Heterogeneous catalyst \cdot Olefins \cdot Cu(CH_3CN)_4PF_6

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Introduction

Oxidation of allylic C–H bonds in olefins to obtain allylic alcohols and allylic esters is a valuable synthetic route in organic chemistry to generate additional functionality at the allylic position while leaving the C=C bond intact, which distinguishes allylic C–H bond oxidation from hydroxylation or epoxidation. The functionalized olefins obtained via this reaction can be further functionalized to furnish a variety of products. More importantly, this process is considered to be a simple and cost-effective protocol to introduce oxygen atom. This reaction is promoted in the presence of various types of metal salts, particularly those of copper [1-13].

Heterogenization of catalytic species by immobilization on clay is a wellestablished methodology [14]. One of the most attractive clays, which has received tremendous attention in recent years, is halloysite (mostly abbreviated as Hal), a biocompatible, kaolin-like, naturally available, nontoxic clay with formula $Al_2(OH)_4Si_2O_5$ ·2H₂O (Al:Si ratio of 1:1) [15]. This type of clay benefits from some unique features such as tubular morphology, chemical and mechanical stability, high surface area, tunable surface chemistry, and oppositely charged inner and outer surface [14, 15–19], rendering it a potent candidate for use in a diverse range of applications [20–29], especially in catalysis. Work to date has confirmed the utility of Hal for immobilization of catalytically active species and the development of heterogeneous catalysts. To achieve efficient immobilization and control the leaching issue, pristine Hal is mostly modified by surface functionalization on one or both sides [16, 17, 30–39].

In continuation of our research on development of heterogeneous catalysts for promoting efficient protocols for chemical transformations, we recently disclosed use of CuO encapsulated in SBA-15 for oxidation of allylic C–H bonds in olefins [40]. Although that catalyst could promote the reaction efficiently, the reaction time was very long. Moreover, the amount of catalyst required was very high. On the other hand, our recent focus on the utility of Hal as a catalyst support confirmed the excellent performance of this clay [41–43]. Inspired by the efficiency of Hal and in attempt to develop a more efficient strategy for oxidation of allylic C–H bonds in olefins, in the work presented herein, we designed and prepared a novel catalyst for oxidation of allylic C–H bonds in olefins by functionalizing Hal with ionic liquid (IL) and 2-aminopyrimidine (P) followed by immobilization of $Cu(CH_3CN)_4PF_6$. The role of IL and P in the catalytic activity as well as the effect of copper salt were investigated. Moreover, the recyclability of the catalyst was studied.

Experimental

All chemicals used in this work were provided by Sigma-Aldrich and used as received. The structure of the catalyst was confirmed by Fourier-transform infrared (FTIR) spectra obtained using a PerkinElmer Spectrum 65 instrument after degassing at 423 K for 2 h using a BELSORP Mini II. Thermogravimetric analysis was carried out using a Mettler Toledo instrument under N₂ atmosphere at heating rate of 10 °C min⁻¹. Inductively coupled plasma (ICP) analysis (Varian, Vista-pro), field-emission transmission electron microscopy (CM30300Kv), and X-ray diffraction (XRD) analysis (Siemens D5000) were also carried out, after degassing of the sample at 423 K for 3 h using a BELSORP Mini II.

Functionalization of Hal surface with Cl to synthesize Hal-Cl

The first step in the synthesis of the catalyst was surface functionalization of Hal with Cl. For this purpose, Hal (1.2 g) was dispersed in dry toluene (50 mL) using ultrasonic irradiation at power of 12 W. Next, (3-chloropropyl)trimethoxysilane (4 mL) was slowly introduced into the Hal suspension. The resulting mixture was then refluxed at 110 °C under inert (N₂) atmosphere for 24 h. Upon reaction completion, the precipitate was simply separated by filtration. To obtain pure Hal-Cl, the precipitate was washed with dry toluene several times, then dried at 90 °C for 14 h.

Incorporation of imidazole to synthesize Hal-I

In the next step, imidazole was incorporated into the structure of the catalyst. Briefly, Hal-Cl (1.5 g) was suspended in 60 mL ethanol. Then, imidazole (1.36 g) was added to the aforementioned suspension, and the resulting mixture was refluxed at 80 °C for 48 h in presence of catalytic amount of triethylamine. Upon reaction completion, the obtained solid was filtrated, washed with diethyl ether (3×10 mL) repeatedly, then dried at 90 °C in an oven for 10 h.

Conjugation of epichlorohydrin and synthesis of IL-decorated Hal (Hal-E)

Introduction of epoxy group on the surface of Hal was achieved by using a previously reported procedure [44]. Typically, Hal-I (1.2 g) was bathed with excess amounts of epichlorohydrin at 90 °C for 2 days. At the end of the reaction, the obtained precipitate was washed with acetonitrile repeatedly, then dried under vacuum at 50 °C for 20 h.

Reaction with 2-aminopyrimidine to synthesize Hal-P

In the next step, to a suspension of Hal-E (1.2 g), dry toluene 2-aminopyrimidine (0.5 g) was added, and the resulting mixture was refluxed at 110 °C overnight. After that, the solid was filtered, washed with dry toluene for several times, and dried in an oven at 60 °C overnight (Fig. 1).



Fig. 1 Schematic procedure for synthesis of the catalyst

In situ immobilization of copper species and oxidation of allylic C–H bonds in cyclic olefins

Initially, Hal-P (15 mg) was preheated under vacuum at 50 °C for 2 h, then tetrakis(acetonitrile)copper(I) hexafluorophosphate (0.04 mmol, 15 mg) and anhydrous acetonitrile (3 mL) were added (Fig. 1). Then, the reaction mixture was stirred for 1.5 h at ambient temperature under N₂. Next, cycloolefin (5 mmol) and *tert*-butyl *p*-nitrobenzoperoxoate (0.85 mmol, 0.203 g) were added to the reaction mixture. When the reaction had completed, as monitored by thin-layer chromatography (TLC), the heterogeneous catalyst was collected by filtration, then washed with methylene chloride (3×8 mL) and air-dried. The filtrate, on the other hand, was washed with saturated aqueous NH₄Cl (10 mL) then saturated aqueous NaHCO₃ (10 mL), and dried over MgSO₄. Finally, the solvent was evaporated under vacuum, and the product was purified by column chromatography (EtOAc/*n*-hexane 2–10 %) to afford white solid at yield of up to 90 %. The products were characterized by FTIR and ¹H and ¹³C nuclear magnetic resonance (NMR) (Supporting Information) [45].



Fig. 2 TEM images of catalyst



Fig. 3 FTIR spectra of Hal, Hal-Cl, Hal-I, Hal-E, Hal-P, and catalyst

Results and discussion

Catalyst characterization

First, the morphology of the catalyst was studied by TEM. As shown in Fig. 2, the catalyst exhibited tubular morphology, confirming that surface functionalization and incorporation of IL and copper species did not cause the tubular morphology to collapse.

To further characterize the catalyst and confirm the success of each step in its preparation, FTIR spectra of Hal, Hal-Cl, Hal-I, Hal-E, Hal-P, and the catalyst were recorded and are compared in Fig. 3. According to literature [46], the most important characteristic bands of Hal can be assigned to Si–O stretching (1037 cm⁻¹), inner –OH (3599 and 3717 cm⁻¹), and Al–O–Si vibration (509 cm⁻¹) [36]. These characteristic bands could be detected in all the recorded FTIR spectra, confirming that the structure of Hal was preserved upon decoration with IL and P and immobilization of copper. The FTIR spectrum of Hal-I was very similar to that of Hal. Notably, the characteristic band of imidazole ring, C=N (1650 cm⁻¹) overlapped with the bands of Hal. Similarly, in the FTIR spectrum of Hal-E, the characteristic band of epoxy functional group (912 cm⁻¹) overlapped with the bands of Hal. In the FTIR spectrum of the catalyst, the intensities of the bands at 1649 cm⁻¹, 1559 cm⁻¹, and 1479 cm⁻¹, which can be attributed to –C=N, –C=C, and –C–N functionality, respectively, were more pronounced.

To further investigate the structure of the catalyst, its XRD pattern was recorded (Fig. 4). The XRD pattern of the catalyst exhibited the characteristic peaks of pristine Hal at $2\theta = 11.8^{\circ}$, 19.9° , 24.8° , 26.5° , 36° , 38.5° , 55.3° , and 62.5° in agreement with Joint Committee on Powder Diffraction Standards (JCPDS) card no. 29-1487 [38, 47] (for better comparison, the XRD pattern of pristine Hal is also shown in Fig. 4). It is worth noting that the characteristic peaks of Hal were not shifted in the spectrum of the catalyst, implying that the functionalities and copper were located on the exterior surface of Hal. Comparison of the two XRD patterns reveals that, apart from the characteristic bands of Hal, some additional peaks can be observed in the XRD pattern of the catalyst, being attributable to the copper species.

To elucidate the effect of conjugation of IL and immobilization of copper species on the textural features, the N_2 adsorption–desorption isotherm of the catalyst was recorded (Fig. 5). The isotherm of the catalyst is similar to that of pristine Hal [48] (Fig. S21), corresponding to type II with H3 hysteresis loops [38]. Moreover, it was found that, upon surface modification of Hal, the specific surface area decreased



Fig. 4 XRD patterns of pristine Hal and catalyst



Fig. 5 N₂ adsorption-desorption isotherm of the catalyst



Fig. 6 TGA results for Hal and catalyst

significantly (from 51 m² g⁻¹ for pristine Hal to 20 m² g⁻¹ for the catalyst), indicating that the functional groups and copper species covered the surface of Hal.

Next, the copper loading on the catalyst was investigated using ICP analysis. The ICP sample was prepared by digesting the organic moiety according to previous reports. ICP revealed that the content of copper on the catalyst was 4 mol%.

TG analysis of the catalyst (Fig. 6) revealed that the isotherm of the catalyst was different from that of pristine Hal. More precisely, Hal exhibited only two weight losses at 150 and 560 °C, assigned to loss of water and dehydroxylation, respectively

[41, 49]. The thermogram of the catalyst, however, showed additional weight loss stages, which can be attributed to loss of IL and P.

Catalytic activity

As mentioned in "Introduction" section, considering the importance of oxidation of allylic C–H bonds in olefins and in an attempt to furnish a solution to the challenging issues related to this reaction, such as long reaction time and the large amount of catalyst required, a novel Hal-based catalyst was developed in this work. To achieve this, Hal was first surface functionalized with IL and P, then used for immobilization of copper species. As the main catalytically active species in this reaction. Moreover, considering the fact that IL in its individual form can exert a catalytic effect, it was postulated that the presence of IL in the structure of the catalyst could influence its catalytic activity. On the other hand, the presence of P on the backbone of the catalyst could provide multiple nitrogen groups that could effectively play a role in preserving the copper species and prevent its leaching. To verify these assumptions, the role of the catalyst support and nature of copper was first studied. For this purpose, the catalytic performance of several copper species, including Cu(OAc)₂, Cu(NO₃)₂,

Table 1 Role of copper salts and catalyst support in oxidation of allylic C-H bonds of cyclohexene



Entry	Catalyst	Support	Time (h)	Yield (%)
1	Cu(OAc) ₂	_	120	62
2	$Cu(NO_3)_2$	-	110	65
3	CuI	_	150	60
4	Cu(CH ₃ CN) ₄ PF ₆	-	30	75
5	Cu(OAc) ₂	Hal-P	70	70
6	$Cu(NO_3)_2$	Hal-P	64	72
7	CuI	Hal-P	83	82
8	Cu(CH ₃ CN) ₄ PF ₆	Hal-P	7	90
9	Cu(OAc) ₂	Hal-E	100	50
10	$Cu(NO_3)_2$,	Hal-E	90	60
11	CuI	Hal-E	96	55
12	Cu(CH ₃ CN) ₄ PF ₆	Hal-E	24	80

CuI, and Cu(CH₃CN)₄PF₆ in homogeneous form (without support), was investigated in the model reaction of cyclohexene with perester as oxidant at room temperature in acetonitrile in comparison with their heterogeneous counterparts (catalysts immobilized on Hal-P). The results (Table 1) confirmed the importance of the copper salt in the catalytic activity. More precisely, in both the homogeneous and heterogeneous cases, Cu(CH₃CN)₄PF₆ showed the best results. Moreover, it was found that, for all the copper sources, use of homogeneous copper salts resulted in lower product yield and longer reaction time, implying a role for the support in the catalytic activity. Next, the role of P in the catalytic activity was studied. For this purpose, a control catalyst Hal-E (without P) was synthesized and applied for immobilization of all copper species. The results (Table 1) confirmed that, in all cases, immobilization of copper on Hal-P was more effective than Hal-E, indicating a role for P in the catalysis. It is worth noting that use of bare Hal as a catalyst support led to lower product yield than with Hal-P or Hal-E, confirming the contribution of IL to the catalysis.

Armed with these data, $Cu(CH_3CN)_4PF_6$ immobilized on Hal-P was selected as the catalyst of choice. Then, the reaction variables, reaction temperature, catalyst amount, and solvent were optimized (Table 2). The results showed that, among various tested solvents (Table 2), acetonitrile led to the best results. Moreover, the yield and reaction rate decreased dramatically at lower temperature. Notably, at elevated temperature, formation of byproducts resulted in decreased yield of the desired product. Regarding the amount of catalyst, it was found that the optimum value was 15 mg; Use of a lower amount of catalyst led to lower yield and reaction rate.

Table 2 E	Effect of solvent and	temperature on	oxidation of allyl	ic C-H bonds of	cyclohexene
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Entry	Solvent	Temp. (°C)	Catalyst (mg)	Time (h)	Yield (%)
1	Acetonitrile	25	15	7	90
2	Acetone	25	15	15	85
3	Dichloromethane	25	15	27	72
4	Chloroform	25	15	56	45
5	Benzene	25	15	110	52
6	<i>n</i> -Hexane	25	15	150	25
7	Acetonitrile	10	15	33	83
8	Acetonitrile	0	15	70	66
9	Acetonitrile	25	5	22	68
10	Acetonitrile	25	10	17	80
11	Acetonitrile	25	20	8.5	90

Entry	Starting material	Products	Catalyst	Time (h)	Yield (%)
1	\bigcirc		Cu(CH ₃ CN) ₄ PF ₆ on Hal-P	45	67
2	\bigcirc		Cu(CH ₃ CN) ₄ PF ₆ on Hal-P	7	90
3		NO ₂	Cu(CH ₃ CN) ₄ PF ₆ on Hal-P	35	80
4			Cu(CH ₃ CN) ₄ PF ₆ on Hal-P	16	95

Table 3 Synthesis of allylic esters in presence of Hal-P-supported Cu(CH₃CN)₄PF₆

Next, the generality of the developed protocol was investigated by using various cyclic olefins (Table 3). The results showed that the yield and reaction rate were strongly dependent on the size of the cyclic olefin. In detail, among substrates with one C=C bond, the best result was achieved in the case of cyclohexene, which is a cyclic olefin with less strain. Study of cyclic olefins with two C=C bonds proved that not only can this protocol be generalized to this group of olefins, but also that they were more active than their counterparts with only one C=C bond. It is worth mentioning that this protocol was not very successful for acyclic olefins, in most cases showing low yield and several byproducts.

To study the merit of this protocol, the catalytic activity of the catalyst was compared with our previously reported one [40], viz. CuO encapsulated in SBA (Cu–B–N–SBA-15). This comparison confirmed that a very low amount of Halbased catalyst, compared with Cu–B–N–SBA-15 catalyst, could promote the reaction in significantly shorter reaction time to furnish the desired products with comparable yield.

Reaction mechanism

According to literature [45, 50–57], a mechanistic rationale for oxidation of allylic C–H bonds of cyclohexene in presence of the heterogeneous catalyst is proposed in Scheme 1. Initially, oxygen–oxygen bond in *tert*-butyl 4-nitrobenzoperoxoate is cleaved by Cu(I) species to afford Cu(II) *p*-nitrobenzoate and *tert*-butoxy radical. Subsequently, the *tert*-butoxy radical attracts a hydrogen atom from allylic position



Scheme 1 Proposed pathway for allylic oxidation of cyclohexene in presence of catalyst

of the cyclohexene to furnish *tert*-butyl alcohol and cyclohexenyl radical [56, 57]. Cu(III) *p*-nitrobenzoate is produced by addition of allylic radical to the Cu(II) *p*-nitrobenzoate [58, 59], which can rearrange via a seven-membered cyclic transition state to give cyclohex-2-en-1-yl 4-nitrobenzoate and regenerate the Cu(I) catalyst [56]. Notably, to confirm the role of the metallic species in the catalysis, the reaction was also performed in absence of copper. This reaction did not proceed, confirming the necessity for copper to promote the reaction.

Catalyst recyclability

Finally, the recovery and recyclability of the catalyst for allylic oxidation of cyclohexene were investigated. To recycle the catalyst, it was simply separated from the model reaction mixture via filtration, washed with methylene chloride, EtOH, and distilled water, and dried at 50 °C for 3 h under vacuum. The recovered catalyst was then applied in the next run of the same reaction under similar reaction condition. The reactions were monitored by TLC, and at the end of each reaction, the reaction time and yield of the product were obtained. This cycle was repeated for five consecutive reaction runs. Figure 7 compares the reaction times and product yields of the recycling runs. When using the recycled catalyst, the reaction rate decreased. However, this decreasing trend was not constant, with the third recycling run showing a greater decrease in the reaction rate. However, the yield of the desired product decreased slowly upon recycling, with a decrease of only 10 % in the fifth run.

To further characterize the recycled catalyst, the FTIR spectrum of the catalyst after five recycling runs was recorded and compared with that of fresh catalyst (Fig. 8). As depicted, after five recycling runs, the intensities of the characteristic bands of the catalyst decreased. To measure the leaching of copper upon recycling, ICP analysis was applied. The results showed that, after five recycling runs, 0.3 wt% of the initial copper loading had been leached.



Fig. 7 Effect of catalyst recycling on the reaction time and yield of the model reaction



Fig. 8 FTIR spectra of fresh and recycled catalysts

In the final part of this study, the nature of the catalysis was studied via hot filtration test, carried out according to the standard protocol [60]. Briefly, the reaction was stopped at short reaction time and the catalyst separated from the reaction mixture. Then, the reaction of the filtrate was continued and its progress traced. As no significant progress was observed in the absence of the catalyst, it can be concluded that the catalysis was heterogeneous.

Conclusions

An efficient protocol for oxidation of allylic C–H bonds in olefins based on a novel Hal-based catalytic system was developed. The catalyst was prepared by prefunctionalization of Hal with ionic liquid (IL) and 2-aminopyrimidine (P) followed by immobilization of $Cu(CH_3CN)_4PF_6$. Study of the catalytic activity of various copper salts and control supports confirmed that the nature of the copper source could significantly affect the reaction. Moreover, both IL and P could contribute to the catalysis. Study of the catalytic activity of the catalyst confirmed that a low amount of catalyst could promote the target reactions under mild conditions, affording the desired allylic esters in good yield and shorter reaction time compared with previous reports. Investigation of the generality of this strategy established that it could be applied to cyclic olefins with one or two C=C bonds. However, the size of the cyclic substrate could effectively affect the yield and reaction rate. Moreover, this protocol was not successful for acyclic olefins. The results of recycling tests confirmed that the catalyst was recyclable and could be recovered and recycled for five consecutive reaction runs.

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