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Novel catalytic system: *N*-hydroxyphthalimide/hydrotalcite-like compounds catalysing allylic carbonylation of cyclic olefins

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N-hydroxyphthalimide (NHPI) combined with stable and recoverable transition metal–aluminium binary hydrotalcite-like compounds (M-Al HTLcs, M = Cu, Ni, Co) as an unprecedented catalytic system was demonstrated for the allylic carbonylation, as the model reaction, of cyclic olefins with *tert*-butyl hydroperoxide (TBHP), using isophorone (IP) to ketoisophorone (KIP). The results showed NHPI combined with Cu-Al HTLcs to be an efficient catalytic system and the influences of various reaction conditions of the catalytic reaction were optimised. A maximum IP conversion of 68.0 % with 81.8 % selectivity to KIP was afforded under the optimal reaction conditions. Experiments of repeatability and restorability showed Cu-Al HTLcs to be stable for at least five cycles without noticeable loss of catalytic activity. Expanding substrates could also be efficiently converted to the corresponding ketones under the optimised reaction conditions with appreciable yields. A plausible catalytic reaction mechanism was proposed.

Keywords: allylic carbonylation, isophorone, hydrotalcite-like compounds, *N*-hydroxyphthalimide, *tert*-butylhydroperoxide

Introduction

In recent decades, the direct and selective allylic carbonylation of cyclic olefins to the corresponding α,β-enones, such as isophorone (IP) to ketoisophorone (KIP), has been investigated for the extensive application of this functional transformation in organic synthesis and industrial chemistry (Chen et al., 2014; Gao et al., 2015; Skobelev et al., 2013), which can substantially simplify reaction procedure and reduce energy consumption; it also results in less pollution than the traditional transformation schemes including the multi-step reaction (Wang et al., 2010; Zalomaeva et al., 2009). However, no general synthetic methodology is readily available due to the unsatisfactory conversion or selectivity and rigorous reaction conditions (Liu et al., 2010; Qiao et al., 2014; Zhou & Tang, 2005). At present, the development of "green", simple, benign, and recyclable catalysts to functionalise the C—H bonds of hydrocarbons with satisfactory conversion and selectivity under moderate conditions is one of the most interesting areas in the field of allylic oxidation (Nakamura & Nakada, 2013; Yang et al., 2009).

N-hydroxyphthalimide (NHPI) and its derivatives have been identified as extraordinary catalysts for the redox reaction of various hydrocarbons via hydrogen abstraction by intermediate phthalimide-*N*-oxyl (PINO) radical (Chen et al., 2015; Liu et al., 2009; Orlińska, 2010; Wang et al., 2005). However, co-catalysts are required as promoters for achieving the PINO radicals through the precursors NHPI due to its low activity in allylic oxidation (Wang et al., 2010; Yang et al., 2009; Yao et al., 2009). Yang and co-workers (Yang et al., 2005) employed an anthraquinones/NHPI-catalysed system, in which different alkenes were readily oxidised to the desired ketones. Unfortunately, this homogeneous catalytic system for the oxidation of substrates suffers from the drawback of being unrecoverable. Yang et al. (2008)

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reported ZSM-5-supported metal ions/NHPI and Rajabi and co-workers (Rajabi et al., 2011) employed a silica-supported cobalt salen complex/NHPI as a heterogeneous catalytic system for allylic/benzyl oxidation by improving the Ishii system to circumvent contamination of the products with a transition metal. Although these investigations reported promising results, limitations such as low yield and complicated catalyst render them unacceptable for the practical application of the process (Shaabani & Rahmati, 2008; Zheng et al., 2009). An eco-friendly way for carrying out the redox reactions is urgently needed. Hence, a recoverable co-catalyst assisting NHPI may be one feasible catalytic system for eliminating the drawbacks (Melone & Punta, 2013).

On the other hand, inorganic metal mineral hydrotalcite-like compounds (HTLcs), having an ideal and stable formula $[\mathrm{M(II)}_{1-x}\mathrm{M(III)}_x(\mathrm{OH})_2]^{x+}(\mathrm{A}^{n-})_{x/n} \cdot m\mathrm{H_2O}$ with a sheet structure, have attracted considerable attention (Mikulová et al., 2007; Wang et al., 2013; Zhao et al., 2011) in fields such as anion adsorbents, anion exchangers, medicine stabilisers, and in catalytic applications. This results from their particular structure and properties, including exchangeable lamellar anions, controllable basicity, tunable composition, and uniform deposition of the active metal (Alejandre et al., 1999; Xu & Zeng, 2001). Specifically, HTLcs materials containing transition metal ions in the sheets have aroused interest as heterogeneous basic catalysts due to their unique selective oxidation behaviour (Kaneda & Ueno, 1996; Wang et al., 2015; Zhou et al., 2015). Recently, Kishore and Rodrigues (2008) reported that Cu/Co/Fe-MgAl ternary HTLcs as a catalyst could efficiently catalyse the allylic carbonylation of IP to KIP with TBHP. Although Cu-MgAl HTLcs could afford an appreciable IP conversion of 74 % and a selectivity of 100 % for KIP, the long reaction time required (48 h) renders it an unsuitable catalyst for practical applications. In addition, IP conversion using the recovered catalyst for the third cycle was reduced by about 10 % compared with a fresh catalyst due to the amount of catalyst lost.

The current study investigated NHPI combined with commercially available, stable, and recoverable binary HTLcs as a means to developing a relatively low-cost, highly efficient, and reusable heterogeneous catalytic system for the allylic carbonylation of cyclic olefins. The study is unprecedented in employing inorganic metal mineral HTLcs instead of the previous imperfect co-catalyst involving the Ishii catalytic system and appears to be a promising method for circumventing products' contamination and reducing the costs of converting hydrocarbons into their corresponding carbonyl compounds. A series of the first transition metal–aluminium binary hydrotalcite-like compounds (M-Al HTLcs, M = Cu, Ni, Co) were prepared and characterised so as to investigate their catalytic reactivity in the allylic carbonylation of IP combined with NHPI. By contrast, NHPI/Cu-Al HTLcs was determined as an optimal catalytic system for the allylic carbonylation of IP. Next, various reaction parameters were optimised and the best conversion of 68.0 % with 81.8 % selectivity for IP to KIP was afforded. It was also possible for different cyclic olefinic substrates to be efficiently oxidised to the corresponding ketones under the optimised reaction conditions. On the basis of the promising experimental results and related reports, a plausible catalytic reaction mechanism was proposed.

Experimental

All the chemicals were of analytical grade. The only exception was industrial grade isophorone. Deionised water was used throughout the experiments. Inductively-coupled plasma (ICP) was measured using an Optima 5300 DV (Perkin–Elmer, USA) and the heterogeneous samples were pre-processed by acid digestion with $\mathrm{HNO_3}$. The FT-IR spectra were detected on a Nicolet NEXUS 670 FT-IR spectrophotometer (Nicolet, USA) using KBr discs. The power X-Ray diffraction (XRD) patterns of the samples were measured using a Rigaku D/Max III VC diffractometer (Rigaku, Japan) with Cu KR radiation in the range of $2\theta = 2$–9°. The thermogravimetric analyses were carried out on a Netzsch STA 409 PC thermogravimetric apparatus (Netzsch, Germany) under $\mathrm{N_2}$ and in the temperature range between 0 ℃ and 1000 ℃ at a heating rate of 10 ℃ min^{-1}. The surface area and porosity were measured using Autosorb-iQ instruments (Quantachrome, USA). The specific surface areas were determined using the BET equation and the microspore volumes were investigated using the de Boer's *t*-method. The SEM images were obtained with a FEI QUANTA 200 microscope (FEI, USA). The reaction products of oxidation were monitored using a GC-7890II gas chromatograph with an OV-1701 column and a flame ionisation detector (Techcomp, China). IP conversion and KIP selectivity were calculated using the area normalisation method for quantitative analysis.

The preparation of M-Al HTLcs was based on the synthesis of a typical hydrotalcite material via co-precipitation under low supersaturation reported by Guida et al. (1997). Taking Cu-Al HTLcs as an example: an alkaline solution containing $\mathrm{NaHCO_3}$ (2.5 g/0.03 mol) and NaOH (5.20 g/0.13 mol) in deionised water (100 mL) was added drop-wise over 2 h to a saline solution containing $\mathrm{CuCl_2 \cdot 2H_2O}$ (7.65 g/0.045 mol) and $\mathrm{AlCl_3}$ (2.0 g/0.015 mol) in deionised water (50 mL) at 75 ℃. The pH was maintained at 10 ± 0.5. After 24 h, the precipitate was filtered and washed several times with warm deionised water (60 ℃) until the washing fluid was free of chloride ions (using the $\mathrm{AgNO_3}$ test). Then the sample was ground to a uniform consistency and

Table 1. Physical and chemical properties of M-Al HTLcs

Sample	M/Al ratio		S_{BET}	Total pore volume	Pore diameter
	Starting solution	Isolated solid	m^2 g^{-1}	m^3 g^{-1}	nm
Fresh Cu-Al HTLcs	3	3.11	40.0	0.07	7.5
Recycled Cu-Al HTLcs	–	2.92	31.9	0.05	14.0
Ni-Al HTLcs	3	2.95	42.7	0.05	5.0
Co-Al HTLcs	3	2.87	59.8	0.25	16.5

oven-dried at 105 ℃ for 24 h. The preparation of other HTLcs (M = Co, Ni) was in accordance with the Cu-Al HTLcs as detailed above apart from the transition metal salts ($CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$). $CuCl_2 \cdot 2H_2O$, $AlCl_3$, $NaHCO_3$, NaOH, $CoCl_2 \cdot 6H_2O$, and $NiCl_2 \cdot 6H_2O$ were purchased from Tianjin jin feng Reagent (China).

Typically, the catalytic reactions were carried out in a 50 mL round flask. Cu-Al HTLcs (150 mg), NHPI (0.75 mmol), and acetonitrile (10 mL) were placed in a flask equipped with a magnetic stirrer, then the mixture was stirred vigorously for 10 min to create a finely dispersed heterogeneous system. Sequentially, isophorone (10 mmol) and 70 mass % TBHP (40 mmol) were added and the reaction mixture was refluxed. After the required time, the reaction mixture was cooled and filtered. Next, saturated $NaHSO_3$ solution was added to the solution to remove any extra TBHP and the solution was extracted with ethyl acetate (3 × 10 mL). The organic phase was washed successively with saturated EDTA solution and saturated NaCl solution and dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation and the resulting residue was analysed by GC. Isophorone and acetonitrile were purchased from Sinopharm Chemical Reagent. (China). TBHP was purchased from Aladdin (China). NHPI was purchased from J&K Chemical (China). $NaHSO_3$, EDTA, NaCl, and Na_2SO_4 were purchased from Tianjin jin feng Reagent. (China).

Results and discussion

Hydrotalcite-like catalysts characterisation

The M/Al mole ratios of the samples measured by ICP are shown in Table 1. Clearly, there are slight differences between the M/Al mole ratios of the solids isolated and the starting solutions. It is possible that some part of the ions was not precipitated in the preparation process of the M-Al HTLcs. In addition, the Cu/Al mole ratios of the recycled Cu-Al HTLcs solids isolated decreased slightly from 3.11 to 2.92 in the fresh Cu-Al HTLcs solids isolated. This may have largely been due to a modest copper loss in the catalytic reaction.

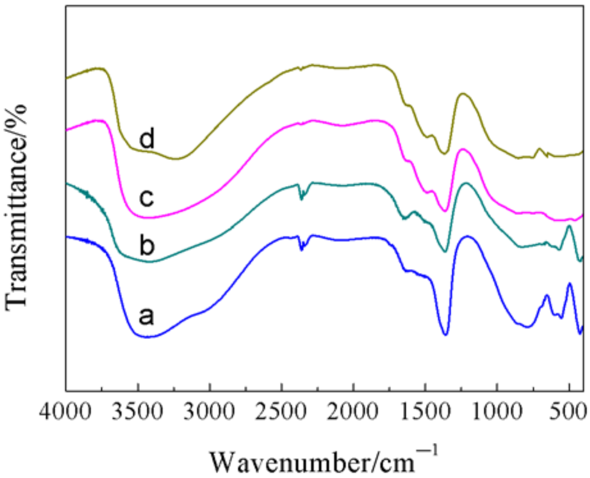


Fig. 1. FT-IR spectra of Co-Al HTLcs (a), Ni-Al HTLcs (b), fresh Cu-Al HTLcs (c), and recycled Cu-Al HTLcs (d).

Fig. 1 shows the FT-IR spectra of all the prepared M-Al HTLcs and recycled Cu-Al HTLcs. For all the samples, the broad and intense absorption peak at 3300–3500 cm^{-1} is attributed to the ν_{as} (O—H) vibration of the interlayer water. Broad absorption peaks at 1500–1600 cm^{-1} corresponding to the δ (O—H) vibration of the interlayer water are perceived. Sharp and intense absorption peaks at 1363 cm^{-1} due to the δ (C—O) vibration of the interlayer CO_3^{2-} are observed. The characteristic absorption peak of the stretching vibration and the framework vibration of M—O—Al can be found at 400–700 cm^{-1}. On comparison, the FT-IR spectra of all the samples are similar to the standard spectra as reported in the literature (Blanch-Raga et al., 2013). The results indicated that well-crystallised M-Al HTLcs were prepared. Clearly, the fresh and recycled Cu-Al HTLcs bear a similarity to each other, suggesting that the structure of the Cu-Al HTLcs after the catalytic reaction did not change significantly.

The XRD patterns of all the samples (Co-Al HTLcs, Ni-Al HTLcs, fresh and recycled Cu-Al HTLcs) are shown in Fig. 2. The sharp and intense characteristic interplanar stacking peaks around $2\theta = 7.54°$ (0 0 3), 23.56° (0 0 6), and 35.64° (0 0 9) are attributed to diffraction by the basal planes of a crystallised hydrotalcite-like compounds. The remaining less intense peaks are consistent with patterns as de-

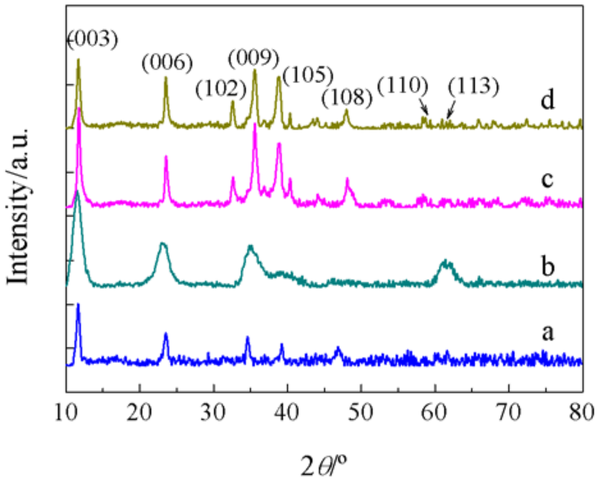


Fig. 2. Powder X-ray diffraction pattern of Co-Al HTLcs (a), Ni-Al HTLcs (b), fresh Cu-Al HTLcs (c), and recycled Cu-Al HTLcs (d).

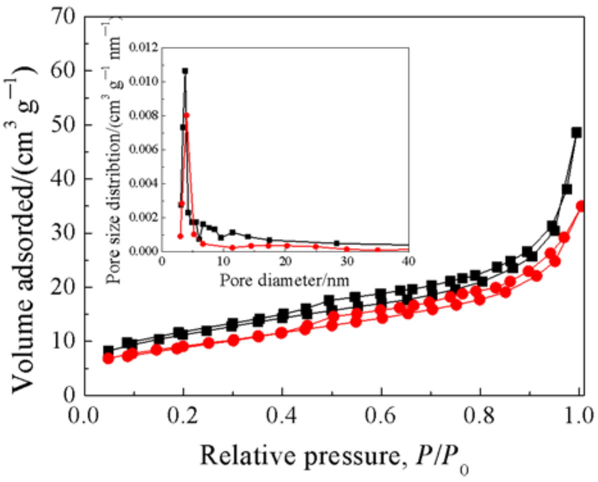


Fig. 4. N$_2$ adsorption/desorption isotherms and corresponding pore size distributions of fresh (■) and recycled (●) Cu-Al HTLcs.

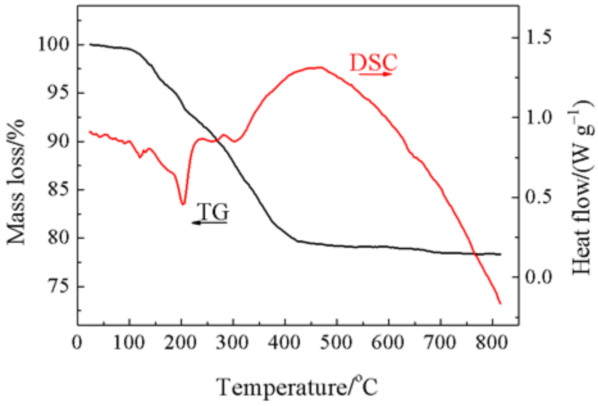


Fig. 3. TG/DSC curves of Cu-Al HTLcs.

tailed in the literature, suggesting the formation of a well-crystallised hydrotalcite (Blanch-Raga et al., 2013; Cunha et al., 2012). The XRD patterns of the recycled catalyst show the retention of the hydrotalcite phase without significant changes, indicating the Cu-Al HTLcs to have a facile chemical stability.

To investigate the process of the thermal decomposition of all the M-Al HTLcs prepared, their TG/DSC analyses were performed and the result for Cu-Al HTLcs is summarised as an example in Fig. 3. From the curves of TG/DSC, it can clearly be seen that two stages of mass loss occurred in the temperature ranges of 120–250 ℃ and 250–400 ℃ and the total mass loss was about 21 %. In the first stage, about 8–9 % of the mass was lost, corresponding to loss of the weakly adsorbed and interlayer water. The second mass loss amounting to 12–13 % was due to the decomposition of hydroxyl and carbonate anions from the interlayer (Wang et al., 2013).

The surface area and total pore volume of all the samples and recycled Cu-Al HTLcs were determined and the results are shown in Table 1. The sample of Co-Al HTLcs shows a maximum specific surface area (59.8 m^2 g^{-1}) and total pore volume (0.25 cm^3 g^{-1}) followed by Ni-Al HTLcs (42.7 m^2 g^{-1}, 0.05 cm^3 g^{-1}) and Cu-Al HTLcs (40.0 m^2 g^{-1}, 0.07 cm^3 g^{-1}). The pore diameters of all the samples range from 5 nm to 16 nm. Clearly, these catalysts possess a small surface area and narrow total pore volume, which are in accord with the morphology of co-precipitated HTLcs materials (Cunha et al., 2012; Zhao et al., 2011). In addition, the N$_2$ adsorption/desorption isotherms of the fresh and recycled Cu-Al HTLcs are presented in Fig. 4. The hysteresis loops are almost similar and can be included in type IV, which characterises mesoporous solids. Their pore size distributions are both in the mesoporous region.

The scanning electron micrographs (SEM) of fresh and recycled Cu-Al HTLcs are presented in Fig. 5. The samples can be seen to be comprised of agglomerates of irregular morphology and the particle size varies widely (Alejandre et al., 1999; Zhao et al., 2011). Following the oxidation reaction, the particle size of Cu-Al HTLcs decreased slightly, which is consistent with the data of BET measurements.

Catalytic performance

The activities of NHPI combined with different M-Al HTLcs were examined in isophorone oxidation using 100 mg catalyst and 40 mmol TBHP in a 70 mass % aqueous solution, and the results are shown in Table 2. KIP was obtained as the main product with small amounts of epoxy isophorone (OIP), hydroxyl isophorone (HIP), and formyl isophorone (FIP) for all the oxidation reactions with *tert*-butyl hydroperoxide at 80 ℃ for 24 h (Fig. 6). The low conversion (approx-

Table 2. Effect of NHPI combined with various M-Al HTLcs on IP oxidation[a]

Entry	Catalytic system	Conversion/%	Selectivity/%			
			KIP	OIP	HIP	FIP
1	None	Trace	–	–	–	–
2	NHPI	8.6	66.8	7.2	12.5	9.6
3	Cu-Al HTLcs	21.6	72.5	4.4	11.1	9.6
4	Ni-Al HTLcs	9.1	71.0	5.5	13.6	8.1
5	Co-Al HTLcs	15.8	73.1	3.2	12.7	9.0
6	NHPI/Cu-Al HTLcs	60.2	78.1	4.3	8.7	5.2
7	NHPI/Ni-Al HTLcs	17.3	74.6	6.7	10.3	6.3
8	NHPI/Co-Al HTLcs	43.7	76.2	3.7	9.1	7.5

a) Reaction conditions: 10 mmol IP, 100 mg M-Al HTLcs and 1 mmol NHPI, 10 mL CH_3CN, 40 mmol TBHP, 80 °C, 24 h.

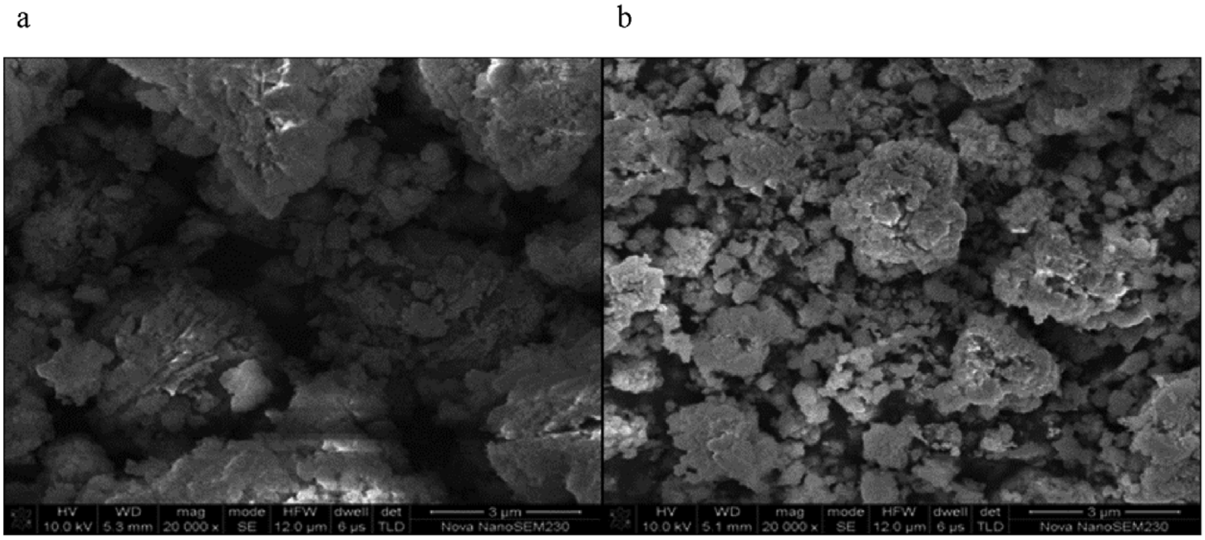


Fig. 5. SEM images of fresh (a) and recycled (b) Cu-Al HTLcs.

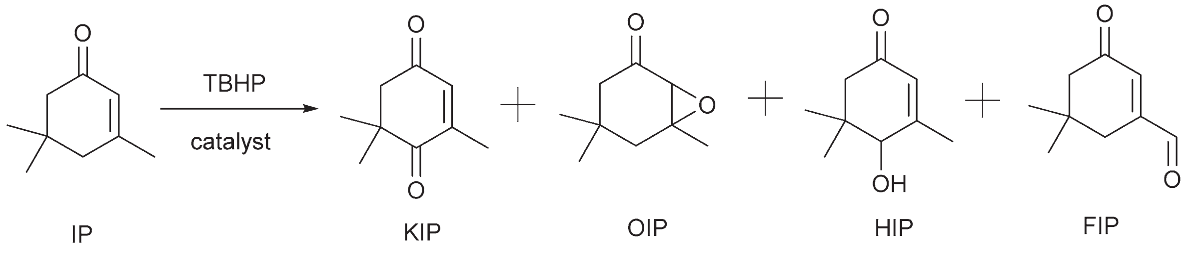


Fig. 6. Allylic oxidation of IP.

imately 10–20 %) was obtained over M-Al HTLcs as the sole catalyst (entries 3–5). However, the accession of NHPI led to the conversion being significantly increased, generally ranging between 8.2 % and 38.7 %, compared with M-Al HTLcs as the sole catalyst under the reaction conditions studied. A maximum IP conversion of 60.2 % with 78.1 % selectivity for KIP was observed with NHPI/Cu-Al HTLcs, followed by NHPI/Co-Al HTLcs (conversion 43.7 %, selectivity 76.2 %) and NHPI/Ni-Al HTLcs (conversion 17.3 %, selectivity 74.6 %) (entries 6–8). It was difficult to perform this transformation with TBHP only (entry 1). The addition of NHPI alone was ineffective in promoting the transformation (entry 2). These results indicate that the interaction between NHPI and M-Al HTLcs significantly influences the catalytic ability of IP oxidation. Since its conversion and selectivity were relatively high, NHPI/Cu-Al HTLcs was selected as the catalytic system for all subsequent studies.

Fig. 7 shows the effect of reaction temperature on the IP oxidation using 100 mg of Cu-Al HTLcs and 1 mmol NHPI as catalysts. The IP conversion in-

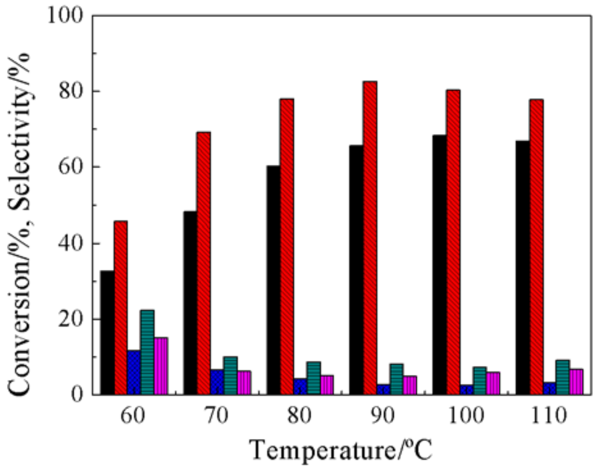


Fig. 7. Effect of reaction temperature on IP oxidation: conversion (■) and KIP (🟥), OIP (🟦), HIP (■), and FIP (■) selectivities. Reaction conditions: 10 mmol IP, 100 mg Cu-Al HTLcs and 1 mmol NHPI, 10 mL CH_3CN, 40 mmol TBHP, 24 h.

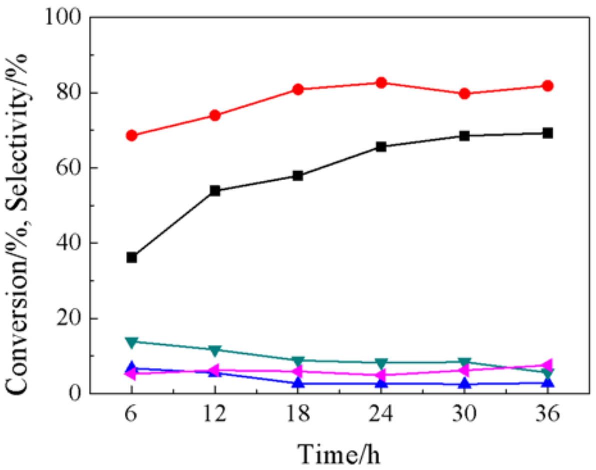


Fig. 8. Effect of reaction time on IP oxidation: IP conversion (■) and KIP (●), OIP (▲), HIP (▼), and FIP (◀) selectivities. Reaction conditions: 10 mmol IP, 100 mg Cu-Al HTLcs and 1 mmol NHPI, 10 mL CH_3CN, 40 mmol TBHP, 90 °C.

creased noticeably from 32.7 % to 65.6 % with gradual increases in the reaction temperature from 60 °C to 90 °C, whereas the conversion of isophorone remained almost unchanged or was reduced with the further increase in temperature. The variation tendency of KIP selectivity was consistent with the IP conversion throughout the increase in temperature. KIP selectivity achieved as high as 82.6 % at 90 °C. On the basis of the IP conversion and selectivity of KIP, 90 °C was selected as the optimal reaction temperature.

The variation in catalytic activity for isophorone at different time intervals is summarised in Fig. 8. A gradual increase in the conversion of IP was found with the increase in reaction time and superior conversion (65.6 %) was observed at 24 h, while further extension of the reaction time did not significantly alter the conversion. Only a small increase in KIP selectivity was noted when the reaction time was prolonged. Hence, 24 h afforded the suitable reaction conditions.

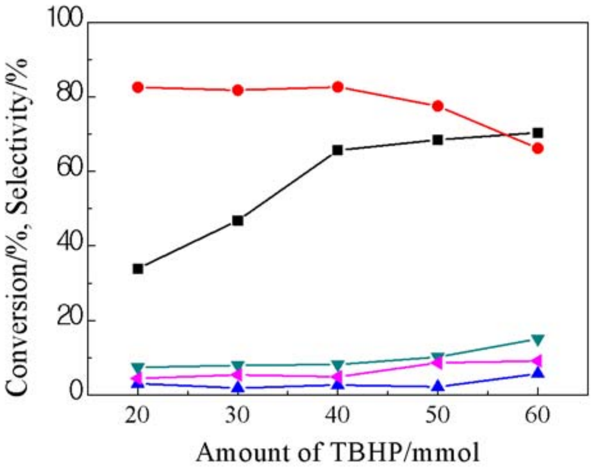


Fig. 9. Effect of TBHP amount on IP oxidation: IP conversion (■) and KIP (●), OIP (▲), HIP (▼), and FIP (◀) selectivities. Reaction conditions: 10 mmol IP, 100 mg catalysts and 1 mmol NHPI, 10 mL CH_3CN, 90 °C, 24 h.

Fig. 9 shows the amount of TBHP to have a significant effect on the oxidation of IP. At below 40 mmol, a positive impact of the amount of TBHP on the transformation was clearly observed. The IP conversion improved from 33.9 % to 65.6 % with increasing the TBHP amount from 20 mmol to 40 mmol, and then remained unchanged. The KIP selectivity did not vary significantly until the amount of TBHP attained 40 mmol, whereas it declined sharply from 82.6 % to 66.2 % with further increase in the amount of TBHP from 40 mmol to 60 mmol as a result of over-oxidation. Hence, 40 mmol was selected as an appropriate amount to retain the highest efficiency of both the conversion of isophorone and the selectivity of ketoisophorone.

The oxidation results using 40 mmol TBHP, different amounts of Cu-Al HTLcs and NHPI at 90 °C for 24 h are displayed in Table 3. An increase in the IP conversion was observed from 43.0 % to 70.9 % with increasing amounts of Cu-Al HTLcs from 10 mg to 150 mg (entries 1–3). IP conversion exhibited no significant change from 150 mg to 200 mg, but it decreased when more of Cu-Al HTLcs was added (entries 4–6). In addition, no marked variation in KIP selectivity was observed until the amount of catalyst reached 200 mg, whereas KIP selectivity decreased slightly if more catalyst was added. This may be because the coke or carbon deposition of the excess Cu-Al HTLcs blocked their active sites, thereby decreasing the activity (Kishore & Rodrigues, 2008). Hence, an opti-

Table 3. Effects of amounts of Cu-Al HTLcs and NHPI on IP oxidation[a]

Entry	Cu-Al HTLcs	NHPI	Conversion/%	Selectivity/%			
	mg	mmol		KIP	OIP	HIP	FIP
1	50	1	43.0	75.3	5.7	10.3	6.1
2	100	1	65.6	82.6	2.7	8.2	4.9
3	150	1	70.9	83.0	3.2	6.5	4.6
4	200	1	72.6	81.3	2.8	10.8	5.3
5	250	1	65.2	78.7	3.1	12.0	6.8
6	300	1	63.0	77.9	3.6	11.4	6.0
7	150	0.25	39.1	70.6	6.8	11.2	8.9
8	150	0.5	55.5	76.8	5.0	8.6	7.2
9	150	0.75	68.0	81.8	2.4	7.3	5.7
10	150	1	70.9	83.0	3.2	6.5	4.6
11	150	1.25	73.3	82.7	3.1	7.6	4.9

a) Reaction conditions: 10 mmol IP, 10 mL CH_3CN, 40 mmol TBHP, 90 ℃, 24 h.

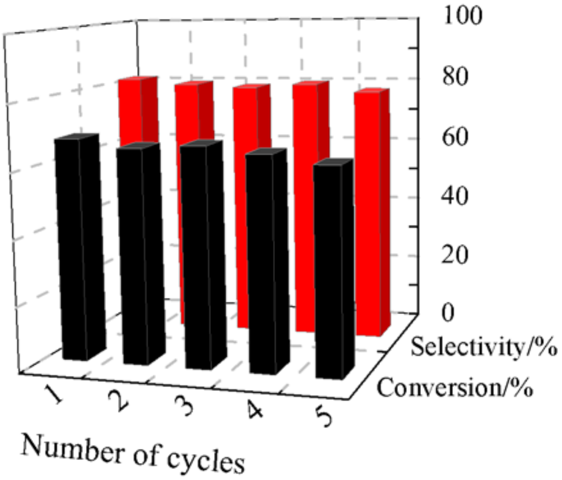


Fig. 10. Recycling of catalyst. Reaction conditions: 10 mmol IP, 150 mg catalysts and 0.75 mmol NHPI, 10 mL CH_3CN, 40 mmol TBHP, 90 ℃, 24 h.

mal amount of 150 mg was selected for all subsequent studies. In addition, the effect of different amounts of NHPI was investigated. A maximum IP conversion of 68.0 % with 81.8 % selectivity of KIP was achieved when employing 0.75 mmol NHPI with gradual increase in the NHPI amount, whereas the IP conversion and selectivity of KIP remained almost unchanged with further increases in the amount of NHPI (entries 9–11). Consequently, 0.75 mmol NHPI was identified as the optimal amount for subsequent investigations.

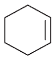
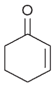
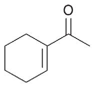
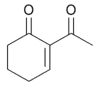
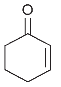
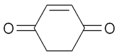
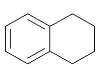
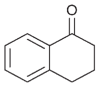
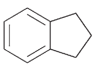
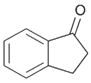
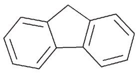
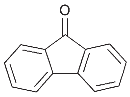
In evaluating the reusability of catalysts, Cu-Al HTLcs was readily and conveniently recovered by separating it from the reaction mixture, successively washing the residue in the acetonitrile, saturated Na_2CO_3 solution, and warm water, and drying in the oven at 105 ℃ for 24 h (yield 93 %) prior to using it in the subsequent run (Kaneda & Ueno, 1996). As a result, no distinct loss in catalytic activity was identified (Fig. 10). IP conversion declined by only 5.9 % and KIP selectivity remained almost unchanged after five repeat uses. Hence, it may be inferred that the catalyst can be recycled and efficient catalysis can be achieved for at least five applications. Consistent with these results, no apparent change could be detected between the FT-IR spectra and the XRD patterns of the fresh and recycled catalysts. These results indicate Cu-Al HTLcs to be a stable, heterogeneous catalyst for allylic carbonylation.

To further explore the general features of this novel catalytic system, a series of various cyclic olefins were examined under the optimised conditions (Table 4). Cyclohexene afforded a remarkably high level of selectivity of 90.5 % towards the formation of 2-cyclohexene-1-one with 80.1 % conversion (entry 1). However, due to the steric and electrophilic effects of the acetyl group, only 52.1 % of 1-acetylcyclohexene was converted into the corresponding 2-acetyl-cyclohex-2-enone with 87.5 % selectivity (entry 2). The conversion of 2-cyclohexene-1-one to the corresponding cyclohex-2-ene-1,4-dione was 54.3 % and the selectivity was 83.6 % (entry 3). The catalytic system was determined as acceptable for converting tetralin into tetralone, affording the appreciable conversion of 72.5 % and selectivity of 87.4 % (entry 4). In addition, indane and fluorene were oxidised to the corresponding indanone and fluorenone, affording the satisfactory conversions of 74.6 % and 79.5 % and selectivities of 92.2 % and 90.4 %, respectively (entries 5 and 6). The cyclohexene, 1-acetylcyclohexene, 2-cyclohexene-1-one, tetralin, indane, and fluorene were purchased from Sinopharm Chemical Reagent (China).

Proposed mechanism for IP oxidation

In view of the above promising results and related published reports (Li et al., 2012; Liu et al., 2014; Melone & Punta, 2013), a plausible catalytic mechanism for the allylic carbonylation of isophorone in the presence of NHPI/Cu-Al HTLcs is proposed and shown in Fig. 11. TBHP was decomposed to highly active

Table 4. Oxidation of different hydrocarbons catalysed by NHPI/Cu-Al HTLcs[a]

Entry	Substrate	Main product	Conversion/%	Selectivity/%
1			80.1	90.5
2			52.1	87.5
3			54.3	83.6
4			72.5	87.4
5			74.6	92.2
6			79.5	90.4

a) Reaction conditions: 10 mmol hydrocarbons, 150 mg catalysts and 0.75 mmol NHPI, 10 mL CH_3CN, 40 mmol TBHP, 90 °C, 24 h.

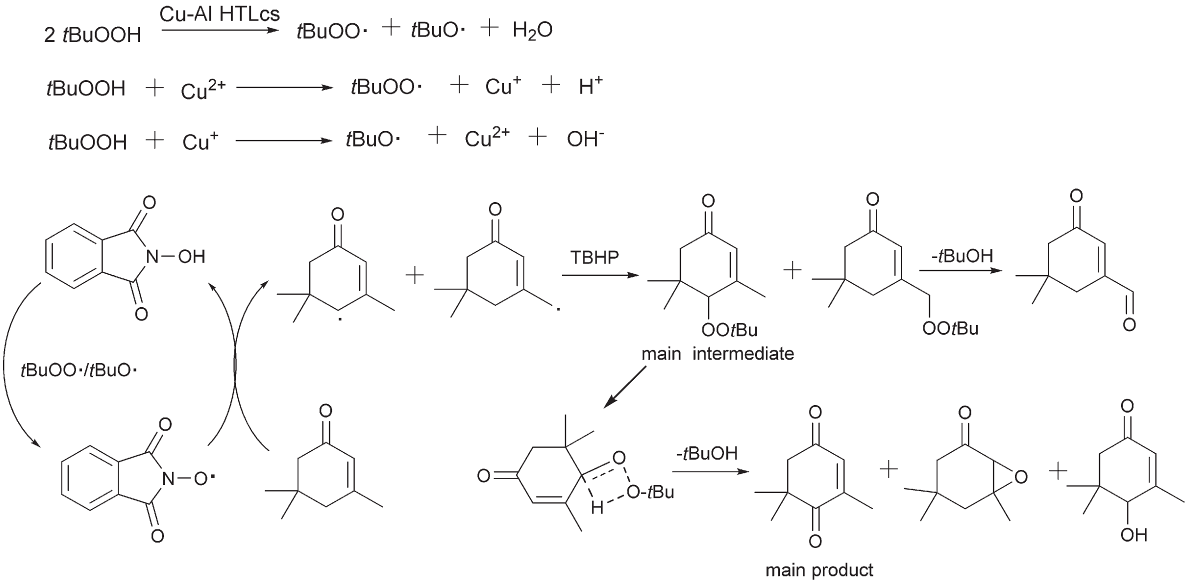


Fig. 11. Plausible catalytic mechanism.

tert-butylhydroxy (*t*BuO) or *tert*-butylhydroperoxy (*t*BuOO) radicals through a Haber–Weiss mechanism in the presence of HTLcs containing a transition metal (Kishore & Rodrigues, 2008). Synchronously, the *t*BuO/*t*BuOO could capture a hydrogen atom from NHPI generating PINO, which could extract a hydrogen atom from IP forming two IP radicals, while the PINO itself is re-converted into NHPI. Then, the newly formed two IP radicals are trapped by TBHP producing two *tert*-butylperoxy ethers, which finally results in oxygenated products (Hermans et al., 2007; Melone & Punta, 2013). Due to their relatively low energy and quite high stability (Chen et al., 2012), *tert*-butyl peroxy isophorone was determined as the main intermediate and KIP as the main product.

Conclusions

The novel heterogeneous catalytic system consisting of NHPI combined with M-Al HTLcs (M = Cu, Ni, or Co) was employed to catalyse the allylic carbonylation of IP to KIP with *tert*-butyl hydroperoxide. After screening and optimisation, a maximum isophorone conversion of 68.0 % of KIP with selectivity of 81.8 % was presented employing the NHPI/Cu-Al HTLcs catalytic system under optimised reaction conditions (10 mmol IP, 150 mg Cu-Al HTLcs, 0.75 mmol NHPI, 40 mmol TBHP, 90 °C, 24 h, and acetonitrile as a solvent). In addition, the repeatability and restorability of Cu-Al HTLcs could avoid contamination of the metal ion. The efficient and eco-friendly transformation process detailed here represents a promising method for oxidising various cyclic olefin analogues.

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