Oxidation of cyclohexane catalyzed by metal-containing ZSM-5 in ionic liquid

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Abstract

Metal-containing ZSM-5 (MZSM-5) molecular sieves were prepared and characterized by XRD, EDX, SEM and N_2-physisorption. The prepared MZSM-5 catalysts were found to be very effective for cyclohexane oxidation with *tert*-butyl-hydroperoxide in ionic liquid [emim]BF_4 under mild conditions. Good yields and high selectivity of products were found in the ionic liquid compared within molecular solvent. The catalytic activity of FeZSM-5 was superior to that of other MZSM-5 and the as-received HZSM-5 in ionic liquid. For cyclohexane oxidation catalyzed by FeZSM-5, 20.9% conversion of cyclohexane and 98.2% selectivity of desired products were obtained in ionic liquid at the temperature of 90 °C. The catalyst/ionic liquid system could be successfully recycled by a simple decantation procedure without significant loss of activity.
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1. Introduction

Partial oxidation of cyclohexane to cyclohexanol and cyclohexanone, the intermediates in manufacturing Nylon-6 and Nylon-6-6, have attracted commercial interest [1]. In the present industrial oxidation process, cyclohexane conversion is less than 3.9% and the selectivity to cyclohexanol and cyclohexanone is 78% [2]. The obvious drawback of this process is the difficulty of separating the catalysts from reaction mixture in homogeneous system. Therefore, the development of effective recyclable catalyst system could offer advantages [3].

Heterogeneous catalyst for the selective oxidation of hydrocarbon is a current challenge [4]. A number of heterogeneous catalysts, which are active and selective for cyclohexane oxidation, including titanium-containing molecular sieves [5], especially titanium silicalite 1 (TS-1), metalloporphyrins [2,6], transition metals (Sn, Zr, Cr, Fe, Mn and Cu) incorporating into zeolite [3,7–9], transition metal complex [10–13], silicalites,

have been studied extensively in recent years. However, most of these reported procedures used volatile organic compounds such as acetonitrile, acetone, acetic acid and methanol as molecular solvents. The recent increased awareness of the detrimental effects of these organic solvents in the environment has led to rapid growth in the research on alternative reaction media. More attention is being given to the reusability of solvents and catalysts for the development of cost-effective chemical processes [14].

There is a considerable interest in the use of room temperature ionic liquids as promising substitutes for volatile organic solvents. These ambient-temperature ionic liquids, especially those based on 1,3-dialkylimidazolium cations, have been emerging as promising green solvents in recent decades. Their low volatility, chemical, physical and thermal stability give them an advantage in recycling and reusing. Moreover, the stability of molecular sieves and other heterogeneous catalysts in ionic liquid is higher than those in molecular solvents [14]. To the best of our knowledge, there has been no report on cyclohexane oxidation with HZSM-5 or metal-containing ZSM-5 molecular sieves in ionic liquid.

In the present work, a series of metal-containing ZSM-5 with an MFI structure were prepared and firstly applied to catalyze the oxidation of cyclohexane with *tert*-butyl-hydroperoxide in ionic

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liquid [emim]BF$_4$, which was used as substitutes for molecular solvent. Good yields and higher selectivity of products were obtained in ionic liquid than in molecular solvent under mild conditions of 90 °C. The catalyst/ionic liquid system could be successfully recycled by a simple decantation procedure without significant loss of activity.

2. Experimental

2.1. Materials

All chemicals and reagents with analytical grade were directly used in the preparation of catalysts and the oxidation of cyclohexane without further purification. HZSM-5 (Si/Al = 25) was a commercial product. Metal sources included nickelous nitrate (Ni(NO$_3$)$_2$·6H$_2$O), cobaltous nitrate (Co(NO$_3$)$_2$·6H$_2$O), cupric nitrate (Cu(NO$_3$)$_2$·3H$_2$O), ferric nitrate (Fe(NO$_3$)$_3$·9H$_2$O), and 50% manganous nitrate aqueous solution (Mn(NO$_3$)$_2$ aq). *Tert*-butyl hydroperoxide (TBHP, 85 wt.% in water) was a commercial reagent.

The required ionic liquids [emim]BF$_4$ was prepared according to a slightly modified literature procedure by the alkylation of 1-methylimidazole with 1-bromoethane followed by substitution of bromide anion with tetrafluoroborate in acetonitrile [15]. The synthesized ionic liquid was finally dehydrated under vacuum over 24 h at 70 °C. Bromide content in [emim]BF$_4$ was 0.2%. Water content of [emim]BF$_4$ was 0.03 wt.%, determined by Karl–Fischer analysis.

2.2. Preparation and characterization of catalysts

A series of metal-containing ZSM-5 (named as MZSM-5) catalyst were prepared using HZSM-5 zeolite (Si/Al = 25) and calcined at 550 °C for 8 h, as a starting material. The incipient wetness impregnation method was used to incorporate metal into the HZSM-5, where the samples were impregnated with an aqueous solution of nitrate, dried at 120 °C for 16 h, and then calcined under O$_2$ flow at 550 °C. The amount of metal contained in MZSM-5 was adjusted to 1.5 wt.% (the metal content was assumed because of the stoichiometric addition of the element in the incipient wetness method).

The structure and particle size of the catalysts were characterized by X-ray diffraction on a X'Pert panalytical diffractometer with Co Kα radiation and scanning electron microscopy. The surface area and pore structure were determined by N$_2$ gas adsorption and desorption isotherms using NOVA 2000 instrument. The surface areas were calculated using the conventional BET method. The elemental analysis was also made by energy dispersed X-ray analysis (EDX).

2.3. Catalytic oxidation reaction

Cyclohexane oxidation reaction was performed in a Teflon-lined 50 ml stainless-steel autoclave equipped with a magnetic stirrer. Typically, 27.8 mmol cyclohexane, 5 ml (6.25 g) ionic liquid, 0.15 g catalyst and 55.6 mmol *tert*-butyl-hydroperoxide (TBHP, 85% in H$_2$O) were introduced into the reactor. The auto-

clave was closed and submerged in a thermostated oil bath at 90 °C. The reaction mixture was vigorously stirred at 1000 rpm for 12 h. After the reactions, the autoclave was removed from the oil bath and maintained for about 2 h, time considered necessary for the system to achieve room temperature. After that period, the autoclave was opened and the upper phase (reaction mixture) was collected carefully via a separating funnel. Recycling tests with repeated use of MZSM-5 and ionic liquid were carried out, the lower phase (ionic liquid/MZSM-5 system) separated was dried in vacuum at 70 °C (16 h) to remove the little amount of water and trace organic compounds. ^{1}H NMR analysis was performed on the recovered ionic liquid. The total mass of the dried ionic liquid and catalyst was measured accurately, ensuring a constant catalyst/ionic liquid/substrate ratio for each run.

For analysis of the products of cyclohexane oxidation, FID gas chromatography (GC, Agilent-6890, capillary column: PEG-20M, 30 m × 0.25 mm, nitrogen as carrier gas) was used for the qualitative analysis. The conversion was calculated based on the starting cyclohexane. Cyclohexyl hydroperoxide (CHHP) contents were determined by decomposition with PPh$_3$ and quantification of the additionally formed cyclohexanol by GC [3,7,11].

TBHP content in the reaction mixture was determined by iodometric titration of the unreacted portion. The efficiencies with respect to THBP (TBHP eff.) were calculated taking into account that 1 mol of TBHP is needed to produce 1 mol of cyclohexanol, 1 mol of CHHP or 0.5 mol of cyclohexanone.

Leaching tests were carried out. After the reaction was complete, the lower suspension was centrifuged for 5 min at 2000 rpm, the liquid phase was decanted, and the metal content in the solvent was determined by atomic absorption spectroscopy (AAS) using Perkin-Elmer 2380 spectrometer. After removal of the liquid phase, the catalyst was washed three times with water and dried for 2 h at 120 °C. The chemical composition of the obtained catalyst was determined by ICP (ICP-9000(N + M)).

3. Results and discussion

3.1. Characterization of catalysts

The particle size of the catalysts, measured by SEM, was around 2 μm. The states of the metals are metal oxides because of the decomposition of nitrate in the atmosphere of O$_2$ at high temperature (550 °C) [16]. The metal distribution on the external surface of the catalysts measured by EDX is given in Table 1. The surface metal concentrations were higher than the bulk concentration (1.5%). This means some part of metal was inserted

Table 1
The amount of metal on the external surface of ZSM-5 catalyst

Metal	The amount of metal on the surface of ZSM-5 (%)
Cu	1.69
Co	1.75
Mn	1.79
Ni	1.73
Fe	1.87

Table 2
Pore structure of different metal-containing ZSM-5 zeolite

Sample	Surface area (m^2/g)	Average pore diameters (nm)	Pore volume (ml/g)
HZSM-5	294.6	2.56	0.189
CuZSM-5	274.1	2.57	0.174
CoZSM-5	277.8	2.66	0.180
MnZSM-5	275.5	2.65	0.177
NiZSM-5	256.2	2.71	0.172
FeZSM-5	281.9	2.60	0.183

into the zeolite and a large part of metal was located on the external surface of HZSM-5. The order of the amount of metal deposited on the external surface of zeolite was as follows: FeZSM-5 > MnZSM-5 > CoZSM-5 > NiZSM-5 > CuZSM-5.

BET surface area, pore volume and the pore size observed for all the catalysts used are shown in Table 2. Compared with the as-received HZSM-5, all the metal-containing ZSM-5 had a lower BET surface area and a smaller pore volume, indicating that the metal was inserted into the zeolite. This result is in agreement with that of the EDX analysis. As one can be seen from Table 2, among all the metals containing ZSM-5, FeZSM-5 had the largest BET surface area and pore volume. CuZSM-5, CoZSM-5 and MnZSM-5 had the similar BET surface area of 274.1–277.8 m^2/g. However, the NiZSM-5 had a low BET surface area of only 256.2 m^2/g. All the MZSM-5 catalysts displayed relatively close pore volume (0.172–0.183 ml/g).

The powder X-ray diffractogram shows a typical pattern for a highly crystalline zeolite having MFI structure (Fig. 1). It can be seen from Fig. 1 that all of the prepared MZSM-5 samples displayed a characteristic diffraction similar to that of as-received HZSM-5 and no metal oxides were detected, implying that the metal-containing ZSM-5 catalysts prepared by calcinations at high temperature maintaining integrated ZSM-5 frameworks with an MFI topology. These results are in accordance with those reported by Xia and co-workers [16].
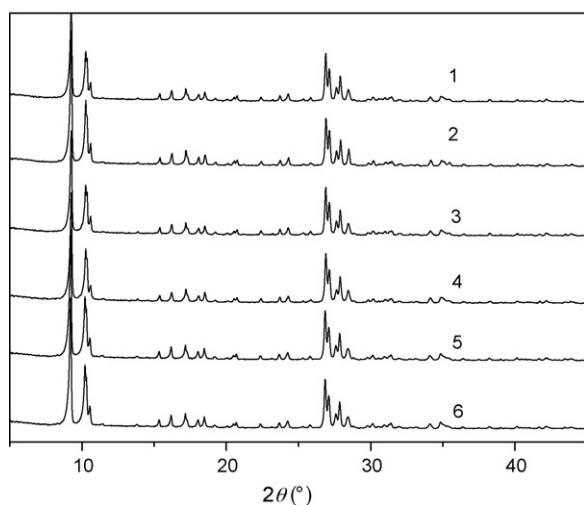

Fig. 1. XRD patterns of ZSM-5 and metal-containing ZSM-5 zeolite: (1) HZSM-5, (2) CuZSM-5, (3) CoZSM-5, (4) MnZSM-5, (5) NiZSM-5, and (6) FeZSM-5.

3.2. Cyclohexane oxidation

3.2.1. Catalytic activity of metal-containing ZSM-5 catalysts for the oxidation of cyclohexane in ionic liquid and molecular solvent

The catalytic performance of the prepared MZSM-5 in ionic liquid [emim]BF$_4$ was investigated in the oxidation of cyclohexane. The results are shown in Table 3. Clearly, for HZSM-5 catalyst, much higher activity was observed in ionic liquid [emim]BF$_4$ compared with in either the conventional molecular solvent or in the absence of a solvent. The as-received HZSM-5 was active, giving a conversion of 15.8% and selectivity of desired products (97.0%), which was higher than the best values reported for 4% conversion in the industrial oxidation process [17]. Compared with the as-received HZSM-5 molecular sieves, all the metals containing ZSM-5 exhibited high selectivity of monofunctional oxidation products (cyclohexanone, cyclohexanol and cyclohexyl hydroperoxide). The best result was observed for the FeZSM-5 which resulted in up to 20.9% conversion of cyclohexane with 98.2% selectivity of desired products, using ionic liquid as solvent. Much higher activity of FeZSM-5 was observed in ionic liquid compared with in acetone. The catalytic activity of the NiZSM-5, CoZSM-5 and MnZSM-5 catalysts was similar to that of the as-received HZSM-5 and cyclohexane conversions of around 15%. CuZSM-5 displayed poor reactivity with low cyclohexane conversions of only 9.5%, while its selectivity reaches up to 100%.

The results obtained with the catalyst MZSM-5 are greater than those reported by Xia and co-workers [16], where a cyclohexane conversion of 4.7–9.3% and a selectivity of desired products of 77.1–96.2% were achieved on metals containing ZSM-5 (Co, Fe, Mn, Cu, Ni, and Cr) catalysts using molecular oxygen and TBHP in a solvent-free system. The highest activity of FeZSM-5 in this study may be due to its largest BET surface area and pore volume. The highest metal content on the external surface of FeZSM-5 may also explain the observed highest activity. The poor reactivity of CuZSM-5 might be attributed to its lowest metal content on the external of catalyst. Compared with CoZSM-5 and MnZSM-5, NiZSM-5 possessed a smaller BET surface area and pore volume, while the activity of NiZSM-5 was similar to that of the CoZSM-5 and MnZSM-5. Therefore, metal types, the metal content on the external of ZSM-5, and the pore structures of molecular sieves had influence on reaction activity and selectivity.

Using CuZSM-5 as catalyst, the ratio of cyclohexanone to cyclohexanol was approximately 1.86, whereas for other MZSM-5 catalysts cyclohexanone formation was more favored and the highest ratio of 3.70 on FeZSM-5 was observed. As shown in Table 3, in contrast to reaction with as-received HZSM-5, all the metal-containing ZSM-5 exhibited low yields of the intermediate product cyclohexyl hydroperoxide (CHHP) which varied in the range of 0–5.15%, accompanied with an increasing order of CuZSM-5, CoZSM-5, MnZSM-5, NiZSM-5, and FeZSM-5. These phenomena might be explained that the metal on the MZSM-5 plays an important role on the decomposition of CHHP.

Table 3
The oxidation of cyclohexane over different metal-containing ZSM-5 materials

Catalyst	Solvent	Conversion (mol%)	Product distribution (mol%)[a]				Selectivity of -one + -ol + CHHP (%)
			-one	-ol	CHHP	-one/-ol	
HZSM-5	No solvent	0.98	0.3	0.68	0	0.44	100
HZSM-5	Acetone	3.29	0	1.29	1.17	0	74.7
FeZSM-5	Acetone	3.81	0.6	1.35	1.03	0.44	78.2
HZSM-5	[emim]BF$_4$	15.8	6.98	2.70	5.64	2.59	97.0
NiZSM-5	[emim]BF$_4$	15.9	8.2	2.84	4.39	2.89	97.1
CoZSM-5	[emim]BF$_4$	14.2	9.82	3.53	0.71	2.78	99.0
MnZSM-5	[emim]BF$_4$	15.5	10.3	3.06	1.77	3.39	97.6
FeZSM-5	[emim]BF$_4$	20.9	12.1	3.27	5.15	3.70	98.2
CuZSM-5	[emim]BF$_4$	9.5	6.15	3.31	0	1.86	100

Reaction conditions: 0.15 g catalyst, 27.8 mmol cyclohexane, 55.6 mmol TBHP (85% in H$_2$O), 5 ml (6.25 g) ionic liquid, 12 h and 90 °C; -one, cyclohexanone; -ol, cyclohexanol; CHHP, cyclohexyl hydroperoxide.

[a] Other than cyclohexanol, cyclohexanone, cyclohexyl hydroperoxide, n-hexanal and adipic acid formed in ionic liquid.

3.2.2. Conversion and efficiency of TBHP in cyclohexane oxidation

It is well known that peroxides are decomposed to alcohols by acid catalysts. Therefore in the case of cyclohexane oxidation, two competing reactions occur, the decomposition of TBHP and the oxidation of substrate. The conversion and efficiency of TBHP had also been studied in cyclohexane oxidation using MZSM-5 catalysts in ionic liquid [emim]BF$_4$ as shown in Table 4. The TBHP conversion was high for all the used catalysts, while the efficiency of the oxidant was very low. For as-received HZSM-5, the TBHP conversion was 74% and the TBHP efficiency was only 15.4%. Around 80% of the oxidant was unselectively decomposed after 12 h. The efficiency with respect to the oxidant is similar to what we observed for the same reaction catalyzed by TS-1 molecular seives in acetic acid [9].

Compared with as-received HZSM-5, all the MZSM-5 catalysts exhibited a higher TBHP conversions. This phenomenon can be explained that the presence of metal accelerates the decomposition of oxidants. In contrast to the as-received HZSM-5, the TBHP efficiency on MZSM-5 was lower except for FeZSM-5. Among all the used catalysts, CuZSM-5 showed the best activity for TBHP conversion and the lowest TBHP efficiency. About 92% of the TBHP was unproductively decomposed. This result is in agreement with the fact that CuZSM-5 has the lowest catalytic activity. In the case of FeZSM-5, the highest TBHP efficiency of 18.5% was observed. This is also

in accordance with our observation that FeZSM-5 has the highest reactivity among all the catalysts. The fact that the TBHP efficiency is rather poor in the reaction using ionic liquid as the solvent can explain that 2 equiv. of THBP was used, a low conversion of cyclohexane (9–21%) on all the catalysts, that is, the non-productive decomposition of TBHP is the reason why the oxidation process is limited to a yield below 21%. This non-productive conversion of TBHP can be analogous to the epoxidation of olefins reported by Luts et al. [18]. Further study should be acquired for the improvements of the efficiency of TBHP in this reaction.

3.2.3. Effect of HBF$_4$ generated in situ on the activity of cyclohexane oxidation and CHHP decomposition

It is known that when the proton form of a zeolite is contacted with imidazolium-based ionic liquids that a cation exchange occurs between the imidazolium cation and the proton on the zeolite to yield the Brønsted acid of the ionic liquid anion, in the case of HBF$_4$ [19]. In order to investigate whether the HBF$_4$ generated in situ and the extent of ion exchange in this system, ion exchange experiment with NaZSM-5 (Si/Al = 25) zeolite was carried out. NaZSM-5 zeolite was stirred in the ionic liquid (containing about 10% water) at 90 °C, the zeolite and ionic liquid were separated by filtration, and the sodium content of both the ionic liquid phase and zeolite was determined by AAS (Table 5). The result shows that about 52% of sodium in zeolite was exchanged. This indicates that ion exchange occurs and HBF$_4$ can generate in the reaction using HZSM-5 as catalyst. This phenomenon is in accordance with those reported by Hardacre et al. [19]. The Na-exchange results indicate that the amount of acid formed from HZSM-5 in [emim]BF$_4$ was 8.2 mg (0.093 mmol) in a typical reaction, that is 54.7 mg of

Table 4
TBHP conversion and efficiency as a function of solvent and catalyst after 12 h reaction

Catalyst	TBHP conversion (%)	TBHP efficiency (%)
HZSM-5	74.0	15.4
CuZSM-5	97.6	8.00
CoZSM-5	87.8	13.6
MnZSM-5	84.3	15.1
NiZSM-5	85.5	13.8
FeZSM-5	88.3	18.5

Reaction conditions: 0.15 g catalyst, 27.8 mmol cyclohexane, 55.6 mmol TBHP (85% in H$_2$O), 5 ml ionic liquid (6.25 g), 12 h and 90 °C.

Table 5
Sodium exchange from NaZSM-5 with ionic liquid [emim]BF$_4$

The sodium amount of zeolite (×10^{-3} g)	1.98
The sodium amount of ionic liquid (×10^{-3} g)	2.13
The extent of ion exchange (%)	52

Experimental conditions: 0.154 g NaZSM-5, 0.8 ml H$_2$O, 5 ml (6.25 g) ionic liquid, 12 h and 90 °C.

HBF$_4$ is produced per gram of zeolite used. Therefore, in a typical reaction only 0.3% ionic liquid loss corresponding to approximately 52% of the acid sites on the zeolite exchanged by [emim]$^+$.

In order to investigate whether the HBF$_4$ generated in situ has catalytic activity of cyclohexane oxidation, another series of cyclohexane oxidation reactions were performed using HBF$_4$ (0.1, 0.5, and 1 mmol) as catalyst in a solvent-free system under the conditions similar to Table 3. Although large excess of acid used in the reaction, no activities were observed, implying that the HBF$_4$ (0.093 mmol) generated in situ in the reaction system had no activity on catalytic reaction of cyclohexane oxidation. Additionally, to test whether the HBF$_4$ formed have an effect on the decomposition of CHHP, designed experiments were carried out. Two parallel decomposition reactions of raw material of CHHP were performed using 0.1 mmol HBF$_4$ (equal to the amount of HBF$_4$ liberated in situ in a typical reaction) as catalyst or in the absence of catalyst at 90 °C for 7 h. Results are shown in Table 6. The conversion of CHHP without catalyst and in the presence HBF$_4$ catalyst was 46.3 and 45.1%, respectively. For CHHP decomposition reaction without catalyst, the amount of cyclohexanone, cyclohexanol (the main products of CHHP decomposition) was 2.16 and 1.33 mmol, respectively, which was very similar to that of the decomposition reaction with addition of HBF$_4$. These phenomena indicated that the little amount of HBF$_4$ formed have no obvious activity on the decomposition of CHHP.

3.3. Catalyst leaching and recycling

After reaction for 12 h, the amount of the unreacted TBHP in the upper phase and ionic liquid phase was determined by iodometric titration, respectively. For FeZSM-5, the amount of TBHP in the reaction mixture (upper phase) and in the ionic liquid phase was 14.5 and 0.7 mmol, respectively. This means that only a little amount of the unreacted TBHP was in ionic liquid phase. After the ionic liquid phase containing MZSM-5 was dried, ^{1}H NMR analysis was performed on the recovered ionic liquid and the results show that there is little change compared

Table 6
Effect of HBF$_4$ on the decomposition of CHHP

Entry	Distribution of reaction mixture (mmol)				CHHP conversion (mol%)
	Cyclohexane	CHHP	-one	-ol	
Raw material[a]	22.4	1.62	2.04	0.85	–
1[b]	22.1	0.87	2.16	1.33	46.3
2[c]	22.3	0.89	2.14	1.35	45.1

-one, cyclohexanone; -ol, cyclohexanol; CHHP, cyclohexyl hydroperoxide.

[a] 6 ml raw material; raw material of CHHP is cyclohexane solution obtained by cyclohexane oxidation performed for 18 h over HZSM-5 catalysts in ionic liquid; reaction conditions of cyclohexane oxidation: 0.30 g catalyst, 55.6 mmol cyclohexane, 111.2 mmol TBHP (85% in H$_2$O), 10 ml (12.5 g) ionic liquid, 18 h and 90 °C.

[b] Decomposition reaction of CHHP (6 ml raw material) in the absence of HBF$_4$ at 90 °C for 7 h.

[c] Decomposition reaction of CHHP (6 ml raw material) in the presence of HBF$_4$ at 90 °C for 7 h.

Table 7
Recycling experiment results for both [emim]BF$_4$ and catalyst[a]

Entry	Conv./Sel. (mol%)[b]	Yield (mol%)[c]
1	15.8/97.0	15.3
2[d]	15.4/97.2	15.0
3[d]	15.7/96.9	15.2
4[d]	15.2/97.5	14.8
5	20.9/98.2	20.5
6[e]	20.6/98.6	20.3
7[e]	20.8/98.1	20.4
8[e]	20.5/98.4	20.2

[a] Reaction conditions: 0.15 g catalyst, 27.8 mmol cyclohexane, 55.6 mmol TBHP (85% in H$_2$O), 5 ml (6.25 g) ionic liquid, 12 h and 90 °C.

[b] Cyclohexane conversion and selectivity of monofunctional oxidation products (cyclohexanone, cyclohexanol and cyclohexyl hydroperoxide).

[c] Yield of monofunctional oxidation products (cyclohexanone, cyclohexanol and cyclohexyl hydroperoxide).

[d] Recycling experiment for both [emim]BF$_4$ and catalyst HZSM-5.

[e] Recycling experiment for both [emim]BF$_4$ and catalyst FeZSM-5.

with the fresh ionic liquid. This indicates that the little amount of organic species and water can be removed after drying for 16 h at 70 °C.

It is important to note that the ionic liquid/MZSM-5 systems are very easily separated from the product mixture by simple decantation. Catalyst recycling experiments were carried out with repeated use of ionic liquid/MZSM-5 system. After each run, the separation step was operated carefully in order to ensure that there was no loss of the catalyst used in ionic liquid. The total amount of the recovered ionic liquid phase containing catalyst was measured accurately. Fresh ionic liquid, which was equivalent to the amount of ionic liquid being lost (about 2%), was added to the recovered ionic liquid/catalyst phase to make up to the initial concentration of ionic liquid, and then the next run was performed by adding 27.8 mmol cyclohexane and 55.6 mmol TBHP (85% in H$_2$O). The results of three consecutive catalytic reactions using the same system are given in Table 7. It can be seen that the desired product were obtained in the similar conversion, selectivity, and yield, indicating that both the ionic liquid and the catalyst were recoverable and reusable. Either ionic liquid/MZSM-5 or ionic liquid/HZSM-5 catalytic system was stable and efficient for three more recycling without detectable loss of catalytic capability. Little amount of metal ferric leached from catalyst (less than 0.5% Fe leaching found for FeZSM-5) was found with AAS and ICP analysis on the lower ionic liquid phase and the separated FeZSM-5 catalyst. This analytical result further confirms the stability of catalyst in ionic liquid and the recyclable applicability of FeZSM-5/ionic liquid system for the oxidation of cyclohexane.

4. Conclusion

Metal-containing ZSM-5 (MZSM-5) molecular sieves were prepared by incipient wetness impregnation method. The characterization of catalysts obtained confirms that metals existed in the zeolite and all the metal-containing catalysts maintained integrated ZSM-5 frameworks with an MFI topology. The liquid phase oxidation of cyclohexane was performed using *tert-*

butyl-hydroperoxide/MZSM-5 in ambient-temperature ionic liquid [emim]BF$_4$. All the prepared metal-containing HZSM-5 catalysts showed high catalytic activity and stability in the cyclohexane oxidation in ionic liquid compared with the molecular solvent. Among all the prepared MZSM-5 catalysts, FeZSM-5 exhibited the highest catalytic activity and can achieve 20.9% conversion of cyclohexane and 98.2% selectivity of desired products. The HBF$_4$ liberated in situ by a cation exchange between the imidazolium cation and the proton on the zeolite has no effect on the activity of cyclohexane oxidation. The products can be easily isolated from the ionic liquid phase containing catalyst by decantation. The process is simple and mild. Most importantly, the ionic liquid/catalyst system can be subsequently reused for three more recycling without significant loss of catalytic capability.

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