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Research Article

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Ionic liquids modified cobalt/ZSM-5 as a highly efficient catalyst for enhancing the selectivity towards KA oil in the aerobic oxidation of cyclohexane

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Abstract: The industrial oxidation of cyclohexane is currently performed with very low conversion level, i.e. 4-6% conversion and poor selectivity for cyclohexanone and cyclohexanol (K-A oil), i.e.70-85%, at above 150oC reaction temperature and above 10atm reaction pressure using molecular oxygen oxidant and homogeneous catalyst. Several disadvantages are, however, associated with the process, such as, complex catalyst-product separation, high power input, and low safe operation. Therefore, the oxidation of cyclohexane using heterogeneous catalyst oxygen oxidant from air at mild conditions has received particular attention. Aerobic oxidation of cyclohexane over ionic liquids modified cobalt/ZSM-5 (IL-Co/ZSM-5) in absence of solvents was developed in this article. The prepared catalysts were characterized by XRD, FT-IR, N_2 adsorption-desorption, SEM, TEM and XPS analyses. The influence of reaction parameters on the oxidation of cyclohexane was researched, such as the various catalysts, reaction temperature, reaction time, and the reaction pressure, on the process. Highly selective synthesis of KA oil was performed by aerobic oxidation of cyclohexane using ionic liquids modified cobalt/ZSM-5 (IL-Co/ZSM-5) as the catalyst in absence of solvents for the first time. A selectivity of up to 93.6% of KA oil with 9.2% conversion of cyclohexane was produced at 150°C and 1.5 MPa after 3 h, with about 0.1 mol cyclohexane, $C_7mimHSO_4$-Co/ZSM-5 catalyst equal to 6.0 wt%, respectively. The induction period of oxidation was greatly shortened when the ionic liquid was supported on ZSM-5. The catalyst was easy to centrifuge and was reused after five cycles. ***It was found that*** both the characterization and performance of the catalysts revealed that both the presence of oxygen vacancies with incorporation of Co ions into the framework of ZSM-5 and the introduction of $C_7mimHSO_4$ into the ZSM-5 leads to the both satisfactory selectivity and robust stability of the $C_7mimHSO_4$-Co/ZSM-5 heterogeneous catalyst.

Keywords: The oxidation of cyclohexane; Ionic liquids modified ZSM-5; Heterogeneous catalyst.

1 Introduction

In the modern chemical industry, selective oxidation of cyclohexane is an important chemical process. Partial oxidation of cyclohexane to cyclohexanol and cyclohexanone (KA oil), which are intermediates in Nylon-6 and Nylon-6-6 manufacturing, has attracted commercial interest [1-3]. The selectivity towards KA oil is significant in the commercial process under mild conditions [4-6]. Therefore, many catalytic systems, such as cobalt salt [7], metal complex [8], biomimetic [9-10], transition metal oxide [11-13] and molecular sieve [14] combined with molecular oxygen were developed to improve the selectivity and efficiency.

In the chemical industry, aluminosilicates zeolite ZSM-5 has been used as one of the important heterogeneous catalysts [15-16]. Hydrogen peroxide is often used as a green oxidant in the oxidation of cyclohexane catalyzed by metal-supported ZSM-5 catalysts. Copper-doped ZSM-5 presented excellent catalytic performance and selectivity for KA oil in the presence of H_2O_2 as oxidant [17].

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Aerobic oxidation of hydrocarbons has a low cost and is an environmentally friendly nature of oxidant, which has generated interest[18]. Due to the high energy of C-H bond, the aerobic oxidation of cyclohexane could be conducted under more benign conditions by using NHPI (*N*-hydroxyphthalimide) or TBHP (*tert*-butylhydroperoxide) as free radical initiators [19-20]. Gold containing ZSM-5 can achieve the direct aerobic oxidation of cyclohexane without any additives [21]. But the extensive application of this catalytic process is seriously limited due to the expensive cost of catalyst. Therefore, the development of non-noble metal supported ZSM-5 catalytic system is particularly important. However, the selectivity of KA oil is generally not high in the system of direct catalytic cyclohexane oxidation of metal/ZSM-5. It has been reported that the stability of molecular sieves in ionic liquids could be improved [22]. The anionic or cationic groups of ionic liquids may interact with the surface of the molecular sieve, which will be favorable for improving the selectivity of products.

Even though this is promising research is related to industrialization, there is little reported, especially for the aerobic oxidation of cyclohexane in absence of solvents, are relatively scanty. In this work, ionic liquids were used to modify the metal supported on ZSM-5 to prepare one kind of stable catalyst, which was applied in the aerobic oxidation of cyclohexane under solvent-free conditions. The effects of different reaction conditions on cyclohexane oxidation were studied, such as the various catalysts, reaction temperature, reaction time, and the reaction pressure, on the process.

2 Experimental

2.1 General

The reagents involved are as follows: ZSM-5, $Co(NO_3)_2$×$4H_2O$, Cyclohexane (A.R., Sinopharm Chemical Reagent Co. Ltd.); $C_7mimHSO_4$, $C_7mimH_2PO_4$, C_7mimNO_3 and $C_7mimTsO$ (A.R., Lanzhou Institute of Chemical Physics, 1-heptylimidazole, abbreviated as C_7mim); Before use, ZSM-5 was first milled and screened by a 20-mesh sieve.

2.2 Preparation of Co/ZSM-5

Co/ZSM-5 was obtained as followed: 0.5g of the ZSM-5 calcined at 550°C was immersed in 1mol $Co(NO_3)_2$×$4H_2O$. The mixture was stirred at 333K for 10 h, filtered and washed with ethanol, separated by centrifugation. At 120°C, the product was dried in an air oven overnight. Co/ZSM-5 was obtained after the calcination at 550°C for 10h.

2.3 Preparation of ionic liquids modified Co/ZSM-5

IL-Co/ZSM-5 was obtained as followed: In a three-neck glass flask, 0.5g Co/ZSM-5 and 0.75g ionic liquid were added to 30 mL of ethanol. The mixture was stirred at 60°C for 4 h. The product was obtained after filtration, washing with ethanol, separation by centrifugation and drying, and is denoted as IL-Co/ZSM-5.

2.4 Characterization of the catalysts

Microphotography (SEM) images were generated on a Hitachi S3400N instrument equipped.

Transmission electron microscope (TEM) images were carried out using a JEM-2010HR transmission electron microscopy.

On a Phi Quantum 2000 Scanning ESCA Microprobe, X-ray photoelectron spectroscopy (XPS) was performed with Al Ka radiation. A C1s binding energy of 284.6 eV was used as the reference.

X-ray diffraction (XRD) spectroscopy was performed on a Rigaku-Ultima III with Cu with Cu K*a*1 radiation. Its Scanning radiation were a range of 2θ = 6-80º and a rate of 1º/min.

FT-IR spectra was recorded by Bruker-TENSOR 27. The precise Co loading was measured by ICP-OES on a PerkinElmer-Optima 8300. Thermogravimetric analysis was conducted by a STA 449F3 Jupiter. The BET specific surface areas were measured by N_2 adsorption in an ASAP 2020C .

2.5 Catalytic activity studies

The cyclohexane was oxidized in a 100 mL stainless steel autoclave equipped with an automatic temperature controller and a magnetic stirrer. The cyclohexane reacted with IL-Co/ZSM-5 catalyst in the autoclave. The autoclave was rinsed with air three times, then it was pressurized to the desired pressure and heated to the desired temperature with stirring. After the reaction was over, the autoclave was cooled with ice to room temperature and slowly depressurized. The products were analyzed by GC-MS and quantified by GC (Agilent-7890A, capillary column: HP-5, 30 m × 0.25 mm×0.25 μm).

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

3.1 Characterization results

Figure 1 shows the powder XRD patterns of ZSM-5, Co/ZSM-5 and C_7mimHSO$_4$-Co/ZSM-5. The parent ZSM-5 exhibited five XRD diffraction peaks assigned to reflections at (111), (220), (311), (511) and (440), which are characteristic of the lattice structure in hexagonal, mesoporous molecular sieves. Compared to Co/ZSM-5, the XRD diffraction peaks of C_7mimHSO$_4$-Co/ZSM-5 at 2*q* =31.3°, 37.0°, 59.5° and 65.4° were decreased. It indicates that it may be the modification of the ZSM-5 with the ionic liquid and the immobilization of cobalt.

Figure 2 shows the FT-IR spectra of Co/ZSM-5, C_7mimHSO$_4$ ionic liquid and C_7mimHSO$_4$-Co/ZSM-5. The strong broad absorption peak at 1080 cm^{-1} corresponds to the asymmetric and symmetric stretching vibration of Si-O-Si. The peak at 666 cm^{-1} can be due to Si-O bending vibrations. The peaks at 2853 cm^{-1} and 2933 cm^{-1} can be associated to the vibration of C-H bond in 1-heptyl group. The peak 1634 cm^{-1} can be due to the stretching vibration of C-N, and both the peaks at 1218 cm^{-1} and 1460 cm^{-1} can be associated to the vibration of the imidazole ring. Therefore, the results confirmed the existence of both imidazole ring and 1-heptyl group.

Figure 3 shows isotherms and pore size distribution of ZSM-5 by nitrogen adsorption-desorption, Co/ZSM-5 and C_7mimHSO$_4$-Co/ZSM-5. It can be observed that ZSM-5 and Co/ZSM-5 exhibited a type IV isotherm, which was characteristic of highly ordered mesoporous materials. No obvious change in average pore size was observed when ZSM-5 was loaded with cobalt ion, and the surface area and pore volume decreased slightly with the loading of cobalt ion.

However, when the sample Co/ZSM-5 was modified by the ionic liquid, the isotherm had a hysteresis effect under high relative pressure, which was characteristic of macroporous materials. Meanwhile, a sharp decrease in surface area and pore volume were observed. These changes could be attributed to the blockage of micropores and the filling of aggregated particles (Table 1).

The characteristics of the surfaces of the particles were studied with TEM and field emission scanning electron microscopy (SEM) images of ZSM-5, Co/ZSM-5 and C_7mimHSO$_4$-Co/ZSM-5. Figure 4(a)and Figure(d)are the SEM and TEM images of ZSM-5, respectively. It can be seen from the images that the surface of the ZSM-5 molecular sieve particle is smooth and the particle size is about 1.0 to 2.5 microns. After the cobalt ion was loaded, the surface of the particles was coarse, and the cobalt ions are mainly supported on the surface of the ZSM-5. No significant changes of ZSM-5 pore structure was observed with the introduction of cobalt ion (Figure 4(b)and Figure

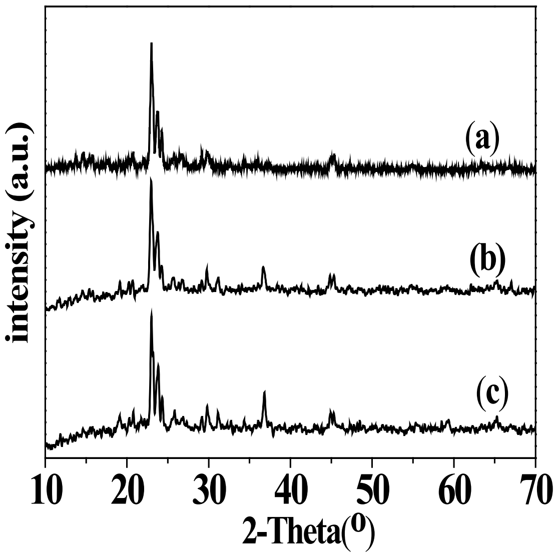

Figure 1: XRD patterns of samples (a) ZSM-5, (b) Co/ZSM-5 and (c) C_7mimHSO$_4$-Co/ZSM-5.

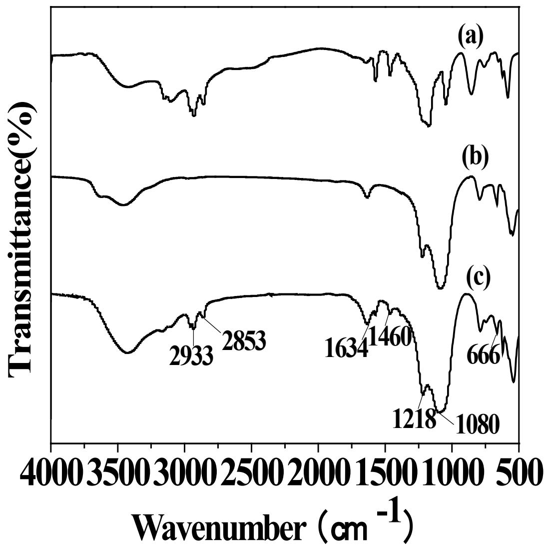

Figure 2: FT-IR spectra of (a) C_7mimHSO$_4$ ionic liquid, (b) Co/ZSM-5 and (c) C_7mimHSO$_4$-Co/ZSM-5.

Table 1: BET surface area and pore characters of catalysts.

Catalyst	BET surface area (m^2g^{-1})	Pore volume (cmg^{-1})	Average pore diameter (nm)
ZSM-5	249.48	0.16	2.51
Co/ZSM-5	196.32	0.13	2.59
C_7mimHSO$_4$-Co/ZSM-5	25.48	0.05	8.22

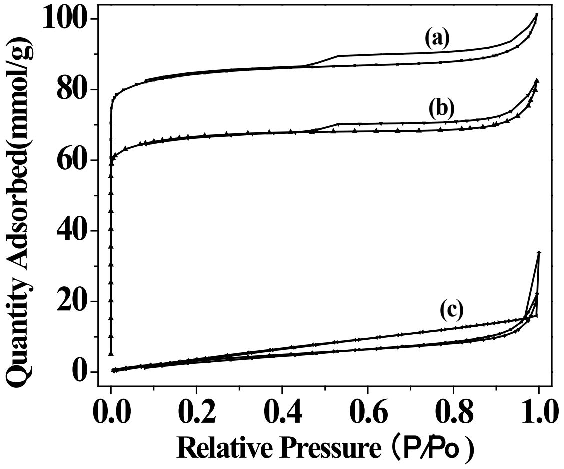

Figure 3: N_2 sorption isotherms of (a) ZSM-5, (b) Co/ZSM-5 and (c) C_7mimHSO$_4$-Co/ZSM-5.

4(e)). The cobalt nanoparticles were still clearly observed when Co/ZSM-5 was modified by the ionic liquid. It can be noticed that the pores and surfaces of ZSM-5 were almost covered with ionic liquid (Figure 4(c)and Figure 4(f)).

In order to obtain the valence states and binding energy of cobalt atoms and oxygen atoms, Co/ZSM-5 and C_7mimHSO$_4$-Co/ZSM-5 were characterized by XPS spectroscopy. The binding energy values in eV corresponding to the individual peaks are presented in Table 2. The binding energy of the $Co_{2p3/2}$ and O_{1s} peaks (Table 2) for Co/ZSM catalyst is respectively found to be 780.49 eV and 532.19 eV, higher than that for Co_2O_3 (780.0eV for the $Co_{2p3/2}$ and 530.0 eV for O_{1s} [23]). This indicates that Co (III) ions, replacing the Al(III) and/or Si(IV), are incorporated into the ZSM-5 framework, resulting in oxygen vacancies from Co (III) doping, and a stronger ability of attracting electrons compared with Co_2O_3. This result is also consistent with that of both the spectra of FT-IR and XRD for Co/ZSM-5. When Co/ZSM-5 was modified by the ionic liquid, the binding energy for Co2$p_{3/2}$ was 0.57 eV higher than that of Co/ZSM-5. While, the binding energy for O1s decreased by 0.90 eV relative to that of Co/ZSM-5. The results suggested that, on the one hand, the lattice oxygen existed on the surface of the C_7mimHSO$_4$-Co/ZSM-5 catalyst, and on the other hand, the introduction of C_7mimHSO$_4$ results in a strong electron

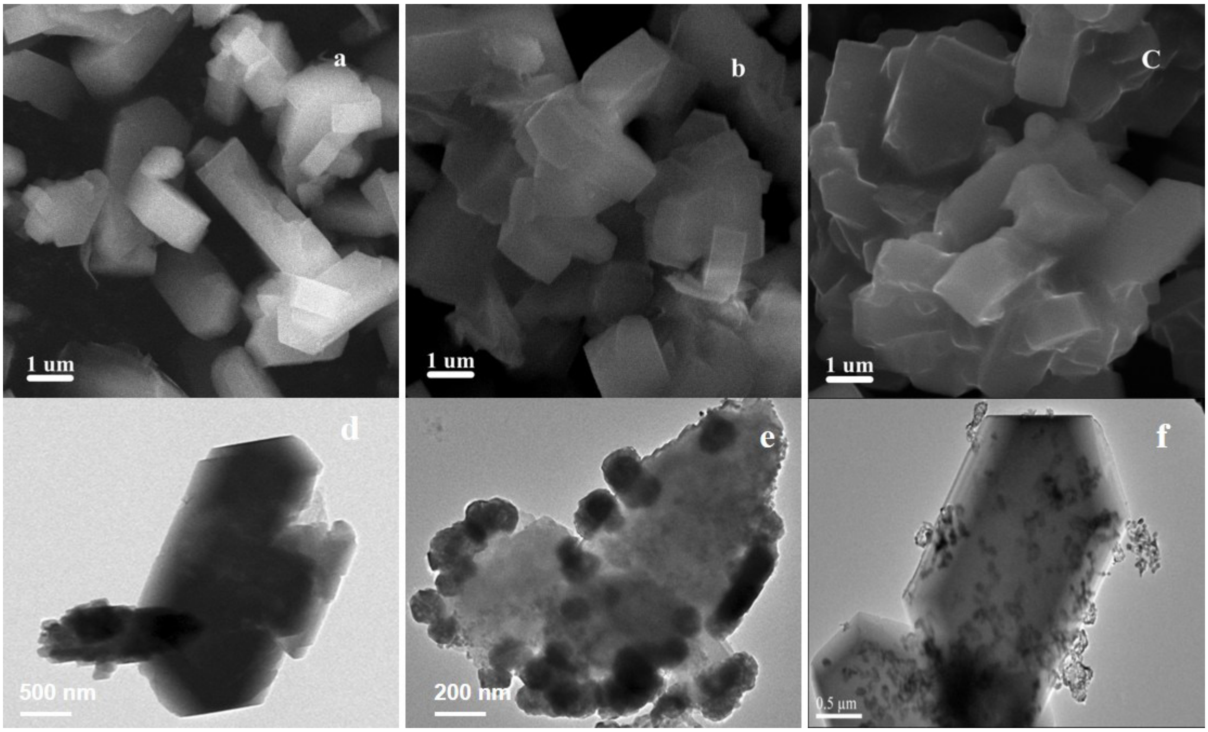

Figure 4: SEM and TEM images of (a, d) ZSM-5, (b, e) Co/ZSM-5 and (c, f) C_7mimHSO$_4$-Co/ZSM-5.

Table 2: XPS analysis of catalysts.

Catalyst	Co2p$_{3/2}$ (eV)	O1s(eV)	Atomic ratio			
			C/Si	Co/Si	O/Si	N/Si
Co/ZSM-5	780.49	532.19	8.32	0.068	1.80	-
C$_7$mimHSO$_4$-Co/ZSM-5	781.06	531.29	7.60	0.074	3.73	1.24

Table 3: Effect of catalyst on the aerobic oxidation of cyclohexane*a*.

Entry	Catalyst	Conv./%	Select./%		
			alcohol	ketone	KA
1	None	1.2	12.3	24.0	36.3
2	ZSM-5	3.1	32.1	28.0	60.1
3	Co/ZSM-5	6.4	38.6	34.3	72.9
4	C$_7$mimHSO$_4$-Co/ZSM-5	9.2	48.4	45.2	93.6
5	C$_7$mimNO$_3$-Co/ZSM-5	8.3	47.8	41.9	89.7
6	C$_7$mimTsO-Co/ZSM-5	7.9	43.8	43.7	87.5
7	C$_7$mimH$_2$PO$_4$-Co/ZSM-5	7.5	45.2	40.2	85.4

a Cyclohexane (0.1 mol), catalyst (6.0 wt%), O$_2$ (1.5MPa), 150°C, 3h.

modification. Thus, the catalytic activity of cobaltous oxide in the oxidation reactions is improved.

3.2 Catalytic oxidation of cyclohexane

3.2.1 Effect of catalyst on the aerobic oxidation of cyclohexane

Table 3 shows the results of cyclohexane aerobic oxidation over various catalysts at 150°C and 1.5 MPa for 3h. As shown in Table 3, the main products in the oxidation of cyclohexane were cyclohexanol and cyclohexanone (KA oil). In the control experiment, almost no obvious conversion was observed (entry 1). In the presence of molecular oxygen, the pure ZSM-5 can promote the oxidation of cyclohexane, which may be due to its large surface area and small amount of acid sites (entry 2). When cobalt was supported on ZSM-5, the activity of the catalyst was increased, in which the selectivity of KA was 72.9% (entry 3). When this type supported cobalt catalyst was modified by the ionic liquid, the activities of catalyst was enhanced, accompanied with the obvious improved selectivity towards KA (entries 4~7). It seems that the activity is related with the anionic group of the ionic liquid with same cation group (1-heptylimidazole). In contrast to the relative catalytic activity of the anionic group of the ionic liquid, the following decreasing order was observed: HSO$_4$>NO$_3$>TsO>H$_2$PO$_4$. The same decreasing order about the selectivity towards KA was observed. Hydrogen bonds could be generated from an interaction between the anionic group and silicon hydroxyl of ZSM-5. The differences in catalytic activity and selectivity towards KA oil maybe related to the intensity of the hydrogen bonds. The mechanistic studies on the influence of the ionic liquids are in progress.

3.2.2 Effect of temperature and pressure on the aerobic oxidation of cyclohexane

The effects of reaction temperature and pressure were researched, as seen in Table 4. The conversion of cyclohexane increased from 2.5% to 9.2% (entries 1~3) when the reaction temperature was increased from 130°C to 150°C. No significant increase was obtained with the continual increase of reaction temperature (entry 4). With increasing temperature, selectivity towards KA oil slightly decreased. However, when the temperature was over 160°C, the reaction rates of side reactions were also obviously accelerated (entry 4). The conversion of cyclohexane increased with increasing molecular oxygen pressure, whereas the selectivity for KA slightly declined with increasing pressure to 2.0 MPa.

Table 4: Effect of temperature and pressure on the oxidation of cyclohexane*a*.

Entry	T/°C	P/MPa	Conv./%	Select./%		
				alcohol	ketone	KA
1	130	1.5	2.5	53.4	42.8	96.2
2	140	1.5	6.6	50.5	43.9	94.4
3	150	1.5	9.2	48.4	45.2	93.6
4	160	1.5	9.7	45.6	42.7	88.3
5	150	1.0	8.5	48.4	45.9	94.3
6	150	2.0	9.3	45.1	45.0	90.1

a Cyclohexane (0.1 mol), $C_7mimHSO_4$-Co/ZSM-5 catalyst (6.0 wt%), 3h

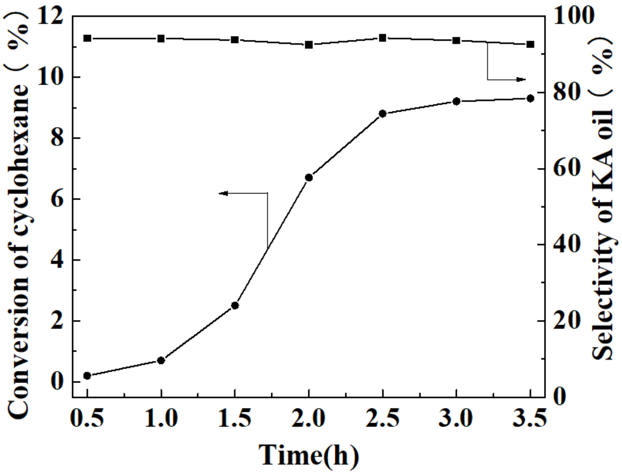

Figure5: Profile of the aerobic oxidation of cyclohexane catalyzed by $C_7mimHSO_4$-Co/ZSM-5 catalyst. Cyclohexane (0.1 mol), catalyst (6.0 wt%), O_2 (1.5MPa), 150°C.

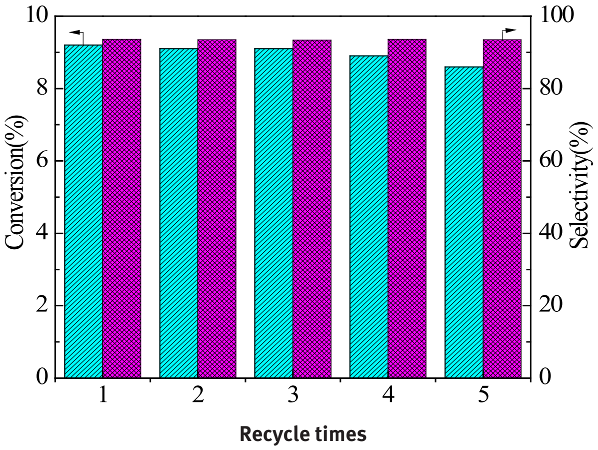

Figure 6: Stability and reusability of $C_7mimHSO_4$-Co/ZSM-5 catalyst in the aerobic oxidation of cyclohexane. Cyclohexane (0.1 mol), catalyst (6.0 wt%), O_2 (1.5MPa), 150°C, 3h.

3.2.3 Effect of time on the aerobic oxidation of cyclohexane

Figure 5 shows the conversion of cyclohexane and selectivity for KA oil at different reaction times. Within the first 1 h, the conversion of cyclohexane slowly increased as the reaction rate rapidly increased. The aerobic oxidation of cyclohexane has an obvious induction period just like any other free radical. For verifying the free radical mechanism, 2,6-*di*-*tert*-butylphenol (1 mmol), serving as the free radical inhibitor was used. After the addition of this inhibitor, the oxidation was subsequently quenched.

3.3 Catalyst reuse and stability

The stability of $C_7mimHSO_4$-Co/ZSM-5 catalyst was monitored using multiple sequential aerobic oxidations of cyclohexane. After the catalyst was recovered by centrifugation, filtration, washed with cyclohexane and dried, it was used in the subsequent run. The results are shown in Figure6.

From Figure 6, the catalyst was without a significant loss of the activity and selectivity for KA oil after it was consecutively reused five times. The results showed that the supported catalyst has good activity and excellent stability for the oxidation of cyclohexane. This can be attributed to the channel range of the ZSM-5 molecular sieve that results in a difficult loss of the $C_7mimHSO_4$ ionic liquid, and on the other hand, a micro-reactor with high concentration of $C_7mimHSO_4$ ionic liquid was constructed with the $C_7mimHSO_4$ ionic liquids were introduced into the pores of ZSM-5 molecular sieve. This further led to good both cyclic stability and reactive activity of the $C_7mimHSO_4$-Co/ZSM-5 heterogeneous catalyst.

4 Conclusions

C_7mimHSO$_4$-Co/ZSM-5 was identified for the the first time as an effective and robust heterogeneous catalyst for the aerobic oxidation of cyclohexane. A selectivity of KA oil for the aerobic oxidation of cyclohexane was obtained as high as 93.6% with 9.2% conversion of cyclohexane using C_7mimHSO$_4$-Co/ZSM-5 as catalyst under relatively mild reaction conditions (150°C,3 h, and 1.5 MPa). The activity of C_7mimHSO$_4$-Co/ZSM-5 heterogeneous catalyst **remains almost unchanged after** five consecutive cycles. Further studies for both the characterization and performance of the C_7mimHSO$_4$-Co/ZSM-5 catalyst revealed that both the presence of oxygen vacancies with incorporation of Co ions into the framework of ZSM-5 and the introduction of C_7mimHSO$_4$ into the ZSM-5 led to the higher catalytic activity of C_7mimHSO$_4$-Co/ZSM-5. In-depth studies for the mechanism of the oxidation of cyclohexane with molecular oxygen over the cobalt/ZSM-5 modified by the ionic liquid catalysts are under way.

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