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Highly selective oxidation of cyclohexene to 2-cyclohexene-1-one in water using molecular oxygen over Fe-Co-g-C_3N_4

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Dexin Yang, Tao Jiang, Tianbin Wu*, Peng Zhang, Hongling Han and Buxing Han*

Efficient and greener oxidation of cyclohexene to 2-cyclohexene-1-one is an interesting topic. In this work, we prepared a series of Fe-Co doped graphitic carbon nitride (Fe-Co-g-C_3N_4) catalysts through simple impregnation and calcination methods. The catalysts were characterized by different techniques, such as transmission electron spectroscopy (TEM), Fourier-transformed infrared spectroscopy (FTIR), nitrogen adsorption–desorption, powder X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) methods. The selective oxidation of cyclohexene to 2-cyclohexene-1-one was carried out in different solvents over the catalysts using molecular oxygen as oxidant. The influence of supports, solvents, Fe/Co molar ratio in the catalysts, pressure of oxygen, reaction temperature and time on the reaction was investigated. It was revealed that the bimetallic Fe-Co-g-C_3N_4 catalysts were very efficient for the reaction. More interestingly, the selectivity of the reaction in water was much higher than that in other solvents. At the optimized conditions, the selectivity of 2-cyclohexene-1-one could reach 95% at a cyclohexene conversion of 36%. Fe-Co-g-C_3N_4 catalyst could be reused at least four times without obvious loss of efficiency.

Introduction

The selective allylic oxidation of alkenes into high value-added chemical product occupies an important position in the chemical industry[1]. Among the oxidation products, 2-cyclohexene-1-one, which is obtained by the allylic oxidation of cyclohexene, is a very important intermediate because it is extensively used in spices, medication, pesticide and insect pheromone[2]. However, it is very difficult to control the selectivity of oxygenated products in the allylic oxidation of cyclohexene due to the existence of two active sites on cyclohexene molecule, where there are C-H bond of allylic site and C=C double bond. Some compounds, such as cyclohexanone, cyclohexanediol and dialdehyde, will be produced if the C=C double bond is oxygenated. On the contrary, 2-cyclohexene-1-ol, 2-cyclohexene-1-one or cyclohexene hydroperoxide will be generated when C-H bond of allylic site is oxygenated[3]. Therefore, it is still challenging and attractive to obtain high selectivity to the target product in the allylic oxidation of cyclohexene.

The traditional oxidants for the oxidation of cyclohexene are usually iodosylbenzene, sodium hypochlorite, and chromium trioxide, *etc*[4]. Although these strong oxidants can enhance the yield of the product, their applications are limited due to the high cost, inconvenient transportation, explosibility, environmental pollution and lower atomic economy[5, 6]. Thus, the development of green processes for the catalytic oxidation of cyclohexene is becoming increasingly important. Recently, some greener oxidants were applied for the oxidation of cyclohexene, including *t*-butyl hydroperoxide (TBHP)[7], H_2O_2[8] and molecular oxygen[9]. Among these oxidants molecular oxygen, which is cheap, abundant, environmentally benign, has received much attention in academic research and industrial aplication[10]. For example, the allylic oxidation of cychohexene over cobalt resinate using oxygen as oxidant was carried out under a solvent-free condition. It was shown that cobalt resinate exhibited high catalytic activity, but the selectivity to 2-cychohexen-1-one was only 44.4%[2]. More recently, magnetic core-shell Fe_3O_4@chitosan-Schiff base Co(II), Cu(II) and Mn(II) complexes were proved to be active catalysts for cyclohexene oxidation with oxygen in the absence of solvents[11]. A conversion of 50.2% and a selectivity of 80.3% to 2-cyclohexene-1-one were obtained over this catalyst. Organic solvents were often used when oxygen was used to oxygenate the cyclohexene. For instance, the allylic oxidation of cychohexene over CoO-catalyst in cyclohexane was studied, and high conversion and selectivity to 2-cyclohexene-1-one could be achieved[12]. Generally, improving the selectivity to 2-cyclohexene-1-one in the allylic oxidation of cyclohexene using oxygen as oxidant is still very interesting topic.

Traditionally, most of the catalysts used for the allylic oxidation of cyclohexene are complexes based on Co, Fe, Mn, Ir and Cu[13-16]. However, it is very difficult to recover these catalysts from the homogeneous systems because these oxidation reactions are usually carried out in the liquid phase.

Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Laboratory of Colloid and Interface and Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: wtb@iccas.ac.cn, hanbx@iccas.ac.cn; Fax: +86-10-62562821; Tel: +86-10-62562821

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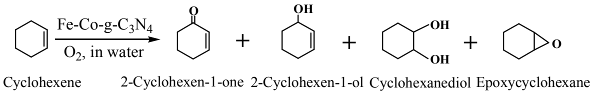
Hence, heterogeneous catalysts have been developed by immobilizing transition metals on solid supports, such as SiO_2, zeolite and Fe_3O_4 for the oxidation of cyclohexene[11, 17, 18]. It has been reported that the noble metal Au nanoparticles immobilized on different supports can improve the catalytic performance for the oxidation of cyclohexene. Donoeva et al. found that the size of gold nanoparticles deposited on SiO_2 support played a crucial role for catalytic activity in aerobic oxidation of cyclohexene without solvent[19]. Recently, gold nanoparticles supported on modified silica and bentonite also showed high conversion and selectivity to 2-cyclohexene-1-one for cyclohexene oxidation with oxygen in the absence of solvents[20]. Graphitic C_3N_4 (g-C_3N_4) as a special support has recently attracted much attention due to its extremely chemical and thermal stability and easy accessibility. g-C_3N_4 exhibited outstanding potential in material science, catalysis, electronic and optical fields due to the excellent optical and photoelectric properties[21,22]. Interestingly, g-C_3N_4 itself has been reported to be excellent catalyst for the oxidation of alcohols, cyclohexene and amines by oxygen under visible light irradiation in the absence of any metal derivatives[23-25]. Moreover, some organic compounds or metal derivatives could bind or intercalate into the matrix of g-C_3N_4 through the numerous anchoring sites on the surface, which undoubtedly greatly improved the catalytic performance and expanded the applications of g-C_3N_4 in catalysis[21, 26]. For example, Fe or Pd doped g-C_3N_4 catalysts exhibited excellent catalytic performance in the oxidation of benzene and selective hydrogenation of phenol and derivatives[27, 28].

Water has been widely applied as a greener reaction medium in catalysis[29-32]. From an environmental point of view, it would be much better to replace organic solvents with water because it is abundant, environmentally friendly, and low-cost. It is well-known that transition metals are of great importance and have played irreplaceable role in chemical reaction[33]. Fe and Co are abundant and cheap transition metals. In this work, we designed Fe-Co doped g-C_3N_4 (Fe-Co-g-C_3N_4) catalysts for the selective allylic oxidation of cyclohexene using oxygen as oxidant (Scheme 1). The results showed that the bimetallic Fe-Co-g-C_3N_4 catalysts were highly effective for the oxidation of cyclohexene to 2-cyclohexene-1-one. Especially, the selectivity of the reaction in water could be very high, and was much higher than that in other solvents at similar conversion. As far as we know, this is the first work to use the bimetallic Fe-Co-g-C_3N_4 as catalyst for the selective oxidation of cyclohexene.



Scheme 1 The oxidation of cyclohexene catalyzed by Fe-Co-g-C_3N_4 catalyst with molecular oxygen in water.

Results and discussion

Characterization of the catalysts

In order to understand well the existent state of bimetallic Fe-Co on the surface of g-C_3N_4 support, the morphologies of the g-C_3N_4 and 5-Fe-Co-g-C_3N_4 were characterized by TEM techniques, as shown in Figure 1 (a) and (b). It can be seen that there are no significant differences in morphologies between g-C_3N_4 and 5-Fe-Co-g-C_3N_4. Both of them showed similar sheet-like structure of graphene, indicating that Fe-Co doped g-C_3N_4 did not significantly change the texture of carbon nitride polymer. Although Fe and Co species could not be observed on the surface of g-C_3N_4 by TEM, they were proved to be existed by element mapping images of 5-Fe-Co-g-C_3N_4 in the Figure 1 (c), probably due to the interaction between Fe or Co and g-C_3N_4 by the formation of Fe-N or Co-N bonds.

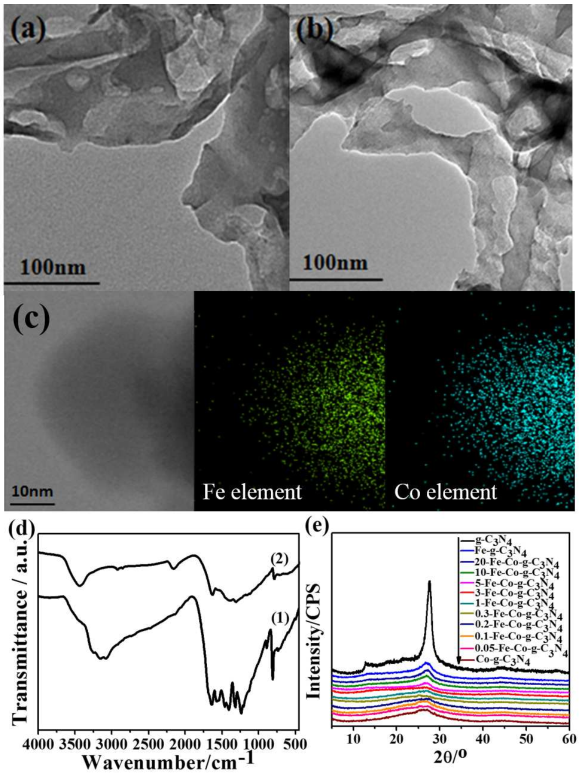


Figure 1 TEM images of g-C_3N_4 (a) and 5-Fe-Co-g-C_3N_4 catalyst (b); Element mapping images of 5-Fe-Co-g-C_3N_4 (c); FT-IR spectra of g-C_3N_4 (1) and 5-Fe-Co-g-C_3N_4 (2) catalyst (d); XRD patterns of g-C_3N_4 and Fe-Co-g-C_3N_4 catalyst with the different molar ratio of Fe to Co (e).

The FT-IR spectra of g-C_3N_4 and 5-Fe-Co-g-C_3N_4 catalyst were shown in Figure 1 (d). The bands between 1200 and 1650 cm^{-1} corresponding to the typical stretching modes of CN heterocycles, and the characteristic mode of the triazine units (C_6N_7) at 803 cm^{-1} are observed for g-C_3N_4[34, 35], indicating the presence of typical structure of g-C_3N_4. It is also notable that the spectrum of the 5-Fe-Co-g-C_3N_4 was similar to that of the g-C_3N_4, expect that the characteristic bands were relatively weak, suggesting that the doping of bimetallic Fe-Co had no obvious influence on the typical structure of g-C_3N_4 support. This can be further confirmed by the XRD patterns of the g-C_3N_4 and Fe-Co-g-C_3N_4 catalyst with different molar ratios of Fe and Co. As showed in Figure 1 (e), the strong peak at 27.6° and weak peak at 12.9° were observed for the g-C_3N_4, corresponding to the graphitic materials as the (002) peak of layered stacking of the conjugated aromatic system and the in-plane structural packing motif of tri-s-triazine units, respectively[36]. Interestingly, the XRD patterns of Fe-Co-g-C_3N_4 catalysts with the different molar ratios of Fe and Co were similar to that of pristine g-C_3N_4, but the overall intensity of the peaks decreased with increasing content of Co in the Fe-Co-g-C_3N_4. There were no peaks originating from Fe or Co species. This is presumably caused by the formation of Fe-N or Co-N bonds through the chemical coordination of Fe or Co species with g-C_3N_4 in the preparation of Fe-Co-g-C_3N_4 catalysts under flowing nitrogen atmosphere.

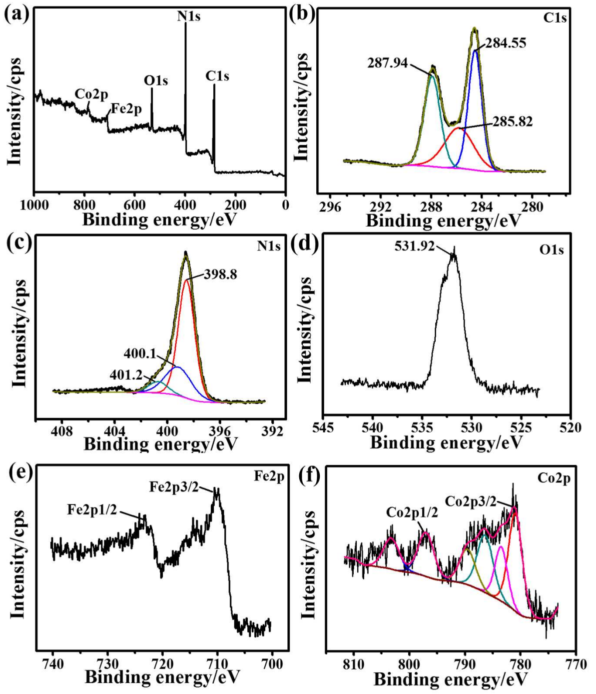


Figure 2 XPS spectra of the 5-Fe-Co-g-C_3N_4 catalyst; Survey spectra (a), High resolution spectra of C1s (b), N1s (c), O1s (d), Fe2p (e), and Co2p (f).

The 5-Fe-Co-g-C_3N_4 catalyst was further investigated by XPS analysis, as shown in Figure 2. The surface of the catalyst concentrations of Fe and Co species obtained from XPS were 1.91% and 1.1%, respectively. It can be seen from the full XPS spectrum that the main elements were C, N, O, Fe and Co in 5-Fe-Co-g-C_3N_4 catalyst. The photoelectron peaks of these elements were clearly observed at binding energies of 288.0 eV (C1s), 399.0 eV (N1s), 530.9 eV (O1s), 710.3 eV (Fe2p) and 781.3 eV (Co2p), respectively. The fitted spectrum of C in Figure 2 (b) shows three main peaks with binding energy of 287.9 eV, 285.8 eV and 284.5 eV, corresponding to sp^2-bonded carbon (N-C=N), C-O and graphitic carbon (C-C), respectively[37]. The high resolution N 1s spectra (Figure 2 (c)) for 5-Fe-Co-g-C_3N_4 displayed typical heptazine repeating units with several N species at different binding energies, including triazine rings (C=N-C, 398.8 eV), tertiary nitrogen ($N-(C)_3$, 400.1 eV), and the handful of amino functions (N-H, 401.2 eV)[34,38]. These representative signals indicated that the framework of g-C_3N_4 was not changed with the doping of Fe and Co species. The high resolution Fe 2p XPS spectrum is shown in Figure 2 (e). A typical binding energy peak at 710.3 eV indicates the existence of Fe (III) valence state in 5-Fe-Co-g-C_3N_4 catalyst, which may be due to the stabilization of Fe species in the electron-rich g-C_3N_4 structure mainly through Fe-N bonds[27,39]. Moreover, the binding energy peaks at 781.3 eV and 783.4 eV were observed in the high resolution Co 2p XPS spectrum (Figure 2 (f)), suggesting the existence of Co (II) valence state in the form of Co-N moieties[40]. These results reasonably explained the fact that Fe and Co species in the 5-Fe-Co-g-C_3N_4 catalyst could not be observed through XRD and TEM methods.

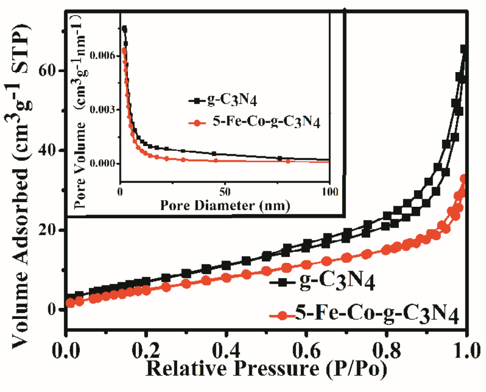


Figure 3 N_2 adsorption-desorption isotherms and corresponding pore size distribution plots (inset) for pure g-C_3N_4 and 5-Fe-Co-g-C_3N_4 catalyst.

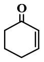
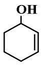
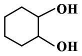
The N_2 adsorption-desorption isotherms and pore size distribution plots for the g-C_3N_4 and 5-Fe-Co-g-C_3N_4 catalyst are shown in Figure 3. Both samples exhibited type H_4 sorption hysteresis loops, indicating the existence of narrow slit-like pores. The pore size distribution of pure g-C_3N_4 and 5-Fe-Co-g-C_3N_4 catalyst calculated by original DFT showed a main peak centered at approximately 2-5 nm. 5-Fe-Co-g-C_3N_4 catalyst had a Brunauer-Emmett-Teller (BET) surface area of 22.9 $m^2\ g^{-1}$ and a pore volume of 0.050 $cm^3\ g^{-1}$. While the BET surface area and pore volume of pure g-C_3N_4 were 29.9 $m^2\ g^{-1}$ and 0.101 $cm^3\ g^{-1}$, respectively.

The contents of C, N, and H in the 5-Fe-Co-g-C_3N_4 catalyst determined by elemental analysis were 32.55%, 56.34%, and 1.15%, respectively. An approximate value of 0.77 was calculated for the C/N ratio, which is close to the theoretical value of 0.75 for g-C_3N_4, indicating that the 5-Fe-Co-g-C_3N_4 catalyst was highly enriched in nitrogen. The result further suggests that the doping of Fe-Co did not change the chemical structure of g-C_3N_4 support. The minor amount of hydrogen (1.15%) and oxygen (5.75%) may be attributed to adsorbed water and imperfections in the condensation process, as confirmed by XPS analyses. The loading of Fe and Co in the catalyst determined by ICP were 3.28 wt% and 0.93 wt%, respectively. The loading of Fe and Co by XPS was less than that by ICP, perhaps due to a part of Fe and Co existing inside the catalysts in the form of Fe-N and Co-N which were not detected through the method of XPS.

Catalytic performance of catalysts with different supports

The oxidation of cyclohexene was firstly conducted with non-catalyst in water using oxygen as oxidant, as shown in Table 1 (Entry 1). It is found that the catalytic activity and selectivity to 2-cyclohexene-1-one were considerably dissatisfactory. It is well-known that the support often plays an important role for the performance of a catalyst. So we loaded Co on activated C, TiO_2, SiO_2, and g-C_3N_4 and studied the selective oxidation of cyclohexene to 2-cyclohexene-1-one in water using oxygen as oxidant, and the results are shown in Table 1. The catalytic activity and selectivity to 2-cyclohexene-1-one over Co-g-C_3N_4 catalyst was much higher than that over Co-C, Co-TiO_2 and Co-SiO_2 catalysts under similar reaction conditions. This indicates that g-C_3N_4 was an excellent support of Co for the selective oxidation of cyclohexene to 2-cyclohexene-1-one, probably due to the fact that the interaction between Co and N in g-C_3N_4 could inhibit the generation of the by-products (such as 2-cyclohexene-1-ol and cyclohexanediol) effectively. As a result, the g-C_3N_4 can be regarded as the promising support for the oxidation of cyclohexene.

Table 1. Catalytic performance of Co on different supports[a]

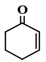
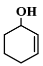
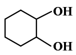
Entry	Catalysts	Conversion (%)	Selectivity (%)			
						Others
1	-	5.5	51.4	18.1	21.9	8.6
2	Co-C	16.7	63.8	25.7	7.6	2.9
3	Co-TiO_2	24.6	67.3	18.6	5.2	8.9
4	Co-SiO_2	19.9	65.0	25.6	5.2	4.2
5	Co-g-C_3N_4	55.9	71.7	23.0	1.9	3.4

[a] Reaction conditions: cyclohexene, 0.5 mL; oxygen pressure, 4 MPa; deionized water, 2.0 mL; catalyst, 0.023 g; reaction time, 5 h; reaction temperature, 90°C.

Catalytic performance of g-C_3N_4 doped with different metals

We investigated the effect of different metals doped in g-C_3N_4 on the oxidation of cyclohexene using oxygen as oxidant and water as solvent, and the results are summarized in Table 2. Without doping metal, g-C_3N_4 showed a relatively high activity for the oxidation of cyclohexene, but the selectivity to 2-cyclohexene-1-one was very low (Table 2, Entry 1). The V or W doped g-C_3N_4 also showed low the activity and selectivity (Table 2, Entries 2 and 3). Although the Cu and Co doped g-C_3N_4 catalysts exhibited higher activity than the V and W doped g-C_3N_4, the selectivity to 2-cyclohexene-1-one was still low (Table 2, Entries 4 and 5). However, when g-C_3N_4 was doped with Fe metal, the selectivity to 2-cyclohexene-1-one increased to 90.4%, but the conversion of cyclohexene was relatively low (Table 2, Entry 6). Based on the results of higher activity of Cu-g-C_3N_4 and Co-g-C_3N_4 for the oxidation of cyclohexene, and higher selectivity of Fe-g-C_3N_4 catalyst to 2-cyclohexene-1-one, we attempted to combine Cu and Fe or Co and Fe with g-C_3N_4 for the reaction. The results showed that the Fe-Co-g-C_3N_4 had higher activity and selectivity than Fe-Cu-g-C_3N_4 (Table 2, Entries 7 and 8), i.e., Fe-Co-g-C_3N_4 catalyst was a very effective catalyst for oxidation of cyclohexene to 2-cyclohexene-1-one with oxygen as oxidant and water as solvent.

Table 2. Catalytic activity of g-C_3N_4 doped with various metals for the oxidation of cyclohexene[a]

Entry	Catalysts	Conversion (%)	Selectivity (%)			
						Others
1	g-C_3N_4	37.6	60.3	26.2	2.9	10.6
2	V-g-C_3N_4	22.2	62.6	25.7	3.3	8.4
3	W-g-C_3N_4	13.8	53.4	29.1	14.0	3.5
4	Cu-g-C_3N_4	45.9	65.2	26.6	5.9	2.8
5	Co-g-C_3N_4	55.9	71.7	23.0	1.9	3.4
6	Fe-g-C_3N_4	13.6	90.4	6.3	1.4	1.9
7	1-Fe-Cu-g-C_3N_4	16.2	79.9	15.2	1.9	3.0
8	1-Fe-Co-g-C_3N_4	27.6	89.9	7.8	0.8	1.5

[a] Reaction conditions: cyclohexene, 0.5 mL; oxygen pressure, 4 MPa; deionized water, 2.0 mL; catalyst, 0.023 g; reaction time, 5 h; reaction temperature, 90°C.

Effect of different solvents on the oxidation of cyclohexene

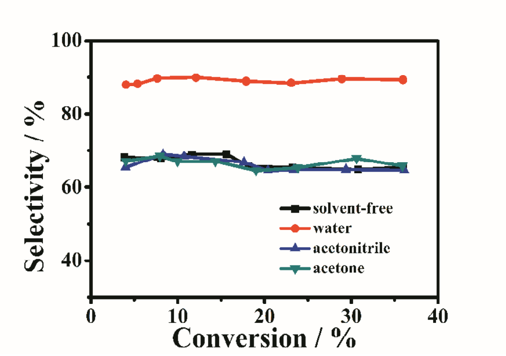
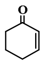
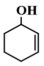
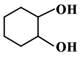


Figure 4 Effect of the different solvents on the oxidation of cyclohexene. Reaction conditions: cyclohexene, 0.5 mL; oxygen pressure, 4 MPa; different solvent, 2.0 mL;1-Fe-Co-g-C_3N_4 catalyst, 0.023 g; reaction temperature, 90°C.

It is known that solvents can often affect reactions significantly. Herein, we studied the effect of different solvents on catalytic oxidation of cyclohexene over the 1-Fe-Co-g-C_3N_4 catalyst with oxygen as oxidant. The results are shown in Figure 4. It is found that the selectivity to 2-cyclohexene-1-one was kept about 90% in the cyclohexene conversion range from 4 to 36% using water as reaction solvent. This indicates that water can suppress formation of byproducts (such as 2-cyclohexene-1-ol and 1,2-cyclohexanediol). However, when acetone or acetonitrile was used as solvent, the selectivity to 2-cyclohexene-1-one was only 65-70% at the conversion range, which is much lower than that in water. Similarly, the resulted selectivity to 2-cyclohexene-1-one was also poor under solvent-free condition. The results suggest that Fe-Co-g-C_3N_4 and water had cooperative effect for the effective catalytic oxidation cyclohexene to 2-cyclohexene-1-one. In addition, water is environmental benign, abundant, and cheap comparing with organic solvents.

Effect of molar ratio of Fe to Co in Fe-Co-g-C_3N_4

Table 3. Effect of molar ratio of Fe to Co in Fe-Co-g-C_3N_4 on the oxidation of cycloheene[a]

Entry	Catalyst	Fe/Co ratio	Conversion (%)	Selectivity (%)			
							Others
1	Co-g-C_3N_4	-	55.9	71.7	23.0	1.9	3.4
2	0.05-Fe-Co-g-C_3N_4	1:20	50.1	73.5	22.1	0.8	3.7
3	0.1-Fe-Co-g-C_3N_4	1:10	45.6	77.4	17.2	2.1	3.3
4	0.2-Fe-Co-g-C_3N_4	1:5	41.3	78.0	18.7	2.3	1.0
5	0.3-Fe-Co-g-C_3N_4	1:3	30.3	82.5	14.0	0.8	2.6
6	1-Fe-Co-g-C_3N_4	1:1	27.6	89.9	7.8	0.8	1.5
7	3-Fe-Co-g-C_3N_4	3:1	24.6	90.3	5.3	1.9	2.5
8	5-Fe-Co-g-C_3N_4	5:1	21.8	95.5	1.2	1.9	1.4
9	10-Fe-Co-g-C_3N_4	10:1	21.3	92.5	3.3	2.7	1.6
10	20-Fe-Co-g-C_3N_4	20:1	20.8	90.2	5.1	2.9	1.8
11	Fe-g-C_3N_4	-	13.6	90.4	6.3	1.4	1.9

[a] Reaction conditions: cyclohexene, 0.5 mL; O_2 pressure, 4 MPa; water, 2.0 mL; catalyst, 0.023 g; reaction temperature, 90°C; reaction time, 5 h.

We also studied the effect of the molar ratio of Fe and Co in Fe-Co-g-C_3N_4 catalyst for the oxidation of cyclohexene with oxygen and water as solvent (Table 3). The molar ratio of Fe and Co influenced the selectivity to 2-cyclohexene-1-one dramatically. Although Co-g-C_3N_4 catalyst showed the highest activity, the selectivity to 2-cyclohexene-1-one was poor (Table 3, Entry 1). With the increase of Fe content in the catalyst, the catalytic activity continuously decreased, while the selectivity to 2-cyclohexene-1-one increased obviously (Table 3, Entries 2-7). When the molar ratio of Fe and Co was 5:1, Fe-Co-g-C_3N_4 catalyst exhibited the highest selectivity to 2-cyclohexene-1-one, which was about 95.5% (Table 3, Entry 8). With the further increase of molar ratio of Fe and Co in Fe-Co-g-C_3N_4 catalyst, the activity and selectivity decreased slightly (Table 3, Entries 9 and 10). In the absence of Co content in the catalyst, the conversion of cyclohexene decreased to 13.6%, while the selectivity to 2-cyclohexene-1-one decreased to 90.4% (Table 3, Entry 11). The results indicate that suitable molar ratios of Fe and Co are required for satisfactory performance of the catalyst. For comparison, Fe, Co or Fe-Co supported g-C_3N_4 catalysts, which were synthesized by conventional impregnation method, were used to catalyze the oxidation of cyclohexene under the same reactive conditions, as shown in supporting information (Table S1, Figure S1, S2 and S3). It can be seen from the results that the catalytic activity and selectivity to 2-cyclohexene-1-one were obviously not as good as the catalysts discussed above. This may be attributed to the fact that Fe and Co existed in the form of Fe_3O_4 and Co_3O_4 on the pristine g-C_3N_4 and the active sites on the support were partly occupied by the metal oxide.

Effect of the pressure of molecular oxygen

The effect of oxygen pressure on the conversion and selectivity was studied over 5-Fe-Co-g-C_3N_4 catalyst in water, and the results are shown in Figure 5. With the increase of oxygen pressure the conversion of cyclohexene increased. The selectivity to 2-cyclohexene-1-one also increased slowly as the pressure was lower than 4 MPa. When oxygen pressure was larger than 4 MPa, the selectivity to 2-cyclohexene-1-one decreased with further increasing pressure.

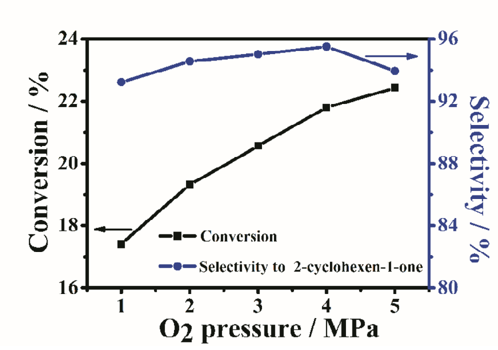


Figure 5 Effect of molecular oxygen pressure on the oxidation of cyclohexene. Reaction conditions: cyclohexene, 0.5 mL; water, 2.0 mL; 5-Fe-Co-g-C_3N_4 catalyst, 0.023 g; reaction temperature, 90°C; reaction time, 5 h.

Effect of reaction temperature

The effect of reaction temperature on the oxidation of cyclohexene is shown in Figure 6. The conversion of cyclohexene was only about 6.7% at 70°C in 5 h, and the selectivity to 2-cyclohexene-1-one was 95.5%. Increasing the temperature from 70 to 90°C could improve the conversion significantly, while the selectivity to 2-cyclohexene-1-one was nearly unchanged. When the temperature was increased to 110°C, the conversion of cyclohexene could reach 36.0% at the experimental condition, but the selectivity to 2-cyclohexene-1-one declined considerably. This indicates that high temperature led to formation of more by-products.

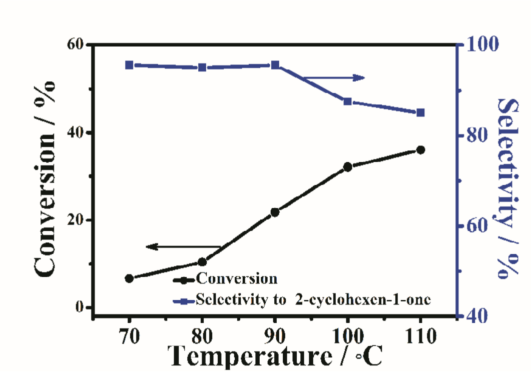


Figure 6 Effect of reaction temperature on the oxidation of cyclohexene. Reaction conditions: cyclohexene, 0.5 mL; oxygen pressure, 4 MPa; water, 2.0 mL; 5-Fe-Co-g-C_3N_4 catalyst, 0.023 g; reaction time, 5 h.

Effect of reaction time

The influence of reaction time on the oxidation of cyclohexene at 90°C is shown in Figure 7. It can be observed that the conversion of cyclohexene increased continuously within 15 h, while the selectivity to 2-cyclohexene-1-one was nearly unchanged. When the reaction time exceeded 15 h, the selectivity to 2-cyclohexene-1-one began to decrease obviously due to the generation of byproducts, such as 2-cyclohexene-1,4-dione, adipic acid, 1,2-cyclohexanediol[9]. It can be known from the figure that 5-Fe-Co-g-C_3N_4 was an excellent catalyst for the reaction in water. The selectivity to 2-cyclohexene-1-one could be as high as 95% at the conversion of 36% at 15 h.

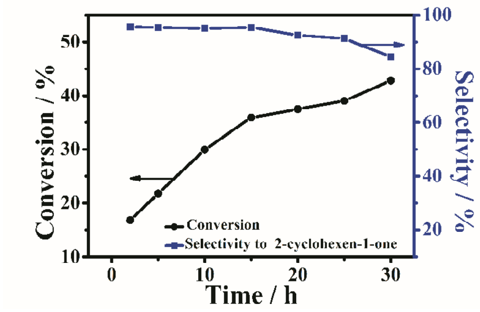


Figure 7 Effect of reaction time on the oxidation of cyclohexene. Reaction conditions: cyclohexene, 0.5 mL; oxygen pressure, 4 MPa; water, 2.0 mL; 5-Fe-Co-g-C_3N_4 catalyst, 0.023 g; reaction temperature, 90°C.

Reusability of the catalyst

The reusability of 5-Fe-Co-g-C_3N_4 catalyst for the oxidation of cyclohexene was investigated and the results are given in Figure 8. The catalyst could be reused at least four times without considerable change in activity and selectivity to 2-cyclohexene-1-one. The conversion of reaction decreased slightly after recycling. The main reason may be that little amount of the catalyst was lost when recovering the catalyst by centrifugation and washing with deionized water. Figure 9 (a) gives the TEM images of the fresh and used catalyst after four cycles. The morphology of the catalyst was not changed notably, as can be known from Figure 1 and Figure 9 (a). Figure 9 (b) compares the XRD pattern of fresh 5-Fe-Co-g-C_3N_4 with that of the catalyst after used four times. The XRD patterns of the virgin and used catalysts were nearly the same, indicating that the crystal structure of the catalysts was unchanged in the reaction.

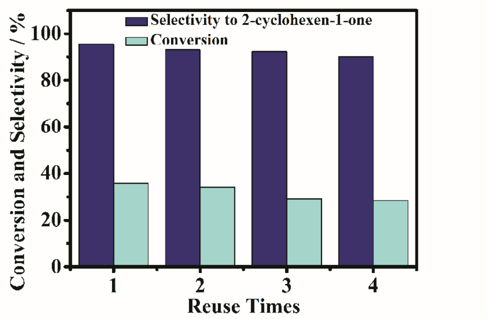


Figure 8 Reuse of 5-Fe-Co-g-C_3N_4 catalyst. Reaction conditions: cyclohexene, 0.5 mL; oxygen pressure, 4 MPa; water, 2.0 mL; 5-Fe-Co-g-C_3N_4 catalyst, 0.023 g; reaction temperature, 90°C, reaction time, 15 h.

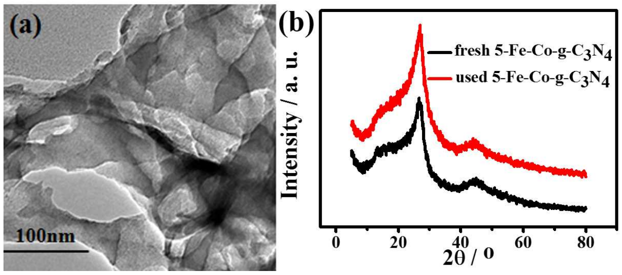


Figure 9 TEM images of 5-Fe-Co-g-C_3N_4 catalyst after used four times (a), and XRD patterns of fresh and used 5-Fe-Co-g-C_3N_4 catalyst after four times (b).

Conclusions

Fe-Co-g-C_3N_4 catalysts have been designed and prepared, and used to catalyze the selective oxidation of cyclohexene to 2-cyclohexene-1-one with oxygen as oxidant in water. It is shown that the metals in the Fe-Co-g-C_3N_4 catalysts are Fe(III) and Co(II) species stabilized by Fe-N bonds and Co-N bonds. The Fe-Co-g-C_3N_4/water catalytic system is very active and selective for the reaction, and the selectivity to 2-cyclohexene-1-one reaches 95% at cyclohexene conversion of 36%. The catalyst can be used at least four times without considerable decrease in activity and selectivity. We believe that Fe-Co-g-C_3N_4/water catalytic system, which is the highly efficient, environmentally benign, prepared from abundant feedstocks, has great potential to application in the selective oxidation of cyclohexene to 2-cyclohexene-1-one.

Experimental

Materials

Cyclohexene, 2-cyclohexene-1-one, 2-cyclohexene-1-ol, ethyl acetate, *n*-heptane, acetonitrile, acetone, ethanol, $Co(NO_3)_2·6H_2O$, NH_4VO_3, $(NH_4)_{10}W_{12}O_{41}·xH_2O$ and $Cu(NO_3)_2$ were all of analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd. Anhydrous ferric chloride and dicyandiamide were provided by Aldrich and used as received. Molecular oxygen (99.99%) was obtained from Beijing Analytical Instrument Company.

Catalyst preparation

Synthesis of g-C_3N_4: Graphitic carbon nitride (g-C_3N_4) was prepared according to the reported procedure[27]. In a typical preparation, 1 g of dicyandiamide mixed with 10 mL of deionized water was stirred and heated at 80°C in an oil bath. The mixed solution was continually heated at 100°C until removal of water. The resulting solid was then grounded in a mortar, transferred into a quartz tube, and heated under flowing nitrogen atmosphere to 300°C at a rate of $3°C·min^{-1}$ and kept at this temperature for 2 h. The mixture was then continuously heated to 600°C at a rate of $3°C·min^{-1}$, and treated for 4 h at this temperature. Finally, the light yellow g-C_3N_4 powder was obtained after cooling to room temperature under flowing nitrogen atmosphere.

Synthesis of different catalysts: Fe-Co-g-C_3N_4 catalyst was prepared similar to the above preparation of g-C_3N_4 material except that metal precursors were added. In a typical preparation, 1 g of dicyandiamide mixed with 10 mL of deionized water was stirred and heated at 80°C in an oil bath. Next, $FeCl_3$ and $Co(NO_3)_2·6H_2O$ with different molar ratios of Fe to Co was added and the total weight of these two metal precursors were 0.2 g. The mixed solution was continually heated at 100°C until removal of water. The resulting solid was then treated similar to the above method for the synthesis of g-C_3N_4. The obtained catalyst was denoted as x-Fe-Co-g-C_3N_4 with x standing for the molar ratio of $FeCl_3$ to $Co(NO_3)_2·6H_2O$. Similarly, 1-Fe-Cu-g-C_3N_4 catalysts were prepared according to the same method as 1-Fe-Co-g-C_3N_4 catalyst except that $Co(NO_3)_2·6H_2O$ was replaced by $Cu(NO_3)_2$. Similar procedures were applied in the preparation of V-, W-, Cu-, Co-, Fe-g-C_3N_4 catalysts except that different metal precursors, including NH_4VO_3, $(NH_4)_{10}W_{12}O_{41}·xH_2O$, $Cu(NO_3)_2$, $Co(NO_3)_2·6H_2O$, and $FeCl_3$, were added, and the weight of the metal precursors was 0.2 g. In addition, Co-activated C, Co-TiO_2 and Co-SiO_2 catalysts were prepared according to the same method as Co-g-C_3N_4 catalyst except that 1 g of dicyandiamide was replaced by 0.4 g of activated C, TiO_2 and SiO_2, respectively.

Catalyst characterization

The morphology of the catalyst was characterized by transmission electron microscopy (TEM, JEOL JEM-2100F) equipped with EDS and HITACHI S-4300 SEM equipped with EDX. The Fourier transform infrared (FT-IR) spectra of the samples through compressing with KBr powder were obtained by using a Bruker Tensor 27 spectrometer with a resolution of 1 cm^{-1} and 32 scans. The nitrogen adsorption-desorption isotherms were measured on a Micromeritics ASAP 2020 sorptometer at 77 K. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 X-ray diffractometer using Cu-Kα radiation (y=0.15406 nm). The tube voltage was 40 kV and the current was 200 mA. X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab 250 Xi using a 200W monochromated Al-Kα radiation. The 500 μm X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about $3×10^{-10}$ mbar. Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon was used for energy referencing. The content of metal in the catalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-AES, Vista-MPX). The elemental analysis of the catalyst was performed on Flash EA 1112 elemental analysis instrument.

Reaction

The oxidation of cyclohexene over Fe-Co-g-C_3N_4 catalyst was carried out with molecular oxygen as oxidant and water as solvent, as shown in Scheme 1. In a typical reaction, 0.5 mL of cyclohexene, 2.0 mL of deionized water, and 0.023 g of catalyst were introduced into a 6 mL Teflon-lined stainless-steel autoclave in which equipped with a magnetic stirrer. After being filled by the desired molecular oxygen, the autoclave was heated to the required temperature and the stirrer was started. After the reaction, the autoclave was placed in ice water and molecular oxygen was slowly released. The reaction product was extracted by ethyl acetate (4 mL×3), and analyzed by an Agilent 6820 gas chromatograph equipped with a flame ionization detector and a PEG-20M capillary column (30m×0.25mm×0.25mm), using *n*-heptane as internal standard. In the recycling experiment, the catalyst was separated from the liquid by centrifugation, washed with deionized water, dried at 60°C under vacuum for 3 h, and then reused for the next run.

Acknowledgements

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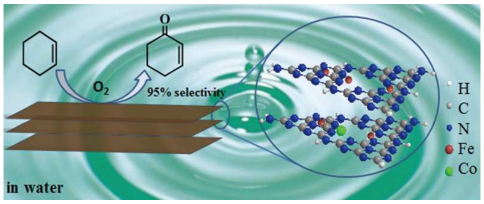
Highly selective oxidation of cyclohexene to 2-cyclohexene-1-one in water using molecular oxygen over Fe-Co-g-C_3N_4

Dexin Yang, Tao Jiang, Tianbin Wu*, Peng Zhang, Hongling Han and Buxing Han*

Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Laboratory of Colloid and Interface and Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190 (China)

E-mail: wtb@iccas.ac.cn, hanbx@iccas.ac.cn



Fe-Co-g-C_3N_4 catalyst is highly effective for the selective oxidation of cyclohexene to 2-cyclohexene-1-one using oxygen in water.