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Article

The synthesis of Co-doped SAPO-5 molecular sieve and its performance in the oxidation of cyclohexane with molecular oxygen

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ABSTRACT

Silicoaluminophosphate (SAPO) molecular sieves doped with cobalt (Co-SAPO-5) were synthesized hydrothermally with different concentrations of Co. Each sample was characterized by X-ray diffraction, N_2 adsorption-desorption, scanning electron microscopy, ultraviolet-visible spectroscopy, temperature-programmed desorption of NH_3 (NH_3 -TPD), and infrared spectroscopy of adsorbed pyridine (Py-IR). The results showed that Co was highly dispersed in the Co-SAPO-5 samples. In addition, a part of the Co content had been incorporated into the SAPO-5 framework, while the remainder existed on the surface as extra-framework Co. The surface areas of the Co-SAPO-5 samples were similar to the SAPO-5 sample. However, the pore volumes of the Co-SAPO-5 samples were lower than that of the SAPO-5 sample. As the concentration of Co increased, the pore volume gradually decreased because extra-framework cobalt oxide was present on the catalyst surface. NH_3 -TPD and Py-IR results revealed that the amount of Brønsted acid and the total amount of acid for the Co-SAPO-5 samples were higher than that for the SAPO-5 sample. These values were also higher for samples with higher Co content. The catalytic activity of the Co-SAPO-5 samples was evaluated for the oxidation of cyclohexane with molecular oxygen. When Co was added to the SAPO-5 catalyst, the catalytic activity of the Co-SAPO-5 catalysts improved. In addition, the conversion of cyclohexane increased as the Co content in the Co-SAPO-5 catalysts increased. However, with a high conversion of cyclohexane (>6.30%), the total selectivity of cyclohexanone (K) and cyclohexanol (A) decreased sharply. The K/A ratio ranged from 1.15 to 2.47. The effects of reaction conditions (i.e., reaction temperature, reaction time, initial oxygen pressure, and the catalyst amount) on the performance of the Co-SAPO-5 catalysts have also been measured. Furthermore, the stability of the Co-SAPO-5 catalyst was explored and found to be good for the selective oxidation of cyclohexane by molecular oxygen.

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1. Introduction

Cyclohexanone and cyclohexanol (KA) are important intermediates in the production of adipic acid and caprolactam,

which are used in the manufacture of nylon-6 and nylon-66 polymers, respectively [1,2]. In addition, they are used as solvents for shellacs, lacquers and varnishes, stabilizers and homogenizers for soaps and synthetic detergent emulsions, and

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as the starting material in the synthesis of insecticides, herbicides, and pharmaceuticals [3]. The oxidation of cyclohexane is an important industrial process to produce cyclohexanone and cyclohexanol; however, the productivity of this process is very low by now [4]. Currently, the most important catalyst system in use for industrial cyclohexane oxidation employs homogeneous Co salts [5]. To prevent the over-oxidation of cyclohexane, conversion is generally kept below 5% and the total selectivity of cyclohexanone and cyclohexanol reaches 70%–80% [6].

The oxidation of cyclohexane with O_2 follows the radical chain mechanism [7]. Transition-metal ions, such as Co^{2+} , Cr^{3+} , Mn^{2+} , and Ce^{2+} , accelerate free radical chain reactions. Consequently, heterogeneous catalysts that contain these ions have been extensively used to catalyze cyclohexane oxidation [8]. On the other hand, molecular sieves based on aluminophosphates have been synthesized and exhibit a huge potential for catalytic applications because of their unique pore structure and low acidity [9,10]. However, doping heteroatoms into the aluminophosphate framework tends to break the charge balance and leads to an improvement in acidity [11–13]. Therefore, because of their mild acidity and shape selectivity, silicoaluminophosphate (SAPO) molecular sieves (such as SAPO-5) have been used as solid acid catalysts for some hydrocarbon reactions. Some of these reactions include the dehydration of ethanol [14], the hydroisomerization of 1-octene [15], the conversion of methanol to olefin [16], the dimerization of propene [17], and the epoxidation of styrene [18]. The enhanced selectivities and decreased deactivation rates were observed for both medium pore-sized SAPO and metalloaluminophosphate molecular sieves.

The main objective of this work was to heterogenize the conventional homogeneous Co salt catalysts by loading them onto a SAPO support. This work also evaluates how the activity for cyclohexane oxidation with O_2 was affected by the doping of SAPO-5 samples with Co. It is worth looking ahead to provide an efficient catalyst for the oxidation of cyclohexane with O_2 .

2. Experimental

2.1. Synthesis of Co-SAPO-5 materials

The Co-doped SAPO-5 molecular sieves were synthesized by the hydrothermal method. The following chemicals were used: triethylamine (TEA) as the template, tetraethyl orthosilicate (TEOS) as the silica source, aluminum isopropoxide as the Al source, and H_3PO_4 as the phosphorus source. In a typical synthesis, a fixed amount of $Co(NO_3)_3 \cdot 6H_2O$ solution was initially mixed with 5.76 g of phosphoric acid and 18 mL of deionized water. Next, 10.21 g of aluminum isopropoxide was added to the mixture and stirred at room temperature until completely dissolved. Then, 3.13 g of the TEOS was added dropwise to the solution and continuously stirring for 1 h. Finally, 3.5 mL of the TEA template was added and stirred for an additional 3 h. The initial gel formed was transferred to a Teflon-lined stainless steel autoclave and heated to 180 °C for 24 h. After crystallization, the product was filtered, washed with deionized water,

dried at 100 °C for 24 h, and calcined in air at 550 °C for 5 h to remove the template. The synthesized samples were recorded as Co-SAPO-5-*x*, where *x* represents the different Co/Si molar ratios in the initial gels.

The SAPO-5 molecular sieve was also prepared with the same procedure, except that no $Co(NO_3)_3 \cdot 6H_2O$ was added.

2.2. Characterization of samples

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 diffractometer using $Cu K\alpha$ radiation ($\lambda = 0.154056$ nm) operating at 40 kV and 40 mA. The morphologies of the catalysts were analyzed with scanning electron microscopy (SEM) using a Hitachi S-3400N operated with a beam energy of 15 kV. The elemental compositions of the samples were analyzed with ICP (TJA IRIS ADVANTAGE 1000) and EDS (EDAX Falcon). The Varian Cary 500 UV-Vis-NIR spectrophotometer was used to record the ultraviolet-visible (UV-vis) spectra in the range of 200–800 nm, with $BaSO_4$ as the reference. Infrared spectra of adsorbed pyridine (Py-IR) of the samples were analyzed using a Nicolet Nexus 670 FT-IR spectrometer.

NH_3 -TPD was carried out in an in-house manufactured equipment. The sample was initially pretreated at 600 °C for 30 min and cooled to room temperature under N_2 . It was then exposed to the 10% NH_3/N_2 mixture gas and allowed to adsorb NH_3 for 1 h. After this adsorption time, the sample was purged at room temperature for 1.5 h under N_2 . Finally, the sample was heated at a rate of 10 °C/min to 600 °C.

2.3. Catalytic activity testing

The catalytic activities of the SAPO-5 and Co-SAPO-5 catalysts were investigated for the selective oxidation of cyclohexane with O_2 as the oxidant. No solvents were added during the process. In the typical reaction, 4 g of cyclohexane and 20 mg of catalyst were introduced into the reactor. After O_2 was charged to 0.5 MPa, the reactor was heated to 140 °C. The samples were stirred continuously and kept at 140 °C for 4 h. After the reaction was completed, the catalyst was separated by centrifugation. The reaction products were analyzed using a flame ionization detector and the Agilent 7890B gas chromatograph, which was equipped with an HP-5 capillary column. Methylbenzene was used as the internal standard.

Recycling tests were carried out on the regenerated Co-SAPO-5-0.2 catalyst. After the reaction was completed, the catalyst was separated from the reaction solution by filtration, washed three times with ethyl alcohol in a glass beaker (while stirring), dried at 100 °C for 6 h, and then calcined in air at 550 °C for 2 h. The regenerated catalyst was supplemented with fresh catalyst and its catalytic performance was tested and compared with the fresh catalyst.

3. Results and discussion

3.1. Characterization of catalysts

The powder XRD patterns of the synthesized Co-SAPO-5-*x*

Fig. 1. XRD patterns of the Co-SAPO-5-*x* samples.

samples are shown in Fig. 1. The most intense diffraction peak of SAPO-5 (100) appeared at $2\theta = 7.4^\circ$. The higher order intense diffraction peaks appeared at $2\theta = 19^\circ$ – 23° . These peaks agreed well with those of the SAPO-5 [19]. After the addition of Co, the XRD patterns of the Co-SAPO-5-*x* samples were similar to that of the SAPO-5 sample. The XRD patterns of the Co-SAPO-5-*x* samples did not show any cobalt oxide diffraction peaks. However, metallic Co was detected on the Co-SAPO-5-*x* samples and is shown in Table 1. These results indicate that Co was highly dispersed on the Co-SAPO-5-*x* samples, even with a Co metal content of 0.64 wt%.

Table 1 shows the BET surface area and pore volume for each sample. These results indicate that the surface areas of the Co-SAOP-5 samples were similar to that of SAPO-5. In contrast, the pore volumes of the Co-SAOP-5 samples were lower than that of SAOP-5, and gradually decreased as the Co content increased. There were no diffraction peaks of cobalt oxide in the XRD patterns for the Co-SAPO-5-*x* samples. Metallic Co was highly dispersed over the Co-SAPO-5-*x* samples. The presence of extra-framework cobalt oxide on the surface was detected by UV-vis spectroscopy, which may result in a decrease in pore volume of the Co-SAOP-5 samples when increasing Co content.

Figure 2 shows SEM images of the synthesized SAPO-5 and Co-SAPO-5-0.2 samples. The SAPO-5 sample exhibited columnar joint morphology. After Co addition, the morphology of the

Fig. 2. SEM images of SAPO-5 (a) and the Co-SAPO-5-0.2 sample (b).

Co-SAPO-5-0.2 sample became disorderly and was composed of bulk and column particles of random sizes.

UV-vis spectroscopy was used to characterize the nature and coordination number of the cobalt oxide species in the Co-SAP-5-*x* samples. The results are shown in Fig. 3. In the case of SAPO-5, there were no adsorption peaks in the wavelength range of 250–800 nm. However, three major groups of absorption peaks appeared at 320, 410, and 525–650 nm for all the Co-SAPO-5-*x* samples. The absorption peaks at 320 and 410 nm are attributed to the mixed oxide of cobalt outside the framework. The group of absorption peaks at 537, 580, and 630 nm is attributed to the tetrahedrally coordinated Co^{2+} in the framework [20–23]. These results suggest that part of the cobalt had been incorporated into the SAPO-5 framework, while the remaining amount existed as the extra-framework cobalt on the surface. Furthermore, the intensities of these absorption peaks increased as the Co content of the Co-SAPO-5-*x* samples increased. This indicates that the amount of cobalt, in both the framework and extra-framework, increased with increasing Co content in the Co-SAPO-5-*x* samples.

Figure 4 shows the NH_3 -TPD curves of the Co-SAPO-5-*x* samples. The results indicate that there are two NH_3 desorption peaks for all samples, which can be ascribed to the weak acid (181°C) and the medium strong acid (285°C), respectively [24]. It is noted that the intensities of the desorption peaks at 285°C increased with increasing Co content. In contrast, the intensities of the desorption peaks at 181°C hardly changed. As a result, the total acid content increased as the Co content in the Co-SAPO-5-*x* samples increased.

Fig. 3. UV-vis spectra of the Co-SAPO-5-*x* samples.

Table 1

Structural and textural parameters of the Co-SAPO-5-*x* samples.

Sample	Co content (wt%)		Surface area (m^2/g)	Pore volume (cm^3/g)
	Theoretical	Actual ^a		
SAPO-5	—	—	242.4	0.365
Co-SAOP-5-0.05	0.05	0.05	236.8	0.279
Co-SAOP-5-0.1	0.1	0.12	263.0	0.207
Co-SAOP-5-0.2	0.2	0.21	238.8	0.191
Co-SAOP-5-0.4	0.4	0.48	245.2	0.192
Co-SAOP-5-0.6	0.6	0.64	244.9	0.180

^a Determined by ICP-AES.

Fig. 4. NH_3 -TPD curves of the Co-SAPO-5- x samples.

Fig. 5. Py-IR spectra of the Co-SAPO-5- x samples.

The Py-IR spectra of the Co-SAPO-5- x samples were recorded between 1400 and 1600 cm^{-1} and are shown in Fig. 5. Three main absorption peaks were seen at 1446, 1489, and 1541 cm^{-1} . The absorption peaks at 1446 and 1541 cm^{-1} were assigned to the Lewis acid and Brønsted acid, respectively. The absorption peaks at 1489 cm^{-1} was assigned to both acids. The amount of acid for the samples was calculated and is shown in Table 2. The results show that the amount of Brønsted acid in the Co-SAPO-5- x samples is higher than that in the SAPO-5 sample. In addition, the amount increased with increasing Co content. However, the amount of Lewis acid did not change significantly. The total amount of acid on the surface of the Co-SAPO-5- x samples increased with Co addition because of the increased Co content. This is consistent with NH_3 -TPD results.

Table 2

Acid properties of the Co-SAPO-5- x samples as calculated by Py-IR spectra.

Sample	m/g	Area of absorption peak		Amount of acid ($\mu\text{mol}/\text{g}$)		
		Assigned to Brønsted acid	Assigned to Lewis acid	Brønsted acid	Lewis acid	Total acid
SAPO-5	0.0422	0.29	7.77	5.4	110.4	115.8
Co-SAPO-5-0.05	0.0396	1.30	6.56	26.1	99.5	125.6
Co-SAPO-5-0.2	0.0470	3.57	5.62	60.4	71.7	132.1
Co-SAPO-5-0.4	0.0461	4.62	5.75	79.6	74.8	154.4
Co-SAPO-5-0.5	0.0433	5.19	7.15	95.2	99.1	194.3

Table 3

The catalytic activities of the Co-SAPO-5- x catalysts for cyclohexane oxidation.

Catalyst	Conversion (%)	Selectivity (%)			K/A ratio
		Cyclohexanol (A)	Cyclohexanone (K)	KA oil	
SAOP-5	4.45	32.14	51.15	83.29	1.59
Co-SAOP-5-0.05	5.22	44.00	50.78	94.78	1.15
Co-SAOP-5-0.1	6.30	40.03	56.96	96.99	1.42
Co-SAOP-5-0.2	10.37	27.29	47.92	75.21	1.76
Co-SAOP-5-0.4	12.36	14.18	35.06	49.24	2.47
Co-SAOP-5-0.6	19.17	9.27	18.00	27.27	1.94

Reaction conditions: cyclohexane 4 g, catalyst 20 mg, initial $p(\text{O}_2) = 1.0$ MPa, 140 $^\circ\text{C}$, 4 h.

In other words, the introduction of Co in the SAPO-5 sample obviously increased the total amount of acid on the surface of the Co-SAPO-5- x samples.

3.2. Catalytic activity for cyclohexane oxidation

This section evaluates the catalytic performance of the Co-SAPO-5- x samples, where cyclohexane is oxidized by molecular oxygen. As shown in Table 3, the SAPO-5 catalyst achieved a 4.45% cyclohexane conversion, with an 83.29% selectivity towards KA oil. When Co was added to the SAPO-5 catalyst, the catalytic activity of the Co-SAPO-5- x catalysts improved. An increase in the Co content of the Co-SAPO-5- x catalysts resulted in an increase in the conversion of cyclohexane. The oxidation of cyclohexane with O_2 is known to proceed via the complex radical-chain mechanism [7,25–27]. The chain initiation proceeds through the homolytic cleavage of cyclohexyl hydroperoxide (CyOOH) according to the reaction $\text{CyOOH} \rightarrow \text{CyO}\cdot + \cdot\text{OH}$. The Co^{2+} ion catalyzes this initiation via the Haber-Weiss cycle [28,29], which leads to an increase in the cyclohexane conversion over the Co-SAPO-5- x catalysts. In addition, the selectivity towards both cyclohexanol and cyclohexanone initially increased, and then decreased violently due to an over-oxidation of the relatively reactive oxygenates. There are two commercial processes: the non-catalytic autoxidation process, and the catalyzed oxidation that uses Co-based homogeneous catalysts. The K/A ratios are generally 1.5 and 0.3–0.5, respectively [30,31]. In the present study, the K/A ratio ranged from 1.15 to 2.47, which indicates that the Co-SAPO-5- x catalyst is real and not simply a promoter of the autoxidation pathways for cyclohexane oxidation. Furthermore, the catalytic role of the Co-SAPO-5- x catalyst during cyclohexane oxidation is different from the Co-based homogeneous catalysts.

3.3. Effects of reaction conditions on the catalytic activity

The effect of reaction temperature on the catalytic activity of the Co-SAPO-5-0.1 and Co-SAPO-5-0.2 samples are shown in Fig. 6. The results show that the conversion of cyclohexane increases as temperature increases from 100 to 140 °C. The selectivity towards both cyclohexanol and cyclohexanone increased to 140 °C before dropping rapidly because of deep oxidation of the products. Both Co-SAPO-5-*x* catalysts exhibited the highest yield of cyclohexanol and cyclohexanone at 140 °C.

Figure 7 shows the influence of reaction time on the catalytic activity of the Co-SAPO-5-0.1 and Co-SAPO-5-0.2 catalysts for the oxidation of cyclohexane. As the reaction time for both catalysts increased, the conversion of cyclohexane gradually increased. In contrast, the selectivity towards cyclohexanol clearly decreased. In addition, the selectivity towards cyclohexanone increased initially and then significantly decreased over both catalysts. However, the reaction time with the maximum selectivity towards cyclohexanone is different for both catalysts because the reaction rates are based on the different Co contents of the catalysts. Taking the yield of KA oil into account, Co-SAPO-5-0.1 and Co-SAPO-5-0.2 exhibited the best reactivity over the reaction time of 6 and 4 h, respectively.

Figure 8 shows the influence of the initial oxygen pressure on the catalytic activity of the Co-SAPO-5-0.1 and Co-SAPO-5-0.2 catalysts for cyclohexane oxidation. As the initial oxygen pressure increased, the conversion of cyclohexane

gradually increased over both catalysts, but the selectivity towards cyclohexanone decreased. The selectivity towards cyclohexanol showed a different trend over both catalysts. In the case of Co-SAPO-5-0.1, selectivity initially increased and then decreased suddenly. In contrast, in the case of Co-SAPO-5-0.2, selectivity consistently decreased. At the initial oxygen pressure of 1.0 MPa, the yield of KA oil reached 6.1% and 7.8% over Co-SAPO-5-0.1 and Co-SAPO-5-0.2, respectively.

Figure 9 shows the influence of catalyst amount on the catalytic activities of both Co-SAPO-5-0.1 and Co-SAPO-5-0.2 catalysts for the oxidation of cyclohexane. As the amount of both catalysts increased from 10 mg to 30 mg, the conversion of cyclohexane increased gradually, and the selectivity towards cyclohexanone decreased gradually. However, the selectivity towards cyclohexanol showed different changing trends over both catalysts: for Co-SAPO-5-0.1, selectivity initially increased and then decreased; in the case of Co-SAPO-5-0.2, selectivity consistently decreased. Consequently, the highest yield of KA oil for the Co-SAPO-5-0.1 and Co-SAPO-5-0.2 catalysts reached 6.9% (with 30 mg) and 7.8% (with 20 mg), respectively.

3.4. Stability test

Based on its high activities for the oxidation of cyclohexane, the reusability of the Co-SAPO-5-0.2 catalyst was examined and the results are shown in Fig. 10. After the Co-SAPO-5-0.2 catalyst was reused six times, no obvious losses in activity or selec-

Fig. 6. The influence of reaction temperature on the catalytic activities of Co-SAPO-5-0.1 (a) and Co-SAPO-5-0.2 (b) catalysts for the oxidation of cyclohexane. Reaction conditions: catalyst 20 mg, cyclohexane 4 g, initial $p(\text{O}_2) = 1.0$ MPa, 4 h.

Fig. 7. The influence of reaction time on the catalytic activities of Co-SAPO-5-0.1 (a) and Co-SAPO-5-0.2 (b) catalysts for the oxidation of cyclohexane. Reaction conditions: catalyst 20 mg, cyclohexane 4 g, initial $p(\text{O}_2) = 1.0$ MPa, 140 °C.

Fig. 8. The influence of initial oxygen pressure on the catalytic activities of Co-SAPO-5-0.1 (a) and Co-SAPO-5-0.2 (b) catalysts for the oxidation of cyclohexane. Reaction conditions: catalyst 20 mg, cyclohexane 4 g, 140 °C, 4 h.

Fig. 9. The influence of the catalyst amount on the catalytic activities of Co-SAPO-5-0.1 (a) and Co-SAPO-5-0.2 (b) catalysts for the oxidation of cyclohexane. Reaction conditions: cyclohexane 4 g, initial $p(\text{O}_2) = 1.0$ MPa, 140 °C, 4 h.

tivity were observed, thereby showing an excellent stability of the catalyst.

4. Conclusions

Co-SAPO-5- x molecular sieves with different Co contents were synthesized using the hydrothermal method. A portion of the cobalt was incorporated into the SAPO-5 framework. The remaining amount existed as extra-framework cobalt on the surface, thereby leading to a decrease in the pore volume of the

Co-SAPO-5- x samples. In addition, the amount of Brønsted acid and the total amount of acid for the Co-SAPO-5 samples were higher with an increase in the Co content. The activity test of the Co-SAPO-5 samples (for the oxidation of cyclohexane with O_2) showed that the conversion of cyclohexane increased with an increase in the Co content. However, the selectivity of KA oil decreased rapidly when the conversion of cyclohexane was higher than 6.3% and when the K/A ratio ranged from 1.15 to 2.47. The Co-SAPO-5- x catalyst was determined to be a real catalyst and not a promoter of the autoxidation pathways for cyclohexane oxidation. Its catalytic role in cyclohexane oxidation is different from the Co-based homogeneous catalysts. The reaction temperature, reaction time, initial oxygen pressure, and catalyst amount influenced the catalytic activities of the Co-SAPO-5- x catalysts. In addition, the Co-SAPO-5-0.2 catalyst possesses excellent stability because its activity remained mostly unchanged after being used repeatedly six times.

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Fig. 10. Reusability of the Co-SAPO-5-0.2 catalyst for cyclohexane oxidation. Reaction conditions: catalyst 20 mg, cyclohexane 4 g, initial $p(\text{O}_2) = 1.0$ MPa, 140 °C, 4 h.

Graphical Abstract

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The synthesis of Co-doped SAPO-5 molecular sieve and its performance in the oxidation of cyclohexane with molecular oxygen

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Cobalt-doped SAPO-5 molecular sieves showed a high activity for the oxidation of cyclohexane with O₂. The catalyst behaved with good stability for this reaction.

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Co掺杂SAPO-5分子筛制备及其催化氧气氧化环己烷反应性能

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摘要: 环己醇和环己酮(KA油)是制备尼龙所需材料己二酸和己内酰胺的重要中间体, 也可用作油漆、农药和染料等的溶剂以及染色和褪光丝的均化剂等。工业上制取KA油的方法主要为苯酚加氢法、环己烯水合法和环己烷氧化法, 其中环己烷氧化法最为普遍, 是非常重要的工业过程。为获得适宜的KA油选择性, 工业上普遍采用Co盐为催化剂, 将环己烷氧化单程转化率控制在5.0%以下, 从而使得产物选择性达到70%以上。该环己烷氧化制KA油过程不仅生产效率较低, 而且所用均相催化剂因分离困难而不能重复使用。因此, 当前关于环己烷氧化反应催化剂的研究均是围绕多相催化剂进行。

氧气选择性氧化环己烷反应因具有更高的原子经济性而逐渐成为环己烷氧化法制KA油研究中最具挑战性的课题。该反应是自由基机理, 而Co²⁺, Cr³⁺, Mn²⁺和Ce²⁺等金属离子可以促进自由基链反应, 因此含有这些金属的多相催化剂被广泛用于该反应。另一方面, AlPO-*n*系列分子筛由于具有特殊的孔结构和一定的表面酸性, 在催化反应中显示出较大的应用潜力。如果进行杂原子掺杂, 通过改变分子筛骨架的电荷平衡, 可以有效提高其表面酸性。例如磷酸硅铝分子筛(SAPO-5)具有中等强度的酸性和良好的择形性, 因而作为固体酸催化剂广泛用于乙醇脱水、甲醇制烯烃、丙烯聚合和苯乙烯环氧化等反应, 表现出较高的选择性和良好

的稳定性.

本文以传统均相Co盐催化剂的多相化为出发点,制备了Co掺杂SAPO-5与分子筛催化剂(Co-SAPO-5),考察了Co掺杂量对催化剂结构、表面性质以及氧气选择性氧化环己烷反应性能的影响.结果表明,一部分Co进入分子筛骨架,同时有少量Co以氧化钴形式高度分散在SAPO-5表面. Co掺杂对SAOP-5催化剂比表面积没有显著影响,但可使其孔体积减小.相反,Co掺杂可以提高SAOP-5分子筛表面B酸性位数量和总酸量.活性测试结果表明,环己烷转化率随着Co-SAPO-5催化剂中Co含量的增加而增加,但KA油选择性在转化率高于6.3%时急剧下降.还考察了反应温度、反应时间、初始氧气压力和催化剂用量对Co-SAPO-5分子筛催化剂性能的影响,得到了最优反应条件.以Co-SAPO-5-0.2 (Co/Si摩尔比为0.2)分子筛为催化剂时,KA油总收率最高可达7.8%.另外,Co-SAPO-5催化剂在环己烷氧化反应中显示出很好的稳定性,Co-SAPO-5-0.2催化剂套用6次后活性几乎没有变化.

关键词: SAPO-5分子筛; 钴; 环己烷; 选择氧化; 氧气

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