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Preparation, Characterization and Catalytic Properties of Porous Tubular Alumina Supported Aluminium Bromide

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Abstract: Tubular gamma alumina was prepared by sol-gel method using cotton as template and aluminium chloride as aluminum resource. Via chemical tailoring method, gamma alumina supported aluminum bromide was obtained. Several techniques such as high-resolution field-emission scanning electron microscopy, N_2 adsorption techniques and X-ray diffraction were employed to investigate their morphology, structures as well as components. Experiments showed, via template synthesis, the gamma alumina fibers well replicated the nanoporous morphologies and hierarchical pore size of original cotton. With different concentration of hydrobromic acid, the morphology, structure and component could be controllablly changed. These preparation methods made these catalysts exhibited unique characteristics, such as environmental friendship, low cost and non-toxicity. The Baeyer-Villiger oxidation reactions of ketones catalyzed by the gamma alumina supported aluminum bromide, together with 30% hydrogen peroxide as an oxidant, were carried out. The experimental results revealed that this type of reactions could proceed in ethylacetate at 70℃ with good yields and high regioselectivity, through an example of oxidized cyclohexanone.

Key words: Cotton; Template synthesis; Chemical tailoring; Baeyer-Villiger oxidation
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At present, there is a tendency to the replacement of homogeneous processes with heterogeneous ones because of recovery and recycling problems, which matched the environmentally friendly and green chemistry [1]. Supported catalysts as heterogeneous reactions met well the requirements of the catalytic processes, which enjoyed the advantages of proceeding efficiently and selectively under milder conditions, and catalyst could be separated easily. By far the used synthesis methods for supported catalysts were mainly referred to impregnation method [2], hybrid method[3], co-precipitation method [4], and ion exchange[5]. On the other hand, different morphology, structure and composition of heterogeneous catalysts exhibited different catalytic properties. Alumina as catalysts or catalyst supports, were controllablly synthesized by many templates [6-9]. It was interesting to note that natural materials such as wood, cotton, bamboo and diatom could be used as templates to synthesize biomorphic materials in the past few decades, during which the morphologies and hierarchical pore sizes of natural materials were well replicated [10-13]. As natural fibers, cotton is composed of 88-96 wt. % cellulose. Cellulose is an oxygen-rich natural polysaccharide including anhydroglucose units joined by an oxygen linkage to form a linear molecular chain. So a variety of special-purposed materials are obtained via series of physical, chemical, biological methods[14-16].

In our previous works, we have found Lewis acid $AlCl_3$[17] and SiO_2-$AlCl_3$[18] could catalytically oxidize ketones to the corresponding lactones or esters with high conversion and selectivity. The primary aims of

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this work were to synthesize another supported Lewis acid catalysts with active component highly dispersed on their support which has highly specific surface and biological structures through template synthesis and chemical tailoring, then to examine their catalytic reactivity toward analogies of ketones with H_2O_2(30%) as oxidant.

1 Experiment

1.1 Materials and equipments

The absorbent cotton, aluminium chloride, hydrobromic acid, cyclohexanone, cyclopentanone, 2-methyl-cyclohexanone, 4-methyl-cycloliexanone, 2-tert-butyl-cyclohexanone, 4-tert-butyl-cyclohexanone, 4-methyl-2-pentanone, diisopropylketone, hydrogen peroxide and ethylacetate were obtained from commercial sources and without further purification. The scanning electron microscopy (SEM) was conducted on a field-emission scanning electron microscopy (FESEM, JEOL JSM- 6701F SEM, Japan) operated at an accelerating voltage of 5 kV. The adsorption-desorption isotherms researches with liquid nitrogen at 77.3 K were performed employing the standard nitrogen adsorption-desorption measuring device (Quantachrome NovaWin 2 1994-2006, Quantachrome Instruments v 2.2). The specific surface area (SSA) was tested with a single point Brunauer-Emmett-Teller (BET) method. Pore-size distribution was reckoned from the adsorption branch of the nitrogen isotherm, using the Barrett-Joyner-Halenda method. XRD were processed on a Bruker D8X-ray diffraction meter using Cu Kα radiation at 40 kV and 30 mA to get a diagram to explain crystal morphology recording in the 2θ range between 10^0 and 90^0 scopes with scanning step of 4^0 min^{-1}. Gas chromatography (GC) analysis was performed in a Shimadzu GC-2010 system equipped with a 15 m × 0.53 mm × 1.5 μm RTX-1 capillary column and a FID detector.

1.2 Preparation of porous tubular γ-Al_2O_3 and tubular γ-Al_2O_3-$AlBr_3$

Dried and loose cotton fibers were impregnated in the aluminium chloride solution (5%) in several minutes. After being dried at 80 ℃ in an oven, the cotton fibers covered with hydrous oxide of aluminium ion were placed into an alundum crucible and then calcined at 800 ℃ in the tube furnace for 6 h, so as to eliminate the cotton templates[19]. The obtained biomorphic Al_2O_3 fibers were immersed in different concentration of hydrobromic acid for about 15 minutes, centrifuged and dried in vacuum below 60 ℃ for 24 h, and then the catalysts of Al_2O_3-$AlBr_3$ were obtained.

The content of aluminum bromide in the chemical tailored tubular alumina was determined by potentiometric titration of the bromide ions with silver nitrate. The bromide contents were summarized in Table 1.

Table 1 The bromide content of tubular alumina tailored with different concentration of hydrobromic acid

Catalyst	The Percentage of Br^- (%)	
	Before reaction	Behind cyclic reaction
Al_2O_3-$AlBr_3$-1	9	5
Al_2O_3-$AlBr_3$-2	23	16
Al_2O_3-$AlBr_3$-3	35	27

1.3 Baeyer-Villiger oxidation

Oxidation of ketones was performed in a 10 mL glass reactor. A typical procedure for the Baeyer Villiger oxidations was as follows: cyclohexanone (10 μL, 0.1 mmol) and 30% hydrogen peroxide (1.5 eq) were dissolved in 3 mL of organic solvent with Al_2O_3-$AlBr_3$ catalysts (0.05 mmol) added; the mixture was heated to 70 ℃ and stirred at this temperature for 15 h. The reaction products were identified by GC analysis. Other cycloketones and chain ketones were also oxidized in this oxidation system to give the corresponding lactones or esters. Some pure products were obtained through column chromatography (silica gel) using petroleum ether and ethyl acetate (10:1, v/v) as eluent.

Cyclopentanone lactone: ^{1}H NMR ($CDCl_3$, 400 MHz): 1.856-1.954 (m, 4H), 2.544-2.578 (s, 2H), 4.341-4.368 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): 18.891, 22.107, 29.651, 69.326, 171.354.

Cyclohexanone lactone: ^{1}H NMR ($CDCl_3$, 400 MHz): 1.772-1.863 (d, 6H), 2.641 (s, 1H), 4.231 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): 22.770, 28.775, 29.118, 34.392, 69.116, 176.133.

4-Methylcyclohexanone lactone: ^{1}H NMR ($CDCl_3$, 400 MHz): 0.995-1.012 (d, 3H), 1.290- 1.553 (m, 2H), 1.737-1.827 (m, 1H), 1.846-1.968 (m, 2H), 2.583-2.666 (m, 2H), 4.157-4.307 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): 22.046, 30.695, 33.126, 35.177, 37.158, 68.007, 175.980.

4-tert-Butylcyclohexanone lactone: ^{1}H NMR ($CDCl_3$, 400 MHz): 0.899-0.921 (s, 9H), 1.315-1.375 (m, 2H), 1.505-1.567 (m, 1H), 2.026-2.098 (m, 2H), 2.534-2.604 (t, 1H), 2.684-2.741 (m, 1H), 4.121-4.366 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): 23.753, 27.434, 30.330, 32.982, 33.447.

2 Results and discussion

The SEM images of the obtained samples were summarized in Fig. 1. Fig. 1 (A) showed the original cotton has morphology of twisted ribbons which are determined by the organization of the cellulose micelles that compose the cell wall. When the fibers dry out,

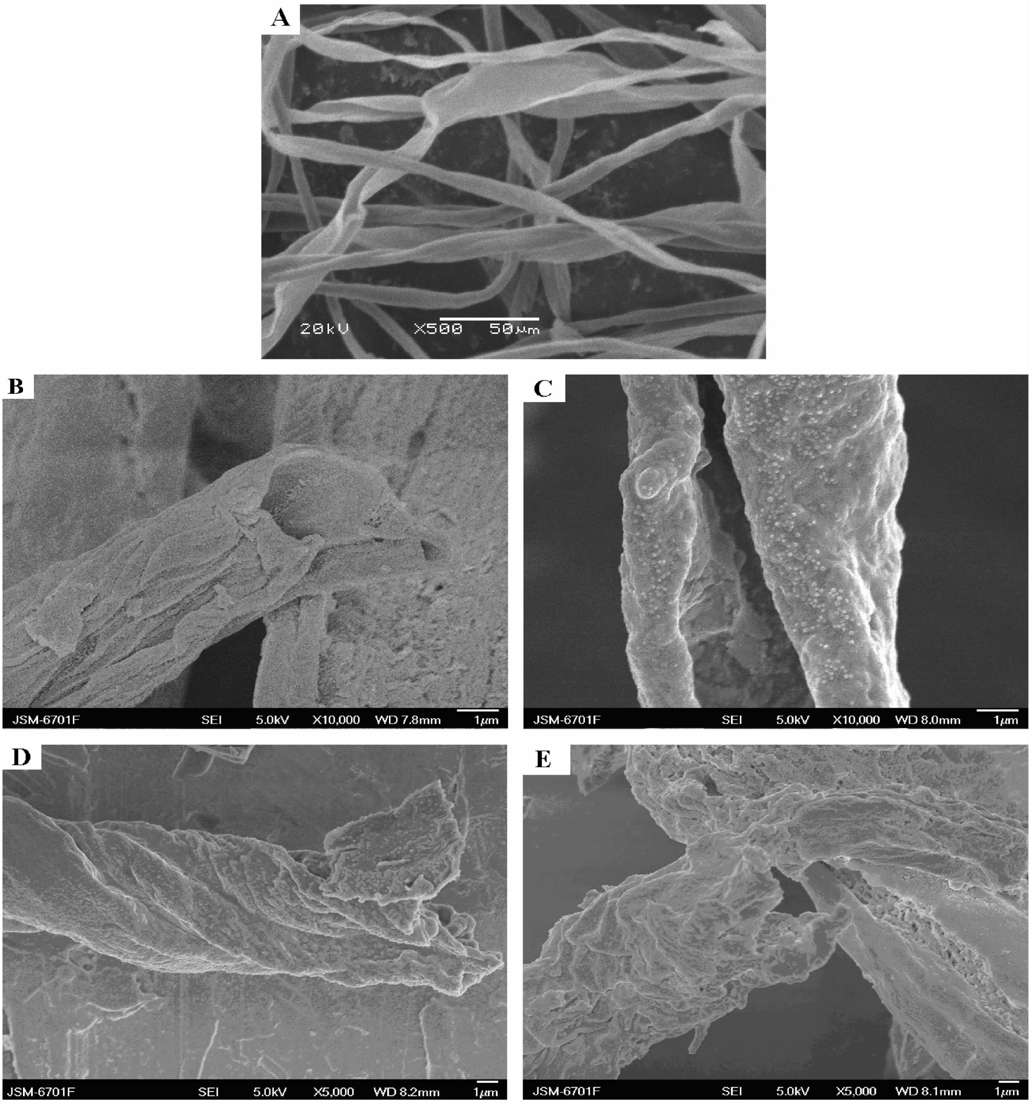


Fig. 1 SEM images of cotton fibers (A), tubular Al_2O_3 (B) and Al_2O_3-$AlBr_3$ obtained with different concentration of hydrobromic acid: (C) 1 mol/L (D) 2 mol/L (E) 3 mol/L

the wall becomes much twisted. Fig. 1 (B) showed the cotton template prepared biomorphic Al_2O_3 fibers were hollow with a wall from 0.5 to 1 μm and inner diameters ranging from 2 to 3 μm. This may be due to the wetting characteristics of cotton fibers during the impregnation process, in which Al^{3+} were distributed on the outer surfaces of the fiber and binded with the ether or hydroxyl oxygen of cellulose then the hollow tubular like fibers were obtained after the cotton templates were removed during calcinations[20]. Figs. 1 (C-E) showed the tailored biomorphic Al_2O_3 fibers using 1 mol/L, 2 mol/L and 3 mol/L hydrobromic acid, respectively. Fig. 1 (C) showed significant changes had taken place in its surface, while the structure remained tubular. With the concentration of hydrobromic acid increasing, the superficial morphology was changed more and more seriously. When the concentration reached at 3 mol/L, the Al_2O_3 fibers tubular structure was almost destroyed Fig. 1 (E). This indicated that appropriate concentration of acid had a dominating impact on its surface topography.

Fig. 2 showed the wide-angle diffraction peak of the synthesized tubular γ-Al_2O_3 (A) and Al_2O_3-$AlBr_3$ obtained with 1 mol/L (B) 2 mol/L (C) and 3 mol/L (D) hydrobromic acid. Compared with the XRD peaks, we could see the samples calcined at 800 ℃ almost shaped pure crystalline γ-Al_2O_3 (A) [21]. After tailored by 1 mol/L hydrobromic acid, the $AlBr_3 \cdot 6H_2O$ crystal peak appeared. With the hydrobromic aicd concentration increased, $AlBr_3 \cdot 6H_2O$ crystal peak was more and more obvious. These results manifested the existence of crystalline γ-Al_2O_3 and $AlBr_3$ $6H_2O$ with hydrobromic acid tailored. It would indicate the catalysts successfully prepared.

Typical nitrogen adsorption desorption isotherms and their corresponding pore size distributions were shown in Fig. 3. As was shown in Fig. 3(A), the adsorption desorption isotherm of biomorphic γ-Al_2O_3 fibers sintered at 800 ℃ belongs to a Langmuir type, with a noticeable inflection point existing in its hysteresis loop[22]. The adsorption curve and it's desorption counterpart overlap in a comparatively low relative pressure range, while a clear hysteresis behavior occurs in the high relative pressure range. These indicate that biomorphic γ-Al_2O_3 fibers contain a large number of mesopores on their surfaces (Fig. 3 insert (A)), giving rise to a strong adsorption behavior[19]. Correspondingly, the Brunauer-Emmett-Teller (BET) surface area was determined to be as high as 76 $m^2 g^{-1}$, and the pore size and pore volume calculated by the nonlocal density functional theory (NLDFT) method was 3.8 nm, and 0.21 $cm^3 g^{-1}$. After being tailored with different concentration hydrobromic acid, the mesoporous structure still remained while it's desorption

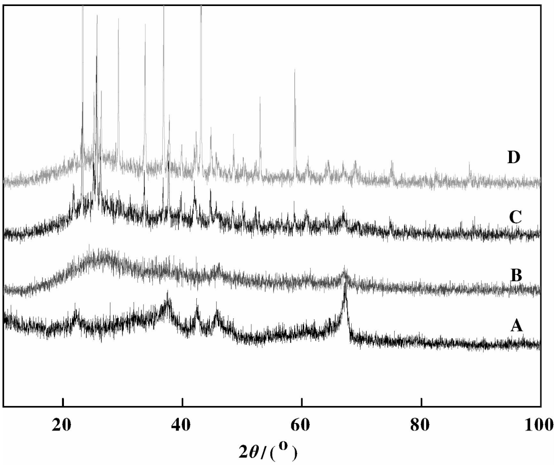


Fig. 2 XRD patterns: tubular γ-Al_2O_3 (A), Al_2O_3-$AlBr_3$ obtained with different concentration of hydrobromic acid: (B) 1 mol/L (C) 2 mol/L (D) 3 mol/L

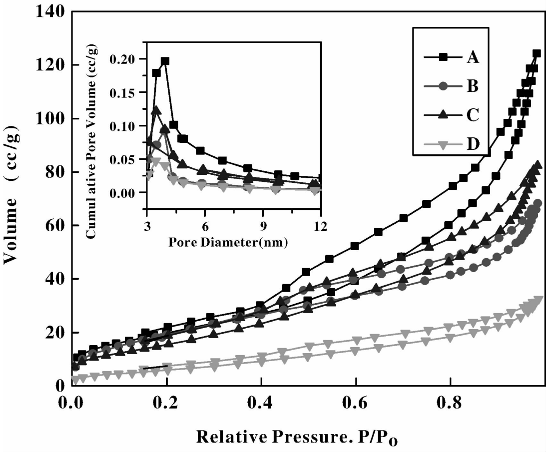


Fig. 3 Nitrogen adsorption-desorption isotherms and BJH pore size distribution: tubular γ-Al_2O_3 (A), Al_2O_3-$AlBr_3$ obtained with different concentration of hydrobromic acid: (B) 1 mol/L (C) 2 mol/L (D) 3 mol/L

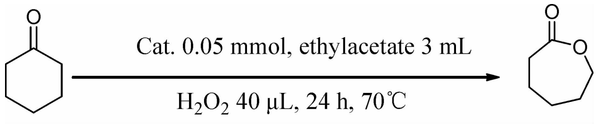
hysteresis loop became smaller with hydrobromic acid concentration increased (Fig. 3 (B, C, D)). Hence, these biomorphic Al_2O_3-$AlBr_3$ fibers exhibited weak adsorption behaviors. A little bit of decrease of BET surface area and mesopore size for the Al_2O_3-$AlBr_3$ (Fig. 3) suggested that the mesopore of the treated Al_2O_3 was well-preserved when the concentration of hydrobromic acid was low. From Fig. 3 (b), the pore size distribution of porous tubular γ-Al_2O_3 fibers and Al_2O_3-$AlBr_3$ was more single. The data of the Brunauer-Emmett-Teller (BET) specific surface area and BJH Pore size and pore volume was shown in Table 2.

Table 2 The specific surface of tubular γ-Al_2O_3 (A) and tubular γ-Al_2O_3-$AlBr_3$ (B) 1 mol/L (C) 2 mol/L (D) 3 mol/L

Sample	BET surface area (m^2/g)	BJH total pore volume (cm^3/g)	BJH pore diameter (nm)
A	76	0.21	3.8
B	74	0.09	3.7
C	61	0.12	3.4
D	24	0.05	3.3

In this work, we screened the commercially available γ-Al_2O_3, together with γ-Al_2O_3 synthesized by cotton template, and γ-Al_2O_3 supported $AlBr_3$ via chemical tailoring approaches, for their catalytic properties toward ketones oxidation. Examination of Table 3 showed that commercially available and cotton template synthesized by γ-Al_2O_3 had little catalytic activity. However, the catalytic activity tended to be high with increasing the concentration of hydrobromic acid on γ-Al_2O_3. This indicated that after chemical tailoring, $AlBr_3$ was evenly distributed on the tubular alumina surface and pore, which could make the oxidation reaction proceed efficiently. This was mainly due to enhancing the surface acidity of Al_2O_3 by Al^{3+} ions of $AlBr_3$.

Table 3 Oxidation of cyclohexanone catalyzed by different γ-Al_2O_3 catalysts



Entry	Catalyst	Conversion (%)	Selectivity (%)
1	γ-Al_2O_3	<5	<5
2	γ-$Al_2O_{3(cotton)}$	<5	<5
3	Al_2O_3-$AlBr_3$-1	66	>99
4	Al_2O_3-$AlBr_3$-2	95	>99
5	Al_2O_3-$AlBr_3$-3	91	>99

Reaction conditions: substrate cyclohexanone 0.1 mmol, 30% H_2O_2 40 μL, ethylacetate 3 mL, catalyst 0.05 mmol, 24 h, at 70 ℃.

Taking into account the impact on γ-Al_2O_3 morphology and pore structure, we selected Al_2O_3-$AlBr_3$-2 as an ideal catalyst. Experiments had been performed to investigate the effects of solvents, reaction temperature, amount of H_2O_2, reaction time and amount of catalyst (Al_2O_3-$AlBr_3$-2), as well as the recycling time of catalyst on cyclohexanone. Table 4 showed the solvents affected Baeyer-Villiger oxidation of cyclohexanone with H_2O_2 oxidant using Al_2O_3-$AlBr_3$-2 as catalyst. However, only in the system of using ethylacetate as solvents was achieved the highest conversion and selectivity. The catalytic activity of Al_2O_3-$AlBr_3$-2 was poor in such solvents as ethanol, 1, 2-dichloroethane, 1, 4-dioxane, cyclohexane and no catalytic activity in acetonitrile and benzonitrile solvents.

Table 4 Catalytic oxidation of cyclohexanone with catalysts in different solvents

Entry	Solvent	Conversion (%)	Selectivity (%)
1	ethanol	93	88
2	ethylacetate	98	100
3	1, 2-dichloroethane	50	50
4	1, 4-dioxane	88	85
5	cyclohexane	60	97
6	acetonitrile	<5	<5
7	benzonitrile	<5	<5

Reaction conditions: substrate 0.1 mmol, 30% H_2O_2 40 μL, catalyst 0.05 mmol, 15 h, at 70 ℃.

Thus, we selected the ethylacetate as solvent to examine the effect of reaction temperature, amount of H_2O_2, reaction time and amount of catalyst (Al_2O_3-$AlBr_3$-2). The results of this study were summarized in Fig. 4. From Fig. 4 (a), the temperature was found to have a significant influence on conversion but little on selectivity. The oxidation occurred at a relatively low temperature. However, the result showed that the conversion increased from 20% to 45% as the reaction temperature increased from 20 to 60 ℃, but when the temperature reached at 70 ℃, the conversion reached at 98% needing 0.05 mmol catalyst and 24 h. Thus 70 ℃ was a decent temperature. The amount of H_2O_2 was another significant factor which could influence the oxidation. Fig. 4 (b) showed when the amount of H_2O_2 in the catalytic system exceeded 40 μL, the conversion of cyclohexanone was reduced as well as the selectivety while the amount of H_2O_2 was exceeded 80 μL needing 0.05 mmol catalysts at 70 ℃ and 24 h. This might be the water in the hydroperoxide, because $AlBr_3$ could be hydrolyzed with increasing water in the system and thus the catalyst activity was reduced. On another hand with water increased, ester also could be hydrolyzed to corresponding acid, and the selectivity was reduced. Fig. 4 (c) showed using 0.05 mmol catalyst at 70 ℃ and within 15 h, the conversion of cyclohexanone reached at 98% and selectivity kept 99%. However, under the same condition the amount of catalyst influenced little on the conversion. From Fig. 4 (d) we could find when the amount of catalyst exceeded

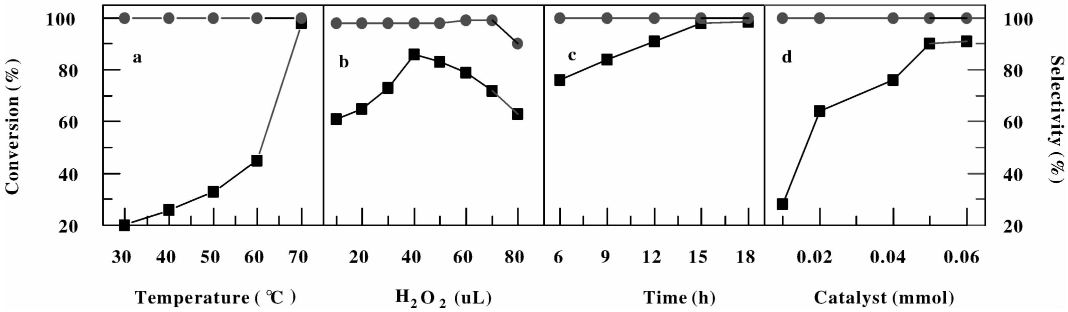
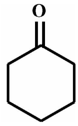
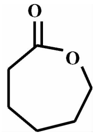
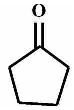
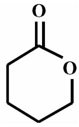
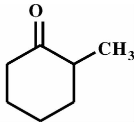
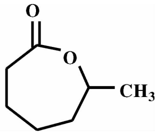
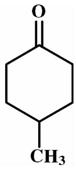
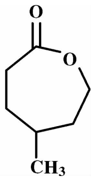
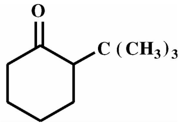
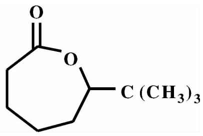
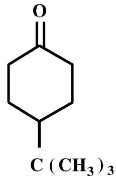
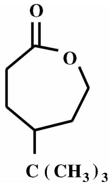
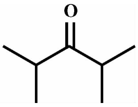
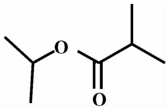
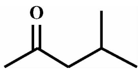
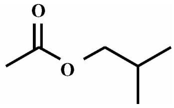


Fig. 4 Optimization of reaction parameters using cyclohexanone

Table 5 Catalytic different ketones with catalysts in the optimal condition

substrate	Conversion (%)	Selectivity (%)	Yeid[a] (%)	product
	98	100	63	
	50	80	54	
	80	62		
	95	63	65	
	40	50		
	50	100	68	
	50	100		
	<5	<5		

Reaction conditions: ethylacetate 3 mL, 30% H_2O_2 40 μL, catalysts (Al_2O_3-$AlBr_3$-2) 0.05 mmol, 15 h, at 70 ℃.

[a] Some pure products was obtained through column chromatography (silica gel) using petroleum ether and ethyl acetate (10:1, v/v) as eluent, the yield was calculated through weighing.

0.05 mmol, the conversion and selectivity were kept constant. According above experiments, the optimum conditions of catalytic oxidation to cyclohexanone were as follows: cyclohexanone 0.1 mmol, catalysts 0.05

mmol, H_2O_2 1.5 eq, ethylacetate 3 mL, 15 h, at 70 ℃. In this reaction condition, several cyclic and chain ketones such as cyclohexanone, 4-methylcyclohexanone, 2-methylcyclohexanone, 2-tertbutylcyclohexanone, 4-tertbutylcyclohexanone, diisobutylketone, 4-methyl-2-pentanone, and cyclopentanone were also catalyzed. As was shown in Table 5, the conversion for some cyclic and chain ketones were more than 50% and for cyclohexanone reached at a maximum of 98%, meanwhile, the product selectivity remained 100% due to some ketones investigated.

In order to investigate the recycle of the catalyst, cyclohexanone was still chosen as the model compound. The reactions were carried out with 30% hydrogen peroxide in ethylacetate at 70 ℃ for 15 h using 0.05 mmol of Al_2O_3-$AlBr_3$-2 as catalyst. When the catalyst was repeatedly filtered out and submitted to a new reaction batch without any further treatment, the activity was lowered to 96%, 87% and 60% from the original 98% after 2, 3, and 4 cycles, respectively. As was shown in Fig. 5, Al_2O_3-$AlBr_3$-2 as heterogeneous catalyst could be recycled although the catalytic activity was lowered by 40% or so, compared with that of the starting reactivity, which might be the aluminium bromide content reduced after the catalyst was recycled four times (Table 1).

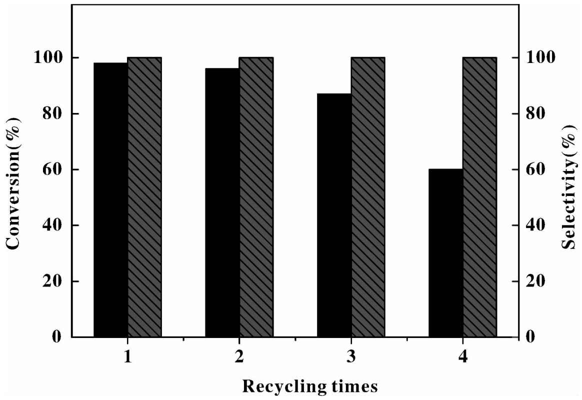


Fig. 5 the recycling of the Al_2O_3-$AlBr_3$

Lewis acid catalysts can activate carbonyl groups[23]. As a hard Lewis acid $AlBr_3$ could coordinate hard basic centres. The ketones which would be oxidated have carbonyl group, and the oxygen atom of the carbonyl group was hard base, therefore Al^{3+} would coordinate the oxygen atom, activating the ketones for a nucleophilic attack.

3 Conclusions

In summary, biomorphic γ-Al_2O_3 which had high specific surface and biological structures could be prepared by sol-gel method using cotton as template. As a catalyst, γ-Al_2O_3-$AlBr_3$ could be controllably prepared by chemical tailoring method. In the structures of these supported catalysts, the nanoporous morphologies and hierarchical pore size of original cotton were well replicated. The active component on the surface of the support pores was well distributed. These preparation methods made these catalysts exhibit some unique characteristics, such as environmental friendship, low cost and non-toxicity. Some ketones could be catalyzed by the catalyst with environmentally friendly 30% hydrogen peroxide as oxidant with high conversion and selectivity. The catalyst could be recycled at least four times and the conversion of cyclohexanone lowered about 40% compared to that of the starting reactivity.

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多孔管状氧化铝及其负载溴化铝的制备,表征及催化性能

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摘　要: 应用棉花为模板,氯化铝为铝源,通过溶胶凝胶法制备了管状 γ-氧化铝。通过化学剪裁制备了 γ-氧化铝负载的溴化铝催化剂。采用高倍扫描电子显微镜,氮气吸附脱附和 X 射线衍射分析等技术对其形态,结构以及组成进行表征。实验表明,γ-氧化铝很好地复制棉花的多孔结构,经过化学剪裁,可以得到形态,结构和组分不同的 γ-氧化铝负载的溴化铝催化剂。此催化剂成本低,环境友好,在 Baeyer-Villiger 氧化反应中,以 30% 的过氧化氢作为氧化剂,乙酸乙酯作为溶剂,70 ℃下,环己酮的转化率达到 98% 和环己内酯选择性达到 100% 。对部分的环酮和直连酮同样具有较高的催化活性。催化剂可以循环使用多次,活性没有明显的降低。

关键词: 棉花; 模板合成;化学剪裁;Baeyer-Villiger 氧化