Environmentally friendly efficient one-pot esterification of cyclohexane with CuO-promoted sulfated zirconia

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Abstract

The production of dibutyl phthalate directly from oxidation and esterification of cyclohexane, catalyzed by CuO-modified sulfated zirconia (SZCu) by one-pot under mild condition, was studied. The esterification reaction process was monitored by UV–vis spectra and the distribution of the products was analyzed by gas chromatograph–mass spectrometry (GC–MS). The result revealed that the SZCu catalyst was efficient in the direct oxidation and esterification of cyclohexane to ester. The selectivity for ester (dibutyl phthalate) can reach up to 72.2 wt.%, and the yield of ester was 29.5 wt.%. The esterification reaction, that offers several advantages such as usage of environmental friendly oxidant, simple work-up procedure, no-solvent conditions, short reaction times, easy recovery and reusability of the catalyst, is necessary for chemosynthesis industry from the environment standpoint. The regeneration property of SZCu was also tested in this work.
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1. Introduction

Transformation of hydrocarbons into oxygenous ramification is of prime economic importance in the petrochemical industry. Generally, the transformation occurs under strong acidic conditions [1]. However, the drawback of conventional liquid acids is that they are corrosive and difficult to recover and reuse. As a replacement of liquid acids, solid acids exhibit a promising alternative because of their environmental friendly characteristics (non-corrosiveness, ease of handling, recovering and reusing). Among several different solid acids, such as clays, zeolites, heteropolyacids and ion exchange resins, metal-promoted sulfated zirconia has been receiving much attention, due to their superior catalytic activity for hydrocarbon conversions [2,3]. Many large volume applications based on metal-promoted sulfated zirconia are reported in the literature, especially in the petroleum industry for alkylation, isomerization and cracking reactions [4–6]. But the effect of the catalysts on oxidation of alkane in the presence of air flow has been paid little attention.

On the other hand, the conversions of the oxidation process are usually kept very low in current oxidation process of hydrocarbons, in order to attain high selectivity for the target products, the success of an industrial reaction depends on the stringent control of the temperature and pressure. Furthermore, long reaction period, formation of by-products, difficulties in after-treatment, corrosion of reaction vessels were all main disadvantages of the current oxidation processes of alkane [7]. Current environmental legislation also reflected a stricter request in the emission of pollutants to the environment. For the above reason, the search for new alternatives with ease of handling, environmentally friendliness and mild conditions in the process of oxidation of alkane is required.

In this work, CuO-modified sulfated zirconia (SZCu) was synthesized and its application in the oxidation of cyclohexane at room temperature and atmospheric pressure was investigated. Unexpectedly, the one-step oxidation of cyclohexane into phthalate ester (dibutyl phthalate) using molecular oxygen (containing in the air flow) as oxidant with the SZCu catalyst was carried out in short reaction time (120 min), with high selectivity (72.2 wt.%) and high yield (29.5 wt.%). The catalytic activity of the regenerated SZCu catalyst was also tested, and the results show the regenerated catalyst showed almost the same yield of ester (25.5 wt.%) as the fresh catalyst at the same

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reaction conditions. In addition, from the environment standpoint, this environmentally friendliness catalyst has the advantages of easy availability, easy handling, high stability, and reusability, this practical oxidation reaction process can be carried out in solvent-free conditions at very short times, with simple work-up procedure, brings us a step closer to preparing the practical catalyst for use in industry for cyclohexane esterification in one-step.

2. Experimental

2.1. Catalyst preparation

All chemicals used were analytical grade and used without any further purification.

The catalyst used in the experimental was prepared by adopting a two-step route [8]. The CuO–ZrO$_2$ binary oxide was prepared by a homogeneous co-precipitation method. For this purpose, an aqueous solution containing the requisite quantities of ZrOCl$_2$·8H$_2$O (100.12 g) and CuSO$_4$ (9.50 g) were prepared separately and mixed together. This solution was hydrolyzed with dilute ammonium hydroxide (25%) with vigorous stirring until the pH of the solution reached to 8–9. At this pH, a white precipitate was formed and the precipitate was allowed to settle for 2 days. The obtained precipitate was filtered off and washed several times with deionized water and then dried at 373 K for 12 h. The powdered oven-dried hydrous CuO–ZrO$_2$ was immersed in 0.5 M H$_2$SO$_4$ solution so as to reach the equivalence of 5 ml of pure H$_2$SO$_4$ per gram of zirconium–copper hydroxide for 24 h to incorporate sulfate ions. The resulting samples were filtered, and then oven-dried at 373 K for 3 h. After that, the samples were calcined at 873 K for 3 h to obtain the catalyst, and finally stored in sealed glass ampoule until use.

2.2. Experimental set-up and analysis of the products

The reactor system for oxidation reaction was the same with the previous paper [9]. The reactor system mainly comprises a glass reactor with a liquid sparger, a fan and several rotameters. The oxidation reaction was performed by loading prepared SZCu into the glass reactor at room temperature (298–303 K) and normal atmospheric pressure. To make the gas–liquid–solid three phrase contacted sufficiently, cyclohexane was added by the liquid sparger at a spray rate of about 100 ml/h, while the fresh air was continuously input into the reaction system. The mole ratio of cyclohexane/oxygen was approximate 1:2. The total volume of the reaction reagent was 500 ml. The moment of addition of overall cyclohexane into the glass reactor was taken as the starting time of the reaction. The oxidation reaction process was monitored by UV–vis spectra. The compositions of reaction mixture were identified by GC–MS and verified by comparing with the retention time (rt) of the relevant standards in GC. The yield of each product was quantified by GC–MS using the internal standard method.

Sulfated ZrO$_2$ (SZ) and ZrO$_2$ were prepared by a conventional method adapted from the literature [8], and were tested at the same condition for comparison.

2.3. Catalyst characterization

X-ray diffraction (XRD) of the catalyst was recorded on a Rigaku apparatus using Cu Kα radiation (λ = 1.5406 Å). The XRD phases present in the catalyst were identified using JCPDS data files. The molecular structure of the fresh SZCu catalyst was recorded on a Bruker EQUINX55 Fourier transform infrared (FT-IR) spectrometry (Germany). The surface composition of the catalyst was analyzed by X-ray photoelectron spectroscopy (XPS) using a XSAM800 (Kratos) equipment with the non-monochromatic Mg X-radiation. The background pressure in the chamber was in the range of 10^{-8} Pa. The catalyst was outgassed in a vacuum oven overnight before XPS measurements.

3. Results and discussion

3.1. Characterization of the catalyst

3.1.1. X-ray diffraction

X-ray diffraction patterns of the catalyst before and after the reaction were shown in Fig. 1. It showed that the crystalline phases for the sample before the reaction were mainly the tetragonal phase of zirconia (t-ZrO$_2$), these were consistent with those reported by others [9–11]. The stabilization of the tetragonal structure was necessary to generate sites of catalytic activity in the catalyst [12,13]. The crystalline phases of the catalyst after the reaction were almost the same with that of the catalyst before the reaction, only little differences between them, suggested that the crystalline phases of the catalyst were very stable during the reaction.

3.1.2. FT-IR spectroscopy

The IR spectrum of SZCu before the reaction shows a huge band with a maximum at around 3500 cm^{-1} in the OH stretching region (Fig. 2), which was attributed to hydroxyls groups coordinated to Zr cation [14,15] or the band of H$_2$O molecule. Two obvious bands observed at 1400–1380 and 1100 cm^{-1}, assigned to the asymmetric stretching vibration and symmetric stretch-
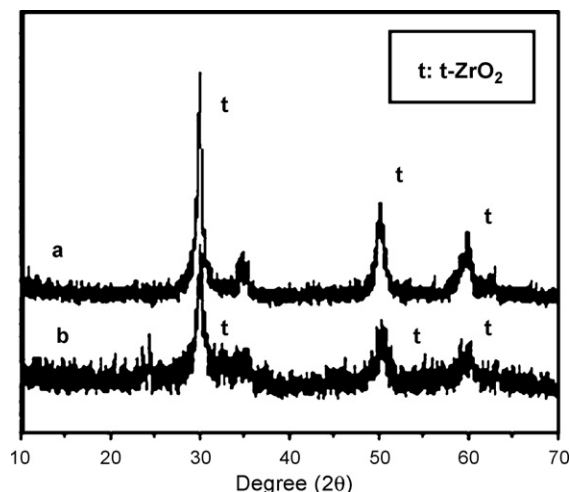

Fig. 1. X-ray diffraction patterns of SZCu before and after the reaction: (a) SZCu before the reaction and (b) SZCu after the reaction.
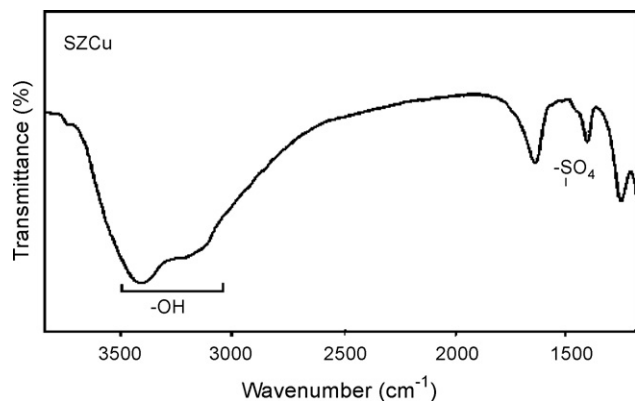
Fig. 2. FT-IR spectra for the catalyst SZCu.

Fig. 4. Zr 3d XPS spectra for SZCu after the reaction.

ing vibration band of the O=S=O, respectively, indicated that a chelate bidentate SO_4^{2-} coordinated to metal oxides such as Zr^{4+} because the highest stretching vibration of the SO_4^{2-} in the samples was above $1200\,cm^{-1}$ [14,15]. It also maybe inferred that sulfur element in the catalyst existed in a six-oxidation state (S^{6+}). These results were very similar to those reported by other authors [14,16,17].

3.1.3. X-ray photoelectron spectroscopy (XPS)

Catalysts before and after the reaction were dried in vacuo and then were investigated by XPS technique. Binding energy of all the elements and the atomic ratios on the surface of SZCu were presented in Fig. 3. The intensity of binding energies of all elements almost unchanged except C and O, indicating the stability of the structure of the modified catalyst, also suggesting that the solid acid may be used repeatedly. The appearance of more intense peak of C 1s after the reaction suggested that the coke or oligomer of carbon was formed and adsorbed firmly on the surface of catalysts, maybe also indicated that the introduction of copper promoter could not inhibit the formation of coke. The O content was increased in the surface of the used catalyst, possibly due to the adsorption of the oxidant. Furthermore, there was no sulfate leaching during the oxidation reaction, also indicating the benign stability of the catalyst.
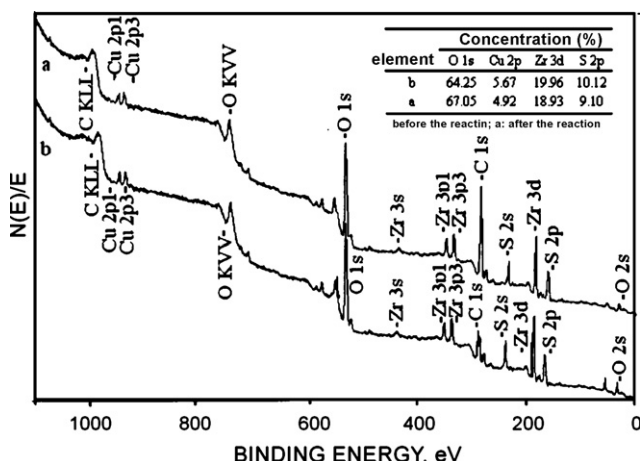
The S=O structure was essential for the generation of active sites on sulfate-promoted oxide samples [17]. The strong ability of S=O in sulfate complexes to accommodate electrons from basic molecules was a driving force for the generation of highly active properties [18]. The acidic properties generated by the inductive effect of S=O bonds in the complex were strongly affected by the environment of sulfate ion. Thus, it can be proposed that catalytic properties would be modified by the type of S=O in sulfate complex, especially the coverage of sulfate species on catalyst surface [19]. So a well-defined S 2p feature must be analyzed for the catalytic activity. Seen from the result of XPS spectra, the binding energy of S 2p for SZCu was observed at 168.70 eV, agreed with that of $Zr(SO_4)_2$ [19], suggesting that the element sulfur in SZCu existed in a six-oxidation state (S^{6+}) and resulting in the remarkable acidity on the surface of SZCu, this was also consistent with the result of FT-IR. Besides, from the binding energy of Zr 3d (Fig. 4), it obviously displayed that, the spin-orbit doublets, Zr $3d_{3/2}$ and Zr $3d_{5/2}$, were located at 184.87 and 182.44 eV, respectively, with a separation of 2.43 eV, indicating the steady formation of ZrO_2 support [20].

3.2. Characterization of the products

3.2.1. UV–vis spectra

The oxidation reaction process was monitored by UV–vis spectra and the result was shown in Fig. 5. With the time pro-

Fig. 3. Binding energy of all elements in SZCu before and after the reaction.
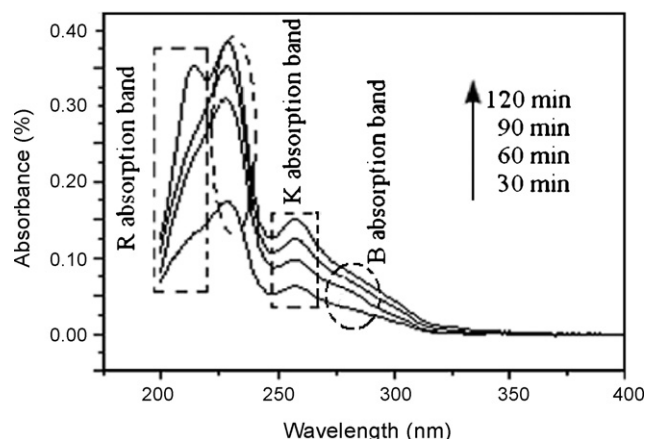

Fig. 5. UV–vis spectra for the reaction process catalyzed by SZCu.

longed, the curve with three obvious absorbed peaks (around 214, 229 and 256 nm) ascended gradually. The R absorption band (around 214 nm) can be attributed to the n–π^* transition, indicating the transition of alkane to carboxylic acid or aldehyde. The increasing of K adsorption band (229 nm) attributed to π–π^* transition, caused by the pair electrons between O atom and C atom of the ester group, indicated that more ester was formed in the reaction system. The absorption bands at 256 nm (the characteristic band of benzene ring) also increased, indicating that formation of the benzene ring. Although precise molecular structure information cannot be extracted from the electronic absorption spectra, the characteristic bands of benzene ring and ester group which increases rapidly with reaction time displayed clearly on the UV–vis spectra, indicated that the formation of aromatic ester, maybe also suggested that the reaction extent was proportioned directly to the reaction time.

3.2.2. GC/MS spectra

To further confirm the result of the UV–vis spectra, the product distribution at different reaction time was taken for GC–MS analysis, which was known for its superior separation of complex organic compounds, greater sensitivity, and shorter measuring time [21]. Fig. 6 showed the total ion chromatogram of the products (the peak of the solvent was taken off) at 120 min. The main peaks were identified by comparing their mass spectra with NIST library data and the result was verified by comparing retention time of the product with that of the standards.

In quantitative analysis of the products, according to the internal standard method, a series of solutions containing the standard molecules and appropriate relative internal standard (IS) in known concentrations was analyzed. The linear calibration curves were traced to quantify the identified compounds in the products: each standard solution was analyzed to calculate the peak area ratio of molecules compared to IS, then the response ratios (y) and the relative molecule concentrations (x)
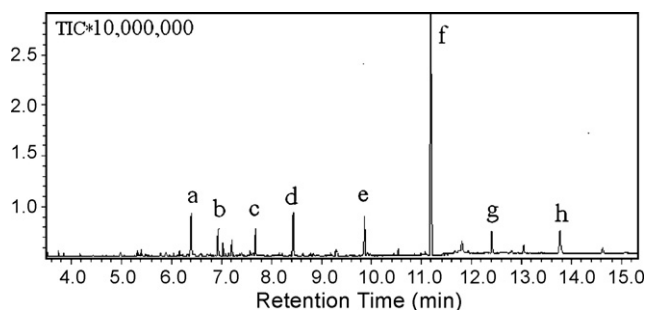

Fig. 6. GC of the products (120 min): (a) cyclohexyl cyclohexane; (b) tetradecane; (c) pentadecane; (d) heptadecane; (e) henicosane; (f) dibutyl phthalate; (g) hexacosane; (h) octacosane.

were used for the construction of the calibration curve. Then, each product with IS in the same concentration of standard solutions was analyzed, and the peak area ratio was used to calculate the concentration of the identified compounds with the curve equation. If the concentration of the identified compounds in the reaction solution was known, the yield of each linear alkane and the conversion of cyclohexane can be calculated. The calibration curve demonstrated acceptable linearity with correlation coefficients $r^2 \geq 0.995$. Quantitative study of each product was independently analyzed for twice. According to the method described as above, it can be calculated that the yield and selectivity of dibutyl phthalate (peak f in Fig. 6) was 29.5 wt.%, 72.2 wt.%, respectively, indicating the strong effectiveness of SZCu on the oxidation of cycloalkane in flow air.

In addition, a small quantity of byproducts identified iso-alkane (cyclohexyl cyclohexane). A large amount of long-straight-chain alkane (C_{14}–C_{28}) was also detected in the product, inferring that the polymerization reaction maybe occurred simultaneously. The selectivity of different products was shown in Table 1. The abundance of the long chain compounds indicated

Table 1
The selectivity of different products after 120 min

Name	Structure	Rate	Selectivity (wt.%)
Cyclohexyl cyclohexane		6.2	Iso-alkane 9.7
Tetradecane		2.3	
Pentadecane		1.9	Linear alkane (C_{14}–C_{28}) 18.1
Heptadecane		4.8	
Henicosane		4.5	
Hexacosane		2.1	
Octacosane		2.6	
Dibutyl phthalate		72.2	Ester 72.2

that this solid catalyst can be effectively employed in the polymerization and opening reaction of cyclohexane ring. Therefore, this approach has highlighted the importance of this kind of solid acid catalyst, not only for cyclohexane esterification under mild conditions, but also for other processes, maybe satisfied the specific requirements in alkane activation in many cases.

For comparison, the reaction system with SZ, non-sulfated ZrO_2 and the reaction system with SZCu without flow air was also investigated. The principal products observed for SZ were almost the same with that of SZCu, but the yield of dibutyl phthalate with SZ was only 9.6 wt.%, much lower than that of SZCu. No ester obtained in the reaction system with non-sulfated ZrO_2, indicating that it was inefficient in catalytic oxidation cyclohexane as a single catalyst. The fact that only trace of oxygenous ramification was present in the reaction system without air suggested that dioxygen was perfect as an oxidant for the one-pot esterification reaction of cyclohexane.

3.3. Regeneration of catalyst

The catalytic activity of the recycled sample was tested in the oxidation reaction, as reported in the experimental section. The recycled catalyst was calcined at 873 K for 3 h after filtration from the reaction mixture to eliminate the coke, oligomer or other impurity deposited on its surface. The regenerated catalyst showed almost the similar yield of the ester as the fresh catalyst, i.e. about 25.5 wt.% yield of dibutyl phthalate, indicating the catalyst can be regenerated easily and reused.

4. Conclusion

SZCu was prepared and characterized by XRD, FT-IR spectroscopy and XPS, its catalytic properties on the oxidation of cyclohexane under mild condition were investigated. The direct oxidation and esterification of cyclohexane, with SZCu as the catalyst and air as the oxidant, has been successively accomplished at room temperature (298–303 K) and normal atmospheric pressure. The simple experimental set-up, mild reaction conditions, inexpensive catalyst, reusability of the catalyst, and environmentally friendliness of the catalyst and the process (solvent-free), make it a very practical and very important addition to the existing methodologies for the synthesis of ester.

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