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Cyclohexane mild oxidation catalyzed by new titanosilicate with hollow structure

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ABSTRACT

Titanium silicalite with hollow structure (HTS), was one new type of titanosilicate used in oxidation process. Its catalytic property on the mild oxidation of cyclohexane with hydrogen peroxide (H_2O_2) in liquid phase was investigated, and the difference of catalytic performance between HTS and compared sample (TS-1) was discussed. The results show cyclohexanone (K) and cyclohexanol (A) are the major products; with the increment of reaction temperature and reaction time, cyclohexane conversion and the yield of K increase, the selectivity to K increases while the selectivity to A decreases. It is found that hollow structure and different distributions of Ti species lead to above differences, and L acidity would be also concerned with their catalytic performance. In one word, HTS is one proper catalyst for application in the cyclohexane oxidation process with H_2O_2 as oxidant under mild conditions.

1. Introduction

Cyclohexanone (K) and cyclohexanol (A) (the mixture is known as K–A oil) are important chemicals and raw materials because they are the key precursors for the production of caprolactam and adipic acid, which in turn are important intermediates in the manufacture of nylon-6 and nylon-66, respectively (Scheme 1) [1,2]. K–A oil are mainly obtained by the oxidation of cyclohexane with air [3,4], current industrial process uses a soluble cobalt carboxylate or metal–boric acid catalyst to produce a mixture of cyclohexanone, cyclohexanol and other products with ~80% selectivity to K–A oil. The air oxidation reaction is usually carried out at ~443 K and ~11 bar of atmospheric pressure, cyclohexane conversion is limited to less than 10% to reduce over oxidation to unwanted products, since the primary products (cyclohexanone and cyclohexanol) are more reactive than the reactant (cyclohexane) [5]. Apart from low conversion (<10%) and extreme reaction conditions, this process produces several by-products, such as mono- and/or di-carboxylic acids, esters, and other oxygenated materials [6]. In addition, the industrial process produces more amount of cyclohexanol, and additional steps are needed to improve the cyclohexanone/cyclohexanol mole ratio (K/A) in the final products [7].

To overcome these defects, attempts have been made to prepare more efficient catalysts or to ameliorate the engineering technologies in cyclohexane oxidation. Moreover, the significant industrial demand in recent years (~10 million ton/year in 2006) of K–A oil has stimulated various studies aiming to find milder, lower-cost, and more environmentally friendly conditions, namely to find alternative greener and more effective catalytic processes for the classic industrial method [8,9], which means that the yield and selectivity to K–A oil should be enhanced in a less polluted process. From the point of view of oxidant, with respect to various of oxidants, hydrogen peroxide (H_2O_2, HP) is a preferable one and as one versatile and green oxidant, because of its containing of a high fraction of active oxygen, simplicity of handling and environmentally benign nature of the co-product (water) in oxidation reaction [10], so the investigation of an efficient catalyst for the oxidation of alkanes especially for cyclohexane with HP as oxidant is very attractive.

Titanium silicalite (TS-1) is a molecular sieve with MFI topological structure, in which small numbers of tetrahedral Si atoms are substituted by Ti atoms in a purely siliceous framework. The discovery of TS-1 zeolite in 1980s [11], offers one new opportunity for the oxidation of cyclohexane with HP as oxidant. With relative high cyclohexane conversion rate and high selectivity to K–A oil under mild conditions in liquid phase, this process is regarded as an alternative environmentally friendly route to substitute for old ones [12]. In our earlier studies, one new titanosilicate with hollow structure was presented (branded by HTS, having large intra-particle voids), which was skillfully synthesized via a route named dissolution-recrystallization process, enhancing the

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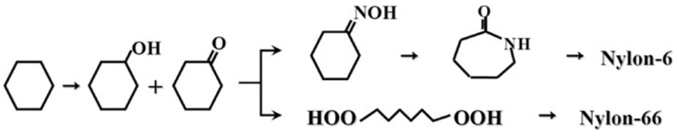


Scheme 1. Simplified route to the production of Nylon-6 and Nylon-66.

dimensions of the intra-particle pores without unduly sacrificing the microporous ones, and thus can intensify the transport of reactants and products in and out of the crystal's channels [13,14]. Here, for the first time, HTS was applied as catalyst to catalyze cyclohexane oxidation with HP, the differences of catalytic performance between HTS and compared sample (normal TS-1) were also discussed extensively. The catalysts were characterized by various instruments, from which the positive role of intra-particle voids within HTS crystals was evaluated. Furthermore, the controlling parameters of this greener oxidation process, such as reaction temperature and reaction time were also investigated, and then their different catalytic performances were tentatively associated with the L acidity of catalysts.

2. Experimental

2.1. Synthesis of HTS and compared sample TS-1

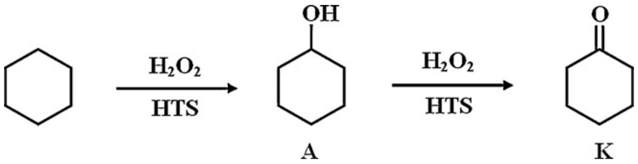
HTS and normal TS-1 (compared sample) were prepared using the procedures similar to that described in the literatures [13,14]. One typical preparation procedures of HTS and normal TS-1 were as follows: (1) 40 g tetraethyl orthosilicate (TEOS) was mixed with the solution containing 12 g tetrapropyl ammonium hydroxide (TPAOH) and 88 g distilled water thoroughly hydrolyzed at 65 °C for 2 h. To the resultant mixture, a solution composed of tetrabutyl orthotitanate (TBOT) and anhydrous isopropanol was added slowly with stirring. The mixture was further stirred at 65 °C for 1 h, then transferred to a stainless steel autoclave with Teflon-coated and shelved at 170 °C for 36 h. The product was recovered by filtration, washed with distilled water, air-dried at 100 °C for 4 h, and calcined in air at 500 °C for 4 h, normal TS-1 was obtained, (2) normal TS-1 was mixed with sulfuric acid solution and treated at room temperature for 5 h, with a weight ratio of normal TS-1:sulfuric acid:water = 10:1.0:150, and (3) the recovered acid-treated TS-1 was mixed with TPAOH solution in a weight ratio of molecular sieve:TPAOH:water = 10:1.5:120. Then, the mixture was treated at 140 °C for 72 h. After cooling and pressure unloading, routine recovery and calcination, HTS was obtained.

2.2. Characterization techniques

Rigaku 3271E X-ray fluorescence spectrometer was used to measure X-ray fluorescence analyses (XRF). Siemens D5005 diffractometer with nickel-filtered Cu Kα radiation was used to record the powder X-ray diffraction data (XRD). Nicolet 8210 infrared spectrometer was used to record the data of infrared spectra (FT-IR). Perkin–Elmer Lambda 20 UV-visible spectrometer was applied to obtain the data of UV–visible spectra (UV–vis). Tecnai G^{2}F20S-TWIN electron microscope was used to perform transmission electron microscopy (TEM) experiments. Philips XL 30 ESEM was used to collect scanning electron microscopy (SEM) images. Micromeritics ASAP 2010M system was used to measure nitrogen adsorption–desorption isotherms of samples.

2.3. Catalytic oxidation of cyclohexane to K–A oil

The experiments for cyclohexane oxidation reaction with HP as oxidant (Scheme 2) were carried out in a stainless-steel reactor equipped with a Teflon beaker, electric stirrer and oil bath. Typically, 1.0 g catalyst, 2.1 g cyclohexane, 15 g acetone and 4.2 g HP (30 wt.% water solution), were charged to the reactor with stirring in one lot, the slurry was shelved and the reactor was kept at reaction temperature for different periods of time. The samples were periodically taken and then analyzed by Agilent 6890N GC equipped with a FID and a HP-5 capillary column (30 m).



Scheme 2. Simplified reaction pathway of cyclohexane oxidation with H_2O_2 as oxidant catalyzed by HTS.

3. Results and discussion

3.1. General characterization of HTS and TS-1

As determined by XRF analysis, HTS is composed of SiO_2 (97.28%) and TiO_2 (2.72%), and normal TS-1 contains SiO_2 (97.26%) and TiO_2 (2.74%) with the same level of Ti content. As examined by X-ray diffraction (Fig. 1), HTS exhibits almost the same main diffraction peaks as those in XRD of normal TS-1, and also accordant with those of the typical ZSM-5, indicating that both HTS and TS-1 are with MFI topological structure [15]. FT-IR spectra of HTS are also consistent well with those of TS-1, further indicating that HTS and TS-1 are with MFI topology and have intra-framework Ti [16,17]. In UV–vis spectra, both HTS and TS-1 give only one strong UV absorption bands at around 210 nm, not only indicating both HTS and TS-1 have intra-framework Ti species, but also demonstrating the Ti species in HTS and TS-1 are mainly existed as isolated tetrahedral

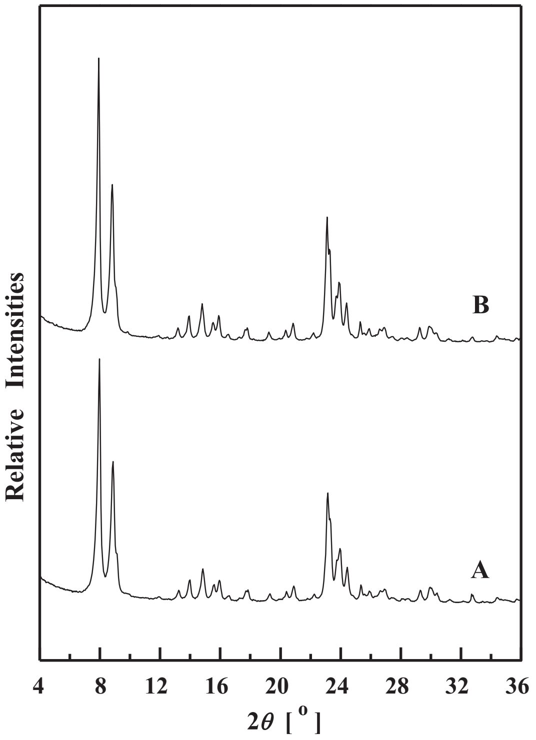


Fig. 1. The XRD patterns of samples: (A) HTS, and (B) TS-1.

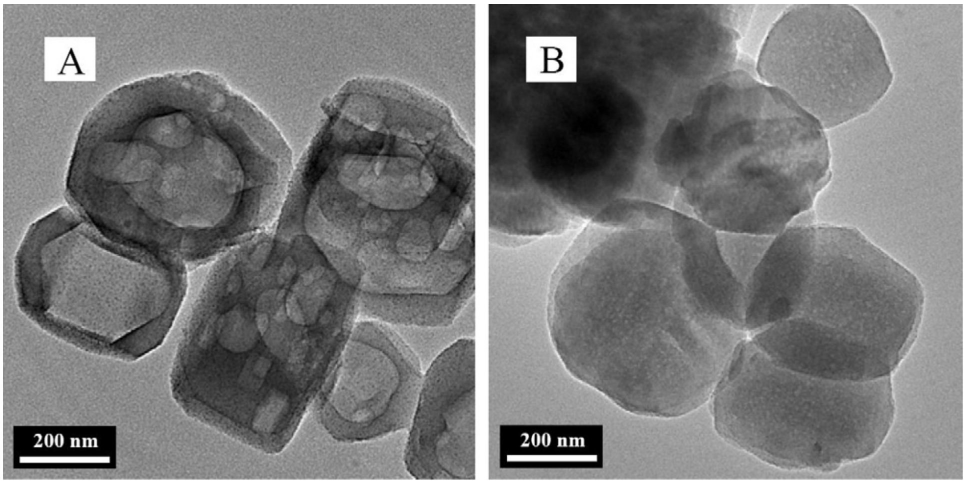


Fig. 2. The TEM images of samples: (A) HTS, and (B) TS-1.

ones [14,18]. As characterized by TEM (Fig. 2) and SEM, the particles of HTS contain large intra-particle voids (mesoporosity and/or macroporosity) and with the average particle size of 150–250 nm, while those of TS-1 display dark images with the same particle size range and appearance morphology (strawberry or cauliflower like) [19,20]. The N_2 adsorption–desorption isotherms curves of HTS exhibit one pronounced hysteresis loop with an abrupt closure on the desorption branch and differ from those of normal TS-1, also indicating the presence of intra-particle voids [14].

So, in one word, from the results of above characterization techniques, the main difference between HTS and normal TS-1 is that HTS is with hollow structure (large intra-particle voids), while TS-1 shows solid structure.

3.2. Catalytic oxidation of cyclohexane to K–A oil

The results of catalytic cyclohexane oxidation performance of HTS and TS-1 are presented in Table 1. Under such mild evaluating conditions (reaction temperature is at 60 °C, reaction time is for 5 h), it can be seen that both HTS and TS-1 exhibit some activity, the cyclohexane conversion ($C_{\text{cyclohexane}}$, mol%) are given at 26.2% & 19.5%, with the selectivity to cyclohexanone (S_K, mol%) at 65% and 44%, and the selectivity to cyclohexanol (S_A, mol%) at 35% and 56%, respectively. The yield of cyclohexanone (Y_K, mol%) are calculated at 17.0% and 8.6%, and cyclohexanol yield (Y_A, mol%) are at 9.2% and 10.9%, respectively. Moreover, the efficiency of H_2O_2 (effective utilization, U_{HP}, mol%) in this process are calculated at 81% and 58% for HTS and TS-1, respectively.

Under such mild reaction conditions, no other by-products (such as cyclohexyl peroxide, mono- and/or di-carboxylic acids and esters) are detected. For the main products in cyclohexane oxidation reaction catalyzed by titanosilicate with HP as oxidant are cyclohexanone and cyclohexanol, cyclohexanone versus cyclohexanol (mole ratio value, K/A) may be used to describe the selectivity, and the bigger of the value of K/A, the better of the selectivity to K. The value of K/A for HTS is at about 1.86, and that for TS-1 is at 0.79.

Above results show that, the catalytic performance of TS-1 are not to be compared with those of HTS. When one mol of cyclohexane was converted to one mol of cyclohexanol, one mol of HP was consumed, while one mol of cyclohexanol was changed into one mol of cyclohexanone, also one mol of HP was expended. Thus, when one mol of cyclohexane was converted to one mol of cyclohexanone, two moles of HP was consumed (see Scheme 2). It can be deduced that the effective utilization of HP in the cyclohexane oxidation catalyzed by HTS is much higher than that catalyzed by TS-1, and this has already been strictly proved by the above U_{HP} data. This may be apparently explained that the preferential formation of ketone on HTS is related to its hollow structure, videlicet, is due to its elimination of molecular diffusions.

We know that in traditional cyclohexane air oxidation process, the formation of cyclohexanol and cyclohexanone are formed by the decomposition of cyclohexyl hydroperoxide as intermediates [21]. Is it possible that the products (cyclohexanol and cyclohexanone) in our experiments are also formed by the decomposition of intermediates (cyclohexyl hydroperoxide) as that in air oxidation? To verify this, two additional compared experiments have been done, the first one is done with the addition of cyclohexane in quite small quantity, i.e., the mole ratio cyclohexane to H_2O_2 is about 1:10, the product is cyclohexanone solely; While in the second experiment, the mole ratio cyclohexane to H_2O_2 is changed into 10:1, it's found that the product is composed only by cyclohexanol. In the traditional mechanism of cyclohexane oxidation by air, the decomposition of cyclohexyl hydroperoxide maybe form two products: cyclohexanol and cyclohexanone, not the only formation of cyclohexanone or cyclohexanol [21]. If the formation mechanism in our experiments is also by the decomposition of intermediates (cyclohexyl hydroperoxide) as hypothesized above, the only product of above two compared experiments is perhaps conflicted with this mechanism. Namely, the decomposition mechanism of intermediates is not fit for the cyclohexane catalytic oxidation with H_2O_2 as oxidant. We think this may be due to their different reaction pathways. Different oxidation processes, i.e., air oxidation and H_2O_2 oxidation, especially for the addition of the catalyst (titanosilicate), perhaps experience different pathways. The catalytic oxidation system composed by titanosilicate and H_2O_2, should be inclined to different product formation mechanism from that of air oxidation.

For the Ti species in titanosilicate are generally regarded as catalytic active centers [22,23], so it can be deduced that the formation of cyclohexanol should occur over Ti species from cyclohexane, while the formation of cyclohexanone should also occur over Ti species from cyclohexanol. As illustrated in Scheme 3, the cyclohexane oxidation process (catalyzed by titanosilicate with HP as oxidant) involves the onsite formation of cyclohexanol followed by its conversion to cyclohexanone, which has also been further testified in a separate experiment with the addition of cyclohexanol instead of cyclohexane, the formation of cyclohexanone at reaction conditions was proved directly. On the basis of above catalytic results, it can be seen that HTS has better catalytic performance than that of TS-1, can oxidize more amount of cyclohexane, and then synthesize more quantities of K, thus HTS can produce more quantities of K–A oil.

Table 1
The catalytic performance results of HTS and normal TS-1 in cyclohexane oxidation process.

Samples	$C_{\text{cyclohexane}}$ (mol %)	U_{HP} (mol %)	S_{K} (mol %)	S_{A} (mol %)	Y_{K} (mol %)	Y_{A} (mol %)	K/A
HTS	26.2	81	65	35	17.0	9.2	1.86
TS-1	19.5	58	44	56	8.6	10.9	0.79

$C_{\text{cyclohexane}}$: cyclohexane conversion, U_{HP}: efficiency of H_2O_2 (effective utilization), S_{K}: selectivity to cyclohexanone, S_{A}: selectivity to cyclohexanol, Y_{K}: yield of cyclohexanone, Y_{A}: yield of cyclohexanol, and K/A: the mole ratio value of cyclohexanone to cyclohexanol.

From Schemes 2 and 3, it can also be seen that cyclohexanol is an intermediate product, which is further oxidized to ketone. Naturally, diffusion limitations will favor "over-oxidation", i.e., the formation of cyclohexanone. From this point of view, TS-1 should produce more cyclohexanone than that of HTS. However, compared with cyclohexane oxidation, cyclohexanol oxidation is preferred in thermodynamics. Linking with above catalytic results, diffusion limitation is perhaps secondary to thermodynamics in cyclohexanol oxidation processing [12]. Moreover, HTS crystals have been subjected to dissolution and recrystallization, and the distribution of Ti species within the crystals may be different. Because during this process, crystals were dissolved from the core of particles, partly due to its lower crystallinity as compared to the external shell [24,25], the dimensions of the intra-particle voids were gradually enhanced; and the Ti species and Si species dissolved, with the presence of template agent (TPAOH), the dissolved Ti and Si species can be recrystallized (regrown) onto the surface of crystals and make HTS into being during recrystallization process without unduly sacrificing the total microporous pores. So, on the whole, this process can make the distribution of Ti atoms in HTS crystals difference from that of normal TS-1 [14]. On the other hand, although HTS and TS-1 crystals are with the same particle size range (measured from XRD and TEM), and the numbers of active Ti species in HTS are almost the same as those in TS-1 (measured from IR and UV-vis spectra), nevertheless the amount of accessible Ti species in both HTS and TS-1 may not be at the same level. Because the same number of Ti atoms does not necessarily imply the same accessible Ti amount, recrystallization process may concentrate Ti ions onto the crystals' surface of HTS, and the Ti species on the surface are more accessible than those in the core of the crystals [14]. Well then the difference of catalytic performance between HTS and TS-1 may be not only attributed to their different substantial structures, but also to their different Ti species' distributions. Namely, the main differences between HTS and TS-1 are HTS with hollow structure while TS-1 with solid structure, and different concentrations of Ti species on their particles' surface (this has been directly proved by the analysis of X-ray photoelectron spectroscopy, the XPS results are not shown here). It can be deduced that the better catalytic performance of HTS, on the one hand, is due to the enrichment of surface Ti concentration, and the better accessibility of Ti species; on the other hand, is probably ascribed to its characteristic hollow structure, which can enhance the accessibility of active centers and diffusion of reactant molecules, thus decrease or even eliminate molecular diffusions and mass transfer resistances, so it can be convenient for the molecular diffusions of reactants (cyclohexane and HP) and products (cyclohexanone and cyclohexanol), finally can increase the cyclohexane conversion and the selectivity to K–A oil, especially the selectivity to K. In other words, the positive effects of intra-particle voids and different Ti distribution in HTS crystals were ultimately reflected from its catalytic performance.

Scheme 3. Simplified scheme of the proposed reaction mechanism of cyclohexane oxidation over titanium silicalites with H_2O_2 as oxidant.

The influences of reaction temperature and reaction time on the cyclohexane oxidation were following evaluated. Firstly, the effect of reaction temperature on the reaction was investigated by maintaining constant amounts of reactants, catalyst and solvent. The results are shown in Table 2, with the increase of reaction temperature, it can be seen that, cyclohexane conversion and K–A oil yield of HTS considerably increase. When reaction temperature is increased from 40 °C to 80 °C, cyclohexane conversion and K–A oil yield increase trebly more, for example, $C_{\text{cyclohexane}}$ of HTS increases from 14.4% to 44.7%, and that for TS-1 rises from 11.9% to 36.2%. At the same time, it can be seen that for both HTS and TS-1, the selectivity to K increases straightly and sharply, and Y_{K} also increases straightly; while S_{A} decreases all along with the increase of reaction temperature, and Y_{A} increases to a maximum and then decreases slightly (also indicating that cyclohexanol is an intermediate). Secondly, the effect of reaction time on the cyclohexane oxidation was examined by another batch of reactions and the results are shown in Figs. 3 and 4. It can be seen that, with the increase of reaction time, the conversion of cyclohexane increases straightly. Synchronously, Y_{K} and S_{K} increase gradually; while S_{A} decreases, the decrease may be due to its further oxidation to cyclohexanone. Y_{A} increase to reach a culmination and then declines gradually. Above phenomena may further indicate that cyclohexanol should be an intermediate product, the cyclohexane oxidation process is composed of the process of converting cyclohexane to cyclohexanol and that of cyclohexanol to cyclohexanone. From the figure, it can be also seen that, for HTS, cyclohexane conversion and K–A oil yield increase faster with the increase of reaction time. Simultaneously,

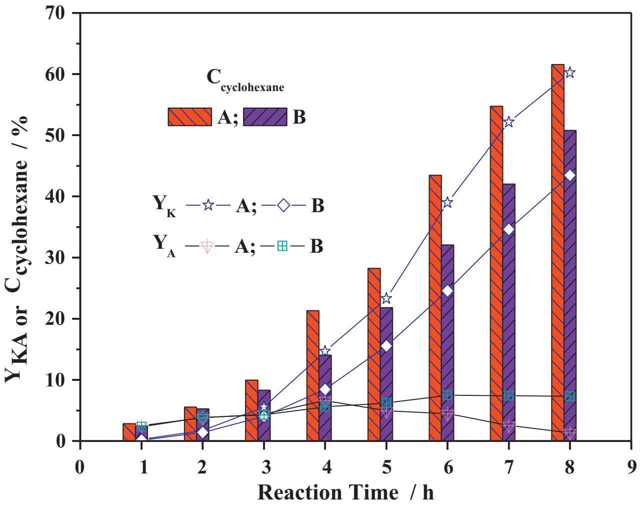


Fig. 3. The yield of K–A oil and the conversion of cyclohexane with different reaction time on the cyclohexane oxidation catalyzed by samples: (A) HTS, and (B) TS-1.

Table 2
The catalytic oxidation results of HTS and normal TS-1 in cyclohexane oxidation process with the increase of reaction temperature.

Samples	$C_{cyclohexane}$ (mol %)				S_K (mol %)				S_A (mol %)				Y_K (mol %)				Y_A (mol %)			
	20 °C	40 °C	60 °C	80 °C	20 °C	40 °C	60 °C	80 °C	20 °C	40 °C	60 °C	80 °C	20 °C	40 °C	60 °C	80 °C	20 °C	40 °C	60 °C	80 °C
HTS	3.1	14.4	26.2	44.7	6	17	65	86	94	83	35	14	0.2	2.5	17.0	38.4	2.9	12.0	9.2	6.3
TS-1	2.6	11.9	19.5	36.2	5	11	44	72	95	89	56	28	0.1	1.3	8.6	26.1	2.5	10.6	10.9	10.1

$C_{cyclohexane}$: conversion for cyclohexane, S_K: selectivity to cyclohexanone, S_A: selectivity to cyclohexanol, Y_K: yield of cyclohexanone, and Y_A: yield of cyclohexanol.

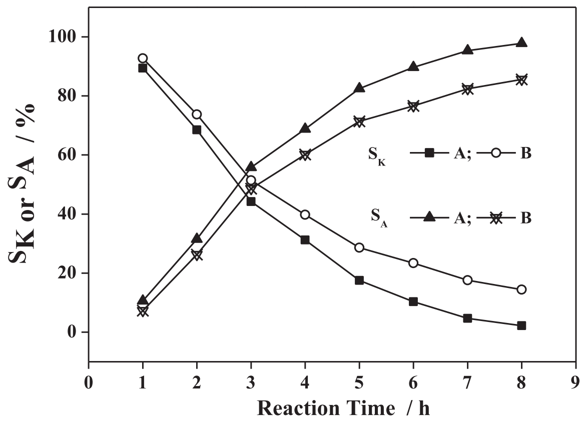


Fig. 4. The selectivity to K–A oil with different reaction time on the cyclohexane oxidation catalyzed by samples: (A) HTS, and (B) TS-1.

the selectivity to cyclohexanone increases, while the selectivity to cyclohexanol decreases along with the increase of reaction time. But for TS-1, cyclohexane conversion and K–A yield increase more tenderly, and the selectivity to K increases more softly at longer reaction time. In other words, at the same reaction time, HTS has higher catalytic oxidation activity than that of TS-1, which indicates that HTS should have better catalytic performance and faster reaction speed than those of TS-1. Such above phenomena might be also due to the hollow characteristic of HTS, the presence of large intraparticle voids would afford facilities for the molecular diffusions of reactants and products in HTS, as discussed above.

In summary, HTS is a proper catalyst for the production of cyclohexanone and cyclohexanol in cyclohexane oxidation with HP under mild conditions.

3.3. Correlation between catalytic performance and L acidity of samples

It is reported that, the main function of Ti species in titanium silicalites is to withdraw electrons in the oxidation process, and reduce the electron density in the O–O bond of intermediate peroxide, i.e., the Ti species in titanium silicalites act as Lewis acid, and the L acidity of Ti is influenced by its coordination environment, so this would be also related to their catalytic property [26,27]. In order to further verify whether this hypothesis can be adapted to suit the reaction of cyclohexane mild oxidation and test the acidity of HTS and TS-1, the types and quantities of acidic sites in HTS and TS-1 were investigated by IR spectra of pyridine adsorbed on samples. As known, for pyridine adsorption IR spectra on samples, the band near at 1450 cm^{-1} is assigned to the adsorption of pyridine on Lewis acidic sites, while that at 1545 cm^{-1} is associated with B acidity [27,28]. Acidity types and quantities of acidic sites in HTS and TS-1 are all calculated from their pyridine adsorption IR spectra and the data are listed in Table 3. It can be seen that, whether desorbed at 200 °C or at 350 °C, all the samples show none but L acidity, implying both HTS and TS-1 only have L acidic sites, no B ones. Moreover, it can be seen that HTS has much more L acidic sites than TS-1, which may be strongly related with their different dis-

Table 3
Acidity types and quantities of HTS and TS-1 calculated from pyridine adsorbed IR spectra.

Samples	200 °C (A cm^2 g^{-1})		350 °C (A cm^2 g^{-1})	
	L acidity	B acidity	L acidity	B acidity
HTS	34.6	0	17.2	0
TS-1	26.3	0	14.3	0

tribution of active Ti species (as discussed above, HTS formed via a dissolution–recrystallization route, during this process, the active Ti species is redistributed) [14]. Above phenomenon might show that L acidity of Ti species in titanosilicate is relevant to their catalytic activity in cyclohexane oxidation reaction with HP as oxidant [3]. The specific relations between L acidity of catalysts and their catalytic performance are under further investigation, the detailed information will be shown in the near future.

4. Conclusions

HTS was a new titanosilicate applied in cyclohexane catalytic oxidation reaction. The results show that K–A oil are the major products; reaction temperature and reaction time have strong effect on cyclohexane conversion and the selectivity to K–A oil. It is found that the hollow structure and the different distributions of Ti species, lead to their different catalytic performance between HTS and TS-1; moreover, L acidity would be relation to their catalytic property. As illustrated by above catalytic results, HTS is an appropriate catalyst for the production of cyclohexanone and cyclohexanol in cyclohexane oxidation with HP as oxidant under mild conditions.

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