Catalysis Today 175 (2011) 546–551

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Highly selective synthesis of enones from benzylic compounds over CrSBA-15

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ARTICLE INFO

Article history:
Received 15 October 2010
Received in revised form 13 February 2011
Accepted 6 April 2011
Available online 25 May 2011

Keywords:
CrSBA-15
pH-adjusting direct hydrothermal method
Oxidation of benzylic compounds
Catalytic activity
Recyclability

ABSTRACT

Mesoporous CrSBA-15 catalysts synthesized with a variety of n_{Si}/n_{Cr} ratios by pH-aDH method were used in the production of enones by the liquid-phase oxidation of benzylic compounds. To investigate the leaching of chromium species on the silica surface, CrSBA-15(8) was chemically treated with ammonium acetate solution while the Cr-containing mesoporous silica catalysts used for these reactions were regenerated by washing and calcinations. The treated catalysts such as washed CrSBA-15 and regenerated CrSBA-15 catalyst were used/reused in these reactions to find their catalytic activities. Furthermore, the influences of various reaction parameters such as temperature, time, ratios of reactant and solvents on the synthesis of tetraline (T═O) have been systematically investigated. Based on the catalytic investigations, CrSBA-15(8) catalyst is found to be a highly active, recyclable and promising heterogeneous catalyst for the selective synthesis of enones, and it has superior catalytic activity in the oxidation of benzylic compounds than CrMCM-41.

1. Introduction

Enone compounds synthesized by oxidation of benzylic compounds over Cr-based reagents are mainly used in many applications, ranging from agricultural products to pharmaceuticals. For example, 1-tetralone (T═O) is an enone and largely used in the production of various products such as dyes, pharmaceuticals and agrochemicals [1], and it is also employed as a starting material above $5 million per year in the production of sertraline (an antidepressant) and naphthyl carbamate (an insecticide) and 18-methylnorethisterone (a contraceptive). T═O is synthesized with a good selectivity by an intramolecular condensation [2], an intramolecular Friedel–Crafts reaction [3] and the selective ionic hydrogenation of 1-naphthol [4], and it is also synthesized by the direct oxidation of tetralin [5] with hydrogen peroxide (HP). In this reaction, 1-tetralin hydroperoxide (THP) intermediate initially forms and decomposes catalytically into a mixture of T═O and 1-tetralol (T–OH). To improve the selectivity of T═O, inorganic salts can be used for the selective transformation of THP [5]. However, we found so many drawbacks from the catalytic systems used in the oxidation of tetralin as follows. (i) The yield of T═O is very low because HP used on direct oxidation of tetralin decomposes easily at an ambient temperature [6]. (ii) The conventional acid catalyst (e.g. chromium oxide) used in this catalytic system is typically associated with the problems of high toxicity and corrosion, (iii) the use of large amounts of environmentally undesirable chromium reagents and the large volume of solvents require in this reaction and (iv) the major problem in this oxidation process is the formation of various products due to uncontrolled oxidation. The above similar problems are practically based on the oxidation of other benzylic compounds viz. indane, fluorine, propylbenzene and *n*-butylbenzene. To overcome these problems, several enone compounds were synthesized over chromium-containing green heterogeneous catalysts [7]. For example, chromium aluminophosphate (CrAPO-5) catalyst (medium pore diameter, 0.73 nm) is used for the production of T═O in the oxidation of tetralin with molecular oxygen under liquid-phase reaction condition [8]. THP is effectively decomposed by this chromium catalyst for giving good selectivity of T═O, but the conversion of tetralin is low due to having medium pore diameter [8]. Although the catalysts give good selectivity of enones (e.g. T═O), several byproducts such as epoxides, alcohols, and alkenes are also obtained, and complicated processes are needed to separate the products.

Mesoporous CrMCM-41 catalysts are selectively used in the oxidation of benzylic compounds with various oxidizing agents [8–13], and they give good selectivity of enones with a few amounts of byproducts. Several researchers tried to use the well uniformly ordered mesoporous SBA-15 synthesized with thicker pore walls [14] to incorporate higher heteroatoms on the surface of silica than MCM-41. However, under strong acidic hydrothermal method, most of them failed to introduce more heteroatomic species into SBA-15 with catalytic active sites of tetrahedral coordination because the formation of metal-oxo species in the mesoporous material is much less. To overcome this problem, pH-adjusting

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doi:10.1016/j.cattod.2011.04.011

Table 1
Structural and textural parameters of Cr-containing SBA-15 catalysts.

Catalysts	$n_{H2O}/n_{HCl(molar\ ratio)}$	n_{Si}/n_{Cr}		A_{BET} (m^2/g)	V_p(cm^3/g)	d_p(Å)	a_o(Å)	$T_w = a_0 - d_p$(Å)
		Gel	Product [a]					
SiSBA-15	40	-	-	908	1.07	87.4	118.2	30.8
CrSBA-15(8)	295	8	9.9	999	1.10	89.4	127.4	38.0
CrSBA-15(16)	295	16	17.3	1015	1.09	88.5	122.7	34.2
CrSBA-15(20)	295	20	45.0	1024	1.08	87.3	121.3	34.0
CrSBA-15(25)	295	25	52.1	1037	1.08	87.2	118.5	31.3
CrSBA-15(50)	-	50	99.8	1063	1.09	86.5	114.5	28.0
CrSBA-15(8) [b]	-	-	12.3	985	1.10	89.4	127.3	37.9
CrMCM-41(40) [c]		40	45	883	0.70	26.9	44.4	17.5

a_o, unit cell parameter; A_{BET}, Specific surface area; $V_{p,}$ pore volume; d_p, pore diameter, T_w, wall thickness value was calculated from unit cell parameter (a_o) and pore diameter (d_p).

[a] nSi/nCr ratios of products are determined by ICP-AES.

[b] Washed catalyst.

[c] The catalyst was synthesized under basic direct hydrothermal method (Reference [11]).

direct hydrothermal (pH-aDH) method has been introduced and used for the synthesis of MSBA-15 catalysts (M = Al, Cr, Mn, Sn, Ga, Ce, Ti, Nb and V) with high metal-content, and the synthesized MSBA-15 catalysts have been used for certain catalytic reactions [15–26]. Selvaraj and Kawi [17] reported the highly ordered CrSBA-15 catalyst synthesized with enhanced hydrothermal stability. The CrSBA-15 catalyst has a huge number of tetrahedral chromium in the framework of silica walls because it has thicker pore walls and higher hydrothermal stability than CrMCM-41 [17]. Our group successfully used the CrSBA-15 catalyst for the selective synthesis of anthraquinone and verbenone with the ranging of selectivity from 88% to 100% [27,28]. However, to the best of our knowledge, the CrSBA-15 catalyst has not been used in the oxidation of benzylic compounds such as tetralin, propylbenzene, *n*-butylbenzene, indane and fluorene for highly selective synthesis of enones, and the catalytic results obtained over CrSBA-15 catalyst have not been clearly reported, in the open literature so far.

Therefore, herein we report the selective synthesis of enones by oxidation of benzylic compounds over Cr-containing mesoporous silica catalysts. The regenerated and washed CrSBA-15 catalysts have been also reused in these reactions to find their catalytic activities. The catalytic results of all mesoporous catalysts are correlated and compared for the selective synthesis of enones.

2. Experimental

2.1. Materials

For the synthesis of Cr-containing mesoporous catalytic materials, all chemicals viz. triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123, molecular weight = 5800, $EO_{20}PO_{70}EO_{20}$), tetraethylorthosilicate (TEOS), hydrochloric acid (HCl), and Cr(III) nitrate nonahydrate (CN) were purchased from Aldrich Chemical Inc. and used as received without further purification. Millipore water was used in all experiments.

For the synthesis of enones, all chemicals viz. tetralin, propylbenzene, *n*-butylbenzene, indane, fluorene, *t*-butylhydrogenperoxide (TBHP), hydrogen peroxide (30% H_2O_2), acetonitrile (MeCN), dichloroethane (DCE), chlorobenzene (CB), dimethylformamide (DMF) and methanol, were also purchased from Aldrich Chemical Inc. and used as received without further purification.

2.2. pH-aDH method

As-synthesized mesoporous CrSBA-15 catalysts with n_{Si}/n_{Cr} = 8, 16, 20, 25 and 50, were synthesized with molar composition in gel, 1 TEOS/0.02–0.125 Cr_2O_3/0.016 P123/0.43 HCl/127 H_2O using pH-adjusting direct hydrothermal method according to the previous published procedure [17]. Finally, the samples were calcined at 813 K in air for 6 h for complete removal of the template. The calcined samples are denoted as CrSBA-15(8), CrSBA-15(16), CrSBA-15(20), CrSBA-15(25) and CrSBA-15(50).

2.3. Synthesis of CrMCM-41(40)

Mesoporous CrMCM-41(40) catalyst was synthesized using cetyltrimethylammonium bromide as the structuring agent with a molar ratio in gel, 1 SiO_2/0.025 Cr_2O_3/0.25 CTMABr/100 H_2O under hydrothermal condition and characterized according to the previous published procedure [11].

2.4. Characterization

The calcined, washed and regenerated CrSBA-15 mesoporous catalysts were characterized by ICP-AES, XRD, N_2 adsorption/desorption, ESR, ^{29}Si MAS NMR, UV–vis DRS, FE-SEM and TEM according to the published procedure [17,28]. Mesoporous CrMCM-41(40) catalyst was also characterized by ICP-AES, XRD, nitrogen adsorption/desorption and UV–vis DRS according to the published procedure [11].

2.5. Oxidation of tetralin and benzylic compounds

Oxidation of tetralin for the synthesis of T=O was performed using a vigorous stirring thermostatted glass vessel reactor under liquid-phase reaction condition. In a typical experimental procedure, 20 mmol of tetralin, 20 ml of CB and 0.1 g of CrSBA-15(8) were taken in the reactor. The reaction mixture was stirred under constant stirring, and subsequently the reaction temperature was slowly raised to 393 K. After that, 40 mmol of TBHP was carefully added through the septum to the reactant mixture and refluxed for 10 h. After the reaction, the CrSBA-15(8) catalyst was filtered, and the products were collected. The oxidation of tetralin was conducted with different catalysts. To find an optimal condition in the presence of CrSBA-15(8), this reaction was further carried out with different reaction conditions such as time, temperature, stoichiometric molar ratios of reactants (tetralin-to-TBHP). For the identification of a better solvent, the oxidation of tetralin was carried out with different solvents like acetonitrile, dichloroethane, chlorobenzene, dimethylformamide. The oxidation of tetralin was also carried out with H_2O_2 and molecular oxygen. Furthermore, oxidation of benzylic compounds such as propylbenzene, *n*-butylbenzene, indane, fluorene was also carried out over CrSBA-15(8) using a vigorous stirring thermostatted glass vessel reactor under various reaction conditions.

The collected products were analyzed with authentic samples by gas chromatography (GC) using a FID (Chromatograph: Varian CP 3800, column: HP-5, 30 m (length) × 0.32 mm (inner diameter) × 0.25 μm (film thickness)). Additionally, the products were further confirmed using combined gas chromatography–mass spectrometry (GC–MS, Hewlett G1800A) with HP-5 capillary column.

2.6. Experimental procedures for stability of catalyst

The regenerated Cr-containing mesoporous catalysts viz. CrSBA-15(8), CrSBA-15(50) and CrMCM-41(40) were collected as follows. In a typical experimental procedure, the CrSBA-15(8) catalyst used in a catalytic run was separated from the reaction mixture, washed with acetone several time and dried at 393 K. Finally, the CrSBA-15(8) catalyst was calcined at 773 K for 6 h in air to remove the adsorbed species. The similar procedure was used for regenerating of other catalysts viz., CrSBA-15(50) and CrMCM-41(40). The regenerated catalysts were reused again to further catalytic runs in the oxidation of tetralin for finding their catalytic activities. After completion of the reaction, the catalysts were filtered and analyzed by ICP-AES to find the percentage of Cr. The conversion of tetralin and selectivity of T=O was calculated using the standard formulas followed by analyzing results of GC and GC–MS. The regenerated CrSBA-15(8) was also reused in the oxidation of benzylic compounds.

In order to find the catalytic stability and remove the extra-framework chromium species, the original CrSBA-15 catalyst was chemically treated with ammonium acetate, according to previously published procedure [28]. Finally, the CrSBA-15(8) catalyst was filtered, calcined at 500 °C for 6 h in air to remove the adsorbed species. This treatment of catalyst is denoted as washed CrSBA-15(8) catalyst. The washed CrSBA-15(8) catalyst was characterized by XRD, N_2 adsorption and UV–vis DRS, and used in the oxidation of benzylic compounds. Subsequently the filtrate solution obtained from the treatment of washing was performed on the oxidation of benzylic compounds under the similar reaction condition.

3. Results and discussion

The CrSBA-15 catalysts synthesized by pH-aDH method have been characterized by ICP-AES, XRD, N_2 adsorption, ESR, FE-SEM, and TEM according to the published procedure [17]. ICP-AES studies show that the high amounts of Cr-ions are highly incorporated on the silica pore walls [17]. The elemental composition of CrSBA-15 catalysts is listed in Table 1. XRD results confirm that the calcined CrSBA-15 catalysts have well ordered 2D-hexagonal mesostructures with space group *p6mm* [17], and the unit cell parameter in the calcined CrSBA-15 catalysts increases with increasing Cr-ion content as shown in Table 1. After washing treatments, the washed CrSBA-15(8) has almost the similar structural integrity [17]. By increasing the Cr-ion content, N_2 adsorption results reveal that the textural parameters of CrSBA-15(8) catalyst increase as compared to other CrSBA-15 catalysts, except surface area (Table 1). The textural parameters of the washed CrSBA-15(8) also remain constant with a good isotherm related to IUPAC classification (Fig. 1). The ESR results prove that the Cr^{5+} and Cr^{6+} ions in the calcined CrSBA-15 catalysts are tetrahedrally coordinated to Si^{4+} on the silica walls [17]. Furthermore, the results of ^{29}SiMAS NMR show that the signal intensity of CrSBA-15 is much less as compared to that of siliceous SBA-15 [17,28]; this observation clearly supports the stabilization of chromium ions via silanol groups (defect sites). However, Cr(VI) polychromate species dispersed on the surface of SBA-15 cannot be found by the ESR analysis. Then the calcined CrSBA-15 catalysts and washed CrSBA-15(8) have been further characterized by UV–vis DRS. The UV–vis DRS results clearly confirm that the Cr^{6+} species can be tetrahedrally coordinated into SBA-15, and small amounts of Cr(VI) polychromate species are dispersed on the SBA-15, as shown in Fig. 2 [28]. Most of polychromate species dispersed on the surface of CrSBA-15(8) are completely removed by the chemical treatments, as shown Figure 2 [28]. The results of TEM and FE-SEM correspondingly show the uniform pore diameter and rope-like hexagonal mesoporous structure of CrSBA-15 [17]. On the basis of characteristic results, it is interestingly to note that the well ordered

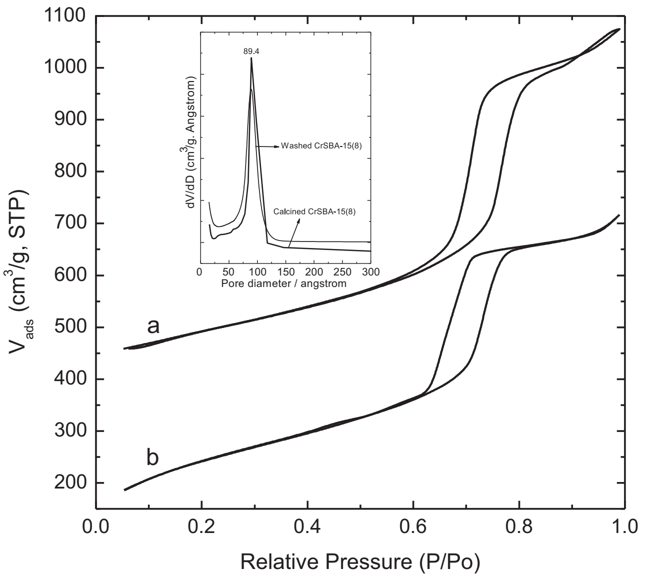

Fig. 1. Nitrogen adsorption isotherms of (a) calcined CrSBA-15(8) and (b) washed CrSBA-15(8).

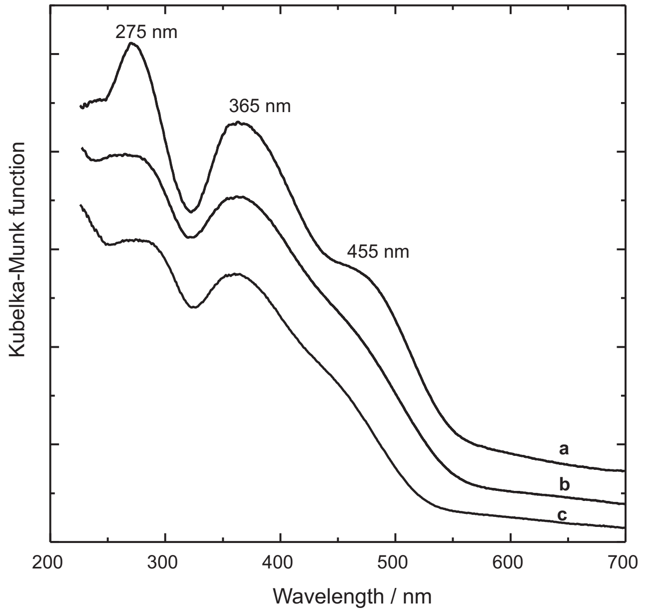

Fig. 2. UV–vis DR spectra of (a) calcined CrSBA-15(8), (b) washed CrSBA-15(8) and (c) recyclable CrSBA-15(8) used for four runs.

Table 2
Oxidation of tetralin over Cr-containing SBA-15 catalysts.[a]

Catalysts	Tetralin conversion (%)	Product selectivity (%)		
		T=O	T–OH	Others
CrSBA-15(8)	96.5	98.5	1.0	0.5
CrSBA-15(16)	83.5	86.3	13.7	–
CrSBA-15(20)	79.6	83.4	16.6	–
CrSBA-15(25)	75.3	80.7	19.3	–
CrSBA-15(50)	50.2	60.3	18.2	21.5[b]
CrMCM-41(40)	69.5	65.4	34.6	–
SiSBA-15	10.6	15.4	26.2	63.2[b]
Blank	6.5	10.4	20.4	69.2[b]

[a] Reaction conditions: 0.1 g of catalyst, 1:2 ratio of tetralin-to-TBHP (20 mmol of tetralin and 40 mmol of TBHP), reaction time = 10 h, 20 ml of CB, temperature = 393 K.
[b] Tetralin hydroperoxide (THP).
Others: T–2OH (1,4-dihydroxytetralin) and T(=O)$_2$ (1,4-naphthaquinone).

Table 3
Catalytic oxidation of tetralin over regenerated Cr-containing mesoporous silica catalysts and washed CrSBA-15(8)[a].

Catalysts	Tetralin conversion (%)	Product selectivity (%)		
		T=O	T–OH	Others
CrSBA-15(8)[b]	85.1	88.5	10.5	1.0
CrSBA-15(50)[c]	45.6	55.7	17.8	26.5[f]
CrMCM-41(40)[d]	63.4	61.5	38.5	–
CrSBA-15(8)[e]	85.4	89.6	10.4	–

[a]Reaction conditions: 0.1 g of catalyst, 1:2 ratio of tetralin-to-TBHP (20 mmol of tetralin and 40 mmol of TBHP), reaction time = 10 h, 20 ml of CB, temperature = 393 K. [b,c,d]The regenerated catalysts were used for four runs. [e]Washed catalyst. [f]Tetralin hydroperoxide (THP). Others: T–2OH (1,4-dihydroxytetralin) and T(=O)$_2$ (1,4-naphthaquinone).

CrSBA-15 with a huge numbers of tetrahedral Cr^{5+}/Cr^{6+} species are successfully synthesized using pH-aDH method.

In order to understand the selectivity of enones by the oxidation of benzylic compounds, firstly, we have systematically investigated the liquid-phase oxidation of tetralin with TBHP over CrSBA-15 catalysts. The oxidation of tetralin proceeds via a radical-chain mechanism [28,29] and has been carried out using the reaction conditions noted in Table 2. This reaction also produces T–OH, as a minor byproduct and very trance amount byproducts such as, 1, 4-dihydroxytetralin (T–2OH) and 1,4-napthaquinone (T(=O)$_2$). The order of catalytic activity found on the selectivity of T=O is as follows: CrSBA-15(8) > CrSBA-15(16) > CrSBA-15(20) > CrSBA-15(25) > CrMCM-41(40) > CrSBA-15(50). CrSBA-15(8) exhibits the best performance with a selectivity of T=O (98.5%). CrSBA-15(8) has higher catalytic activity than other CrSBA-15 catalysts. The higher activity observed in CrSBA-1(8) is tentatively ascribed to its two-dimensional space and very high loadings of tetrahedral Cr^{5+}/Cr^{6+} species on the surface of SBA-15, resulting in high numbers of accessible active sites because the tetrahedral Cr^{5+}/Cr^{6+} species incorporated in the framework of SBA-15 creates the high numbers of Lewis acid sites for enhancing catalytic activity in the oxidation of tetralin. Compared the catalytic results of similar chromium-containing catalysts like CrSBA-15(25) and CrMCM-41(40) as shown in Table 1, the catalytic activity of CrSBA-15(25) is notably higher as compared to that of CrMCM-41(40), as shown in Table 2. A state point can make a decision from this evidence that the well uniformly ordered mesoporosity material plays an important catalytic role in the production of T=O with a high selectivity. Another one point is also indicated from the observation of catalytic studies that the diffusion rate of CrMCM-41(40) may be much less as compared to that of CrSBA-15(25). This reaction was also carried out using SiSBA-15 synthesized by pH-aDH method as well as without catalyst [17]. In both cases, about ~6–10% conversion of tetralin and ~63–70% selectivity of THP were obtained (Table 2), thus indicating that major activity is only due to chromium species incorporated on the silica pore walls of SBA-15.

The regenerated Cr-containing mesoporous catalysts listed in Table 3 have been reused for this reaction, and their catalytic activities decrease in the first two runs (not shown the values in Table 3). On the basis of first two runs, it is observed that the polychromate and pentavalent chromium species can be leached on the catalytic surface (the range of n_{Si}/n_{Cr} ratio obtained by ICP-AES is from 12.2 to 99.9). The leaching studies were also confirmed from the fresh CrSBA-15 catalysts (the range of n_{Si}/n_{Cr} ratio obtained by ICP-AES is from 9.9 to 99.9). The catalytic activities of these catalysts remain constant after four runs (Table 3), indicating that the chromium species cannot be further leached on the mesoporous matrix, which is in good agreement with ICP-AES results of filtrate solutions where no chromium ion was detected while UV–vis DRS also shows that the leaching of chromium ions is not observed after four runs, as shown in Fig. 2. We suspect that the aqueous *t*-butanol generated as a byproduct in this reaction is responsible for the extraction of a small amount of loosely bound pentavalent chromium (extra-framework) in Cr-containing mesoporous catalysts. Furthermore, the washed CrSBA-15(8) was also used in this reaction to find its catalytic activity. Effect of this result is nearly similar to that of CrSBA-15(8) used after four runs, as shown in Table 3. As an important point, the non-framework chromium oxides ($n_{Si}/n_{Cr} = 2.3$) such as polychromate and Cr(VI) oxide are highly toxic and were completely removed by washing treatments. On the basis of recycling results, CrSBA-15(8) is found to be an excellent recyclable catalyst among the other Cr-containing mesoporous silica catalysts.

Since the CrSBA-15(8) is a promising catalyst in this catalytic reaction, it has been further used with a variety of reaction parameters such as reaction temperature, reaction time and ratios of reactant (tetralin: TBHP). When the reaction parameters like temperature and time are decreased from 393 to 313 K and from 10 to 1 h, respectively, the rate of both tetralin consumption and T=O formation decrease. The feasible-tetralin conversion decreases with the decrease of reaction temperature and time (Figs. 3 and 4). This may be due to decreasing the catalytic activity on the surface of the catalyst at low reaction temperature and time, which could not effectively support for the decomposition of THP into T–OH whereas the T=O decreases. Moreover, the conversion of tetralin

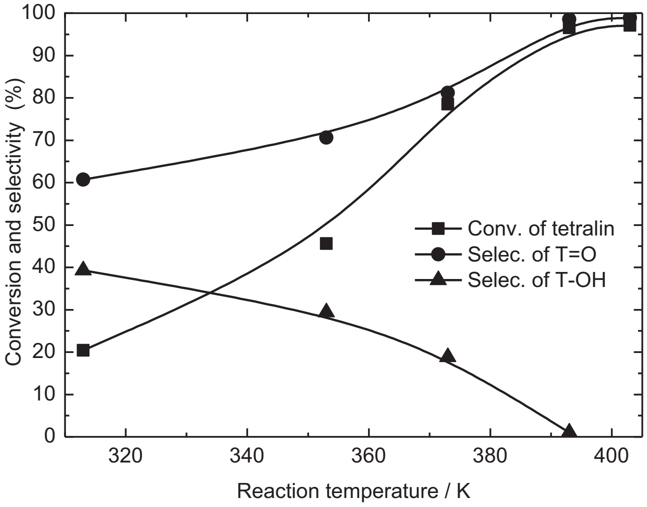

Fig. 3. Variation of reaction temperature on the synthesis of T=O by oxidation of tetralin with TBHP. Reaction conditions: 0.1 g of CrSBA-15(8) catalyst, 1:2 ratio of tetralin-to-TBHP (20 mmol of tetralin, 40 mmol of TBHP), reaction time = 10 h, 20 ml of CB.

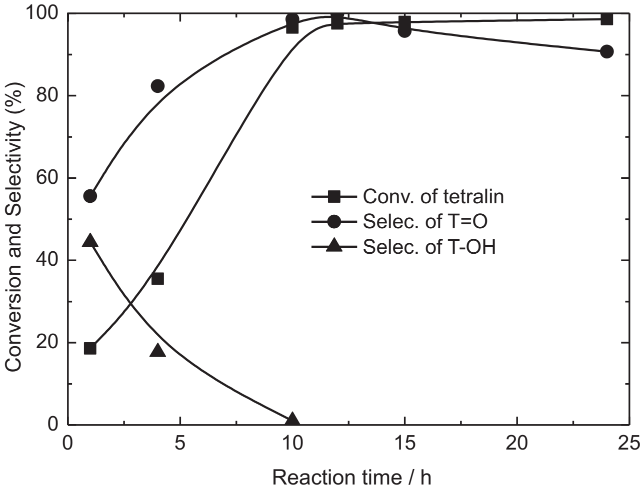

Fig. 4. Variation of reaction time on the synthesis of T=O by oxidation of tetralin with TBHP. Reaction conditions: 0.1 g of CrSBA-15(8) catalyst, 1:2 ratio of tetralin-to-TBHP (20 mmol of tetralin, 40 mmol of TBHP), reaction temperature = 393 K, 20 ml of CB.

as well as selectivity of T=O is not significantly increased when the reaction temperature or time is increased to 403 K/12 h. However, at above 403 K or 12 h the conversion of tetralin as well as selectivity of T=O decreases due to leading the formation of $T(=O)_2$. When this reaction is carried out with 1:2 ratio, a higher conversion of tetralin (96.5%) as well as selectivity of T=O (98.5%) is observed (Table 4). A reason may be that the reactants in 1:2 ratio react with each other on the catalytic surface without deactivation. The selectivity of T=O decreases on the unevenly ratios of reactants viz. 1:1, 1:3 and 2:3 (Table 4). This may be due to the formation of overoxidation byproducts viz., T–2OH and $T(=O)_2$. Pore size of the CrSBA-15(8) catalyst is blocked by the unreacted organics, and its diffusion rate also decreases. Comparing the catalytic results, it is obviously to note that the oxidation of tetralin in 1:2 mmol ratio of tetralin-to-TBHP at 393 K for 10 h gives a higher conversion of tetralin as well as a higher selectivity of T=O. Moreover, the catalytic activity of CrSBA-15(8) at 393 K is higher than that CrMCM-41 due to the high Cr-content [12,13].

The oxidation of tetralin has also been carried out with different solvents like MeCN, DCE, CB and DMF using the reaction conditions noted in Table 5, for obtaining a higher selectivity of T=O. MeCN is a dipolar solvent that cannot be supported to produce a higher conversion of tetralin under the similar reaction conditions because of making a weak interaction between the reactants (tetralin and TBHP) and surface of the catalyst. Moreover, the MeCN is usually low reactivity in the liquid-phase oxidation of cycloaromatics, and the T=O formed from THP is less. DCE is an apolar aprotic solvent that also makes a low selectivity of T=O under the similar reaction condition. CB is a common and high-boiling solvent that has high ability to form the complexes on the catalytic surface for long time in the liquid-phase catalytic oxidations, and it makes higher conversion of tetralin as well as higher selectivity of T=O than MeCN and DCE. Moreover, the CB preferentially attacks the active sites on the surface of catalyst for the higher selectivity of T=O. DMF is a dipolar aprotic solvent and has a high dielectric constant with electron donor properties, and its ability is higher to form the complexes than other solvents. However, the DMF produces a low tetralin conversion but the selectivities of T=O and T–OH are nearly same. Although the DMF solvent has a good polarity, it cannot be fully supported in the oxidation of tetralin under the similar reaction condition. The conversion of tetralin as well as selectivity of T=O is low whereas the formation of T–2OH is ~26% selectivity when the liquid-phase oxidation of tetralin is carried out with H_2O_2 instead of TBHP in the presence of MeCN under the similar reaction condition. A possible reason is that the H_2O_2 decomposes rapidly into O_2 with high exothermicity. When the oxidation of tetralin is investigated with gaseous oxygen instead of TBHP in the presence of CB under the similar reaction condition, the conversion of tetralin (27.4%) as well as selectivity of T=O (36.7%) is low because the gaseous oxygen cannot be completely reacted with THP on the catalytic surface (Table 5). When this reaction is carried out with 10 ml of CB under the similar reaction condition, the conversion of tetralin as well as selectivity of T=O is low, because, the high quantity of tetralin may not be completely dissolved and cannot be completely reacted with TBHP (not shown in Table 5). Moreover, the conversion of tetralin decreases when the CB was conducted with a low temperature (343 K). But, the conversion of tetralin in CB at 393 K is higher than that of other solvents, because, the THP is completely decomposed under the similar condition. Overall, comparing the catalytic activity with different solvents, it is obviously found that CB is the best solvent for highly selective synthesis of T=O.

Table 4
Oxidation of tetralin: different ratios of tetralin to TBHP.[a]

Tetralin to TBHP ratios (mmol)	Tetralin conversion (%)	Product selectivity (%)		
		T=O	T–OH	Others
1:1	60.2	78.9	10.1	11.0
1:2	96.5	98.5	1.0	0.5
1:3	72.4	80.6	8.0	11.4
2:3	50.5	65.4	18.3	16.3

[a] Reaction conditions: 0.1 g of CrSBA-15(8) catalyst; 20 ml of CB, reaction time, 10 h; reaction temperature = 393 K.
Others: T–2OH (1,4-dihydroxytetralin) and $T(=O)_2$ (1,4-naphthaquinone).

Table 5
Oxidation of tetralin with different solvents over CrSBA-15(8).[a]

Temperature (K)	Solvent (20 ml)	Tetralin conversion (%)	Product selectivity (%)		
			T=O	T–OH	others
343	MeCN	69.8	90.6	8.1	1.3
343	DCE	45.6	70.3	29.7	-
393	CB	96.5	98.5	1.0	0.5
343	CB	56.7	65.4	1.0	33.6[d]
393	DMF	25.8	55.2	44.8	-
343	MeCN[b]	10.6	45.0	40.5	25.4[e]
393	CB[c]	27.4	36.7	1.0	62.3[d]

[a] Reaction conditions: 0.1 g of CrSBA-15(8) catalyst, 1:2 ratio of tetralin-to-TBHP (20 mmol of tetralin, 40 mmol of TBHP), reaction time = 10 h.
[b] 20 mmol of 30% H_2O_2 was used instead of TBHP.
[c] Gaseous oxygen (excess) was used instead of TBHP.
[d] Selectivity of THP.
[e] Selectivity of T–2OH.
Others: T–2OH (1,4-dihydroxytetralin) and $T(=O)_2$ (1,4-naphthaquinone).

To explore the scope and limitations of this catalytic system, oxidation of benzylic compounds such as propylbenzene, *n*-butylbenzene, indane and fluorene, has been studied over CrSBA-15(8) using the reaction conditions noted in Table 6. Normally, the oxidation of benzylic C–H bonds in alkylbenzenes is difficult. However, CrSBA-15(8) serves well on the oxidation of benzylic compounds. Alkylbenzenes (propylbenzene and *n*-buylbenzene) have been also oxidized to their corresponding enones with 100% selectivities (Table 6). For comparison, tetralin oxidation data has been also included. Indane has been likewise oxidized with 78% conversion and 98% selectivity of 1-indanone. A fused cyclic compound with aromatic ring, e.g., tetralin and indane has been easily oxidized with present catalytic system. Meanwhile fluorene has been oxidized with 42% conversion and 98% selectivity of 9-fluorenone. It is noteworthy observed that the CrSBA-15(8) gives

Table 6
Oxidation of benzylic compounds over calcined, washed and regenerated CrSBA-15(8).[a]

Substrate	Temperature (K)	Ketone product	Conversion (%)	Selectivity of ketone (%)	Selectivity of alcohol (%)
Propylbenzene (P)[b,c]	353	Propiophenone	58.0	100	–
4th run of P[b,c]	353	Propiophenone	53.0	100	–
CrSBA-15(8) of P[b,c,f]	353	Propiophenone	52.7	100	–
n-Butylbenzene (B)[b,c]	353	Butylacetophenone	55.0	100	–
4th run of B[b,c]	353	Butylacetophenone	48.0	100	–
CrSBA-15(8) of B[b,c,f]	353	Butylacetophenone	48.6	100	–
Indane (I)[d,e]	353	1-Indanone	78.0	98	4
4th run of I[d,e]	353	1-Indanone	73.0	92	8
CrSBA-15(8) of I[d,e,f]	353	1-Indanone	73.0	92	8
Fluorene (F)[d,e]	365	9-Fluorenone	42.0	98	2
4th run of F[d,e]	365	9-Fluorenone	38.0	93	7
CrSBA-15(8) of F[d,e,f]	365	9-Fluorenone	37.9	92	8

[a] Reaction conditions: 0.1 g of CrSBA-15(8) catalyst and reaction time = 10 h.
[b] 1:2 ratio of substrate-to-H_2O_2 (20 mmol of substrate, 40 mmol of H_2O_2).
[c] 20 ml of methanol.
[d] 1:2 ratio of substrate-to-TBHP (20 mmol of substrate, 40 mmol of H_2O_2).
[e] 20 ml of CB.
[f] Washed catalyst.

higher conversion (Table 6) than CrMCM-41 due to the high Cr-content [13]. The regenerated CrSBA-15(8) has also been reused in the oxidation of benzylic compounds under the similar reaction condition, and the conversion of benzylic compounds as well as selectivity of enones is obtained as shown in Table 6. Based on the catalytic activity of each benzylic oxidation reaction, it is noteworthy observed that the catalytic activity of this catalyst remains constant after four runs, and the percentage of Cr-content remains constant. Furthermore, washed CrSBA-15(8) was also used in these reactions to find their catalytic activities. These catalytic results are nearly similar to that of CrSBA-15(8) used after four runs, as shown in Table 6. Overall, on the basis of the catalytic results, it is remarkably noted that the CrSBA-15(8) is a highly active, recyclable and promising heterogeneous catalyst for the highly selective production of enones in the oxidation of benzylic compounds. The CrSBA-15(8) catalyst gives the superior selectivity of enones than CrMCM-41 [13].

4. Conclusions

The CrSBA-15 catalysts have been successfully used for the synthesis of enones. The active sites of these catalysts are highly efficient for the generation and decomposition of benzylic hydrogen peroxide intermediate to enones. CrSBA-15 catalysts are found to be efficient catalysts for the highly selective synthesis of enones. When CrSBA-15(8) is washed with ammonium acetate solution, the non-framework chromium oxides can be completely removed on the surface of the catalyst. From the studies of washing/recyclables, it is found that the CrSBA-15(8) has higher catalytic stability in the liquid-phase oxidation of benzylic compounds as compared to other Cr-containing mesoporous catalysts. On the basis of all catalytic studies, it is clearly found that the CrSBA-15(8) catalyst is a highly active, recyclable and promising heterogeneous catalyst for the selective synthesis of enones. Additionally, CrSBA-15(8) catalyst has higher selectivity of enones than CrMCM-41.

Acknowledgements

This work was supported by a Pusan National University Research Grant (2008) and the National Research Foundation (NRF) of Korea through the Basic Research Program (NRF-2010-002-1933) & Acceleration Research Program (NRF-2011-0000385) for sponsoring this work.

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