

CrAPO-5 catalysts having a hierarchical pore structure for the selective oxidation of tetralin to 1-tetralone

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A novel CrAPO-5 material having a unique microporous–mesoporous hierarchical pore structure (CrAPO-5H) was synthesized using an organosilane surfactant to conventional CrAPO-5 reaction mixture by a one-step hydrothermal process. The materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), N₂-adsorption isotherm and UV-visible diffuse reflectance spectroscopy, and employed as a catalyst for the liquid phase oxidation of tetralin. CrAPO-5H produced higher activity than conventional microporous CrAPO-5. Acylperoxy radicals, *in situ* generated from trimethylacetaldehyde and O₂, were more effective as oxidant than *tert*-butyl hydroperoxide (*t*-BuOOH); 88% conversion of tetralin with 97% selectivity to 1-tetralone was obtained with the former, whereas 57% conversion with 86% selectivity was achieved using the latter at 80 °C after 8 h. The effect of reaction temperature, Cr content, solvent, and the type of aldehyde employed for the *in situ* generation of acylperoxy radicals on catalytic performance was investigated. Activities of CrAPO-5H remained constant after 1st catalyst recycle. A hot filtration experiment coupled with a blank test revealed that oxidation proceeded mostly on Cr sites in the CrAPO-5H, but a minor contribution from trace amount of leached Cr could not be ruled out.

Introduction

Selective oxidation of tetralin (1,2,3,4-tetrahydronaphthalene) produces 1-tetralone, an important source of synthetic precursors and a reactive intermediate for a wide range of products including pharmaceuticals, dyes, and agrochemicals.^{1,2} 1-Tetralone can also be used as an additive to enhance the cetane number in diesel fuels for cleaner combustion.³ For such benzylic oxidation, stoichiometric reagents such as permanganate, manganese oxide, and dichromate have traditionally been used, but because of the large amounts of toxic by-products formed, they are being replaced by a more environmentally benign catalytic oxidation system.

Homogeneous catalytic systems for tetralin oxidation in a liquid phase prior to 1990 were extensively reviewed by Muzart.⁴ Those employing Mn(III) porphyrins,⁵ VO(acac)₂,⁶ vanadium ion-pair,⁷ and Ni complexes with surface active ligands in a biphasic mode⁸ were reported more recently. Heterogeneous catalysts tested for tetralin oxidation include Fe/MgO,⁹ vanadium-substituted polyoxo-metalate,¹⁰ a manganese octahedral molecular sieve,¹¹ Cu(II)/PVP,¹² and Cu/Co MOFs,¹³ and a series of chromium-containing molecular sieves such as CrAPO-5 and CrAPO-11,^{14–18} Cr-MCM-41,^{19–22} and chromium-exchanged zeolite Y,²³ and ZSM-5.²⁴ Chromium-containing molecular sieves appear to

offer higher catalytic activity and selectivity, but possible leaching of the active Cr species from the molecular sieve matrix during the catalytic reaction poses a serious problem.^{24,25} We also reported an efficient benzylic oxidation over the Cr(III) terephthalate metal–organic framework, MIL-101.²⁶

Among the Cr-containing catalysts, CrMCM-41 and CrHMA having mesopores showed higher catalytic activity than microporous CrAPO-5, CrS-1, and Cr-β in the oxidation of tetralin¹⁸ and cyclohexane.²² CrMCM-41 could also be used for the oxidation of bulkier substrates such as anthracene or 9,10-anthraquinone.²⁷ Interestingly, CrMCM-41 was also reported to be an efficient catalyst for solvent-free oxidation of benzylic compounds using dioxygen²⁸ and in vapor phase oxidation of tetralin.²⁹ The mesopore walls of these catalysts, however, are comprised of incompletely cross-linked amorphous silica frameworks and hence structural stability is low. Thus preparation of a mesoporous Cr-containing catalyst with enhanced structural stability is highly desirable.

Various synthetic methods have been reported for the preparation of zeolites or zeotype materials having a hierarchical pore structure.^{30–35} It has been known that mesoporous materials built with microporous crystalline frameworks in zeolites exhibit remarkable stability and high resistance to catalyst deactivation in various organic reactions.³⁴ Recently, such microporous–mesoporous hierarchical structures were formed through a one-step hydrothermal crystallization process by introducing a rationally designed organosilane surfactant as a mesopore director into the conventional zeolite substrate composition.³⁵ The identical synthesis strategy was applied to aluminophosphate compositions in which the mesopore walls are constructed with crystalline microporous

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$\text{AlPO}_4\text{-}n$. No transition metal incorporation to such a hierarchical structure has been reported thus far.

In this work, CrAPO-5 materials having a unique microporous–mesoporous hierarchical pore structure (CrAPO-5H) in different Cr contents were synthesized and tested as a catalyst for the liquid phase oxidation of tetralin. We investigated tetralin oxidation in a liquid phase using *t*-BuOOH as well as *in situ* generated acylperoxy radicals through O_2 at atmospheric pressure in the presence of various sacrificial aldehydes. Rigorous tests were applied to evaluate the catalyst stability of CrAPO-5H .

Results and discussion

Synthetic aspect of CrAPO-5H

The procedure of CrAPO-5H preparation is shown in Scheme 1. Chemical analysis results of CrAPO-5H samples are given in Table 1. The chromium containing aluminophosphates, having microporous–mesoporous hierarchical pore structure, CrAPO-5H , were synthesized by standard synthesis conditions for CrAPO-5 ,¹⁴ with an exception that an organosilane surfactant was additionally employed as a template to create mesopores. The organosilane, 3-(trimethoxysilyl)propylhexadecyldimethylammonium chloride ($[(\text{CH}_3\text{O})_3\text{SiC}_3\text{H}_6\text{N}(\text{CH}_3)_2\text{C}_{16}\text{H}_{33}]\text{Cl}$, TPAC), is used previously as a meso-directing agent in the preparation of various hierarchical zeolite structures.^{30,35} TPAC, a long hydrocarbon chain with alkylammonium group and a hydrolysable methoxysilyl group, is found to be chemically stable in various zeolite synthesis conditions, which showed strong interaction with the growing crystals and prevents phase segregation during crystallization process. As a result, zeolite or zeotype having a hierarchical pore structure was furnished.^{30,35} Triethylamine was used as a usual structure directing agent for $\text{AlPO}_4\text{-5}$ phase, which creates microporosity. These dual templating methods produce a crystalline CrAPO-5H with a high-quality micro- and mesoporosity hierarchical pore

structure. A conventional hydrothermal reaction was used for the crystallization process.

Catalyst characterization

The incorporation of Cr into the $\text{AlPO}_4\text{-5}$ structure has been widely studied.^{14,36–40} The XRD patterns, SEM micrographs, N_2 -adsorption isotherms, and UV-Visible diffuse reflectance spectra of CrAPO-5H and CrAPO-5 samples are shown in Fig. 1–4, respectively.

The wide angle X-ray powder diffraction patterns of both CrAPO-5H and CrAPO-5 in Fig. 1 show identical characteristic peaks at 2θ values of 7.3° , 19.6° , 21.1° , and 22.3° to the previously reported characteristic peaks of high phase purity $\text{AlPO}_4\text{-5}$,^{14,40} confirming that these are structurally identical materials.

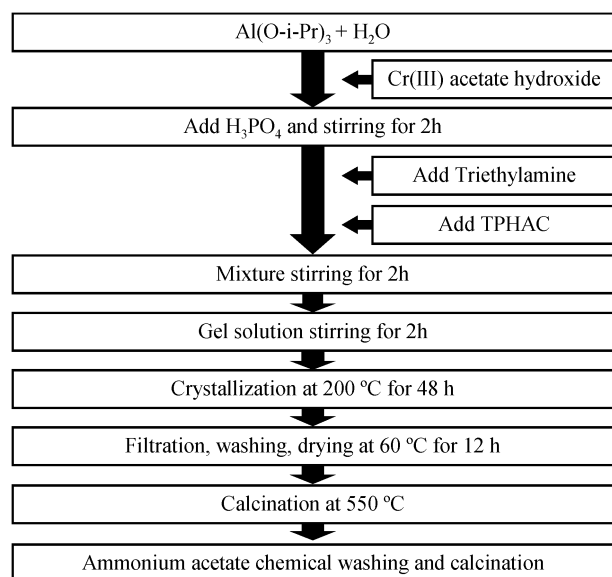
SEM micrographs (Fig. 2) reveal that $\text{Cr}_{1.6}\text{APO-5H}$ particles are cylindrical in shape and composed of 20–50 nm nanocrystals, whereas $\text{Cr}_{1.6}\text{APO-5}$ is comprised of hexagonal slab-shaped crystals. Both particles were found to be covered with smaller amorphous grains with increasing chromium content, but after ammonium acetate washing the grains were mostly removed, as was reported by Sakthivel and Selvam.⁴¹

N_2 adsorption–desorption isotherms of $\text{Cr}_{1.6}\text{APO-5H}$ (Fig. 3b) show a type-IV pattern, indicating mesoporosity of the materials, which originate from intercrystalline voids

Table 1 Chemical analysis^a of CrAPO-5H

Catalyst	(mol%)			
	Cr	Al	P	Si
$\text{Cr}_{0.48}\text{APO-5H}$	0.48	47.76	47.84	3.91
$\text{Cr}_{0.96}\text{APO-5H}$	0.96	47.20	47.72	4.12
$\text{Cr}_{1.6}\text{APO-5H}$	1.61	46.72	47.70	3.97
$\text{Cr}_{3.4}\text{APO-5H}$	3.44	44.87	47.53	4.17
$\text{Cr}_{1.6}\text{APO-5}$	1.64	49.82	48.54	—

^a SEM-EDX.



Scheme 1 Synthetic route of CrAPO-5H .

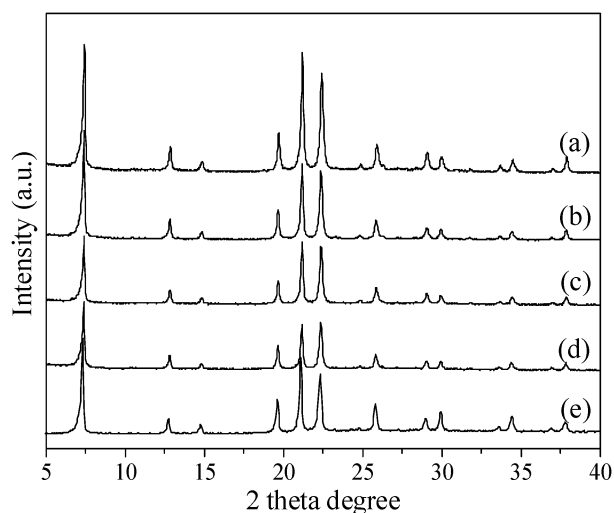


Fig. 1 X-Ray powder diffraction patterns of (a) $\text{Cr}_{1.6}\text{APO-5}$, (b) $\text{Cr}_{0.48}\text{APO-5H}$, (c) $\text{Cr}_{0.96}\text{APO-5H}$, (d) $\text{Cr}_{1.6}\text{APO-5H}$, and (e) $\text{Cr}_{3.4}\text{APO-5H}$.

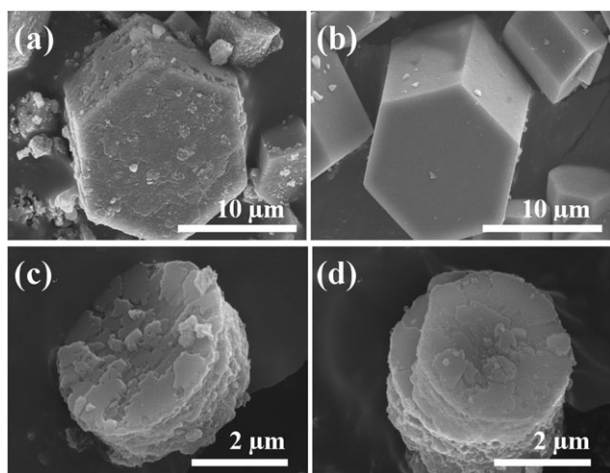


Fig. 2 SEM micrographs of Cr_{1.6}APO-5 (a and b) and Cr_{1.6}APO-5H (c and d): before (a and c) and after (b and d) ammonium acetate washing.

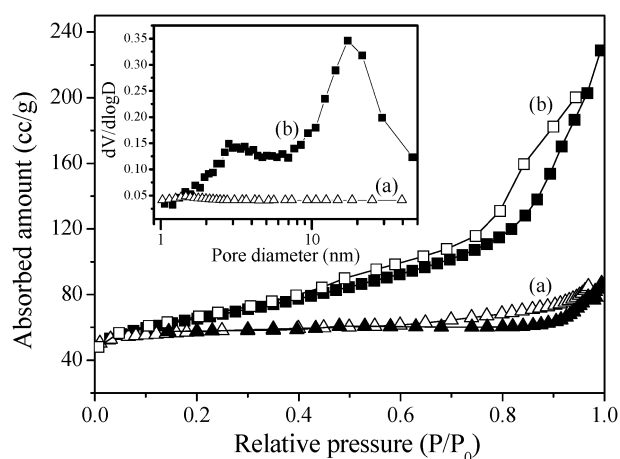


Fig. 3 N₂ adsorption-desorption isotherms of 2 mol% chromium-incorporated (a) Cr_{1.6}APO-5 and (b) Cr_{1.6}APO-5H: (■) adsorption, (□) desorption (inset shows pore size distribution of (a) Cr_{1.6}APO-5 and (b) Cr_{1.6}APO-5H).

between the nano-sized crystallite domains within the particle, whereas Cr_{1.6}APO-5 has a type-I isotherm (Fig. 3a) corresponding to a microporous material. The pore size distribution of Cr_{1.6}APO-5H (Fig. 3, inset) showed two maxima, one at *ca.* 2.8 nm and other at 17.3 nm with a broad pore size distribution. The BET surface area and pore volume of the representative samples of Cr_{1.6}APO-5H and Cr_{1.6}APO-5 were 270 m² g⁻¹ and 0.35 cm³ g⁻¹ and 250 m² g⁻¹ and 0.16 cm³ g⁻¹, respectively.

The diffuse reflectance UV-Visible spectra of both samples display identical features (Fig. 4). The bands appearing at 440 and 600 nm for as-synthesized samples (Fig. 4c and d) are assignable to distorted octahedral coordination of Cr(III),^{38,42} whereas the strong absorption bands at 270 and 360 nm for the calcined samples (Fig. 4a and b) are due to the O → Cr(VI) charge transfer transitions of chromate or polychromate species.⁴³

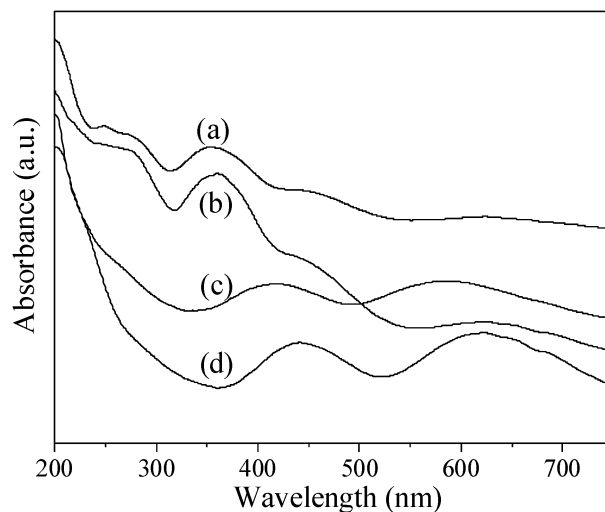
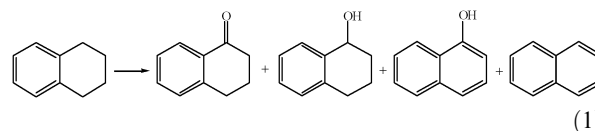


Fig. 4 UV-Visible diffuse reflectance spectra of (a) Cr_{1.6}APO-5, (b) Cr_{1.6}APO-5H, (c) as-syn. Cr_{1.6}APO-5, and (d) as-syn. Cr_{1.6}APO-5H.

Catalyst performances in tetralin oxidation using *t*-BuOOH



Initially, tetralin oxidation over CrAPO-5H catalysts was carried out using *t*-BuOOH and chlorobenzene as a standard oxidant and solvent, respectively (Table 2). Fig. 5 shows the effect of reaction temperature on tetralin oxidation over Cr_{1.6}APO-5H. The selectivity to 1-tetralone was somewhat higher at 80 °C but remained fairly constant at *ca.* 85% as tetralin conversion steadily increased from 50 to 62% in a temperature range of 60 to 120 °C. 1-Tetralol, 1-naphthol, and naphthalene were co-products (eqn (1)). Subsequent catalytic reactions were conducted at 80 °C based upon the obtained yield of 1-tetralone and to guard against a potential catalyst stability problem that may be encountered at higher reaction temperatures.

Catalytic performance by CrAPO-5H with different Cr contents (0.48 to 3.4 mol%) was examined at 80 °C. As shown in Table 2, an increase in Cr content under the given reaction conditions resulted in a gradual increase of tetralin conversion

Table 2 Influence of Cr content in CrAPO-5H on tetralin oxidation using *t*-BuOOH^a

Catalyst	Conversion (%)	Product selectivity ^b (%)			
		1	2	3	4
Cr _{0.48} APO-5H	41	87.1	5.6	5.0	2.3
Cr _{0.96} APO-5H	50	87.0	4.5	6.0	2.5
Cr _{1.6} APO-5H	57	86.2	4.0	7.2	2.6
Cr _{3.4} APO-5H	61	85.8	4.7	6.8	2.7
Cr _{1.6} APO-5	47	82.2	10.2	4.6	3.0
No catalyst	14	59.8	22.7	10.3	7.2

^a Reaction conditions: 8 mmol tetralin, 16 mmol *t*-BuOOH, 5 ml chlorobenzene, 50 mg catalyst, 80 °C and time 8 h. ^b 1-Tetralone, 1-tetralol, 1-naphthol and naphthalene are denoted as **1**, **2**, **3** and **4**, respectively.

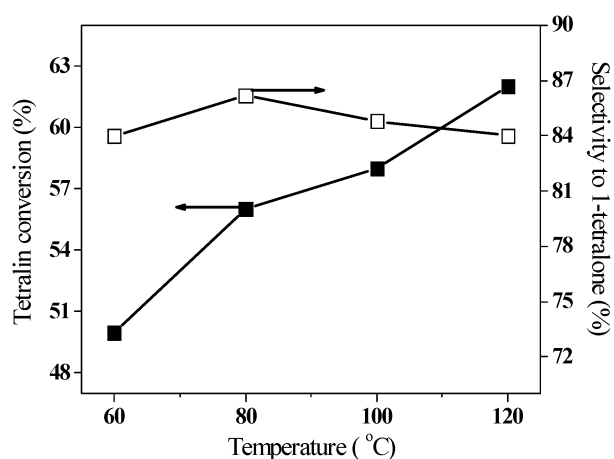


Fig. 5 Effect of temperature on the catalytic activity of Cr_{1.6}APO-5H using *t*-BuOOH (reaction conditions: 8 mmol tetralin, 16 mmol *t*-BuOOH, 50 mg catalyst, 5 ml chlorobenzene, 8 h).

(41 to 61%) but the selectivity to 1-tetralone remained virtually constant. These results indicate that the availability of active chromium sites controls the catalytic oxidation reaction of tetralin, which is fundamentally heterogeneous in nature. Cr_{1.6}APO-5H showed higher conversion and selectivity to 1-tetralone than Cr_{1.6}APO-5; the larger pores in CrAPO-5H are apparently advantageous for enhanced diffusion of the organic substrates as compared to the micropores in CrAPO-5. Identical observations were reported earlier for other catalysts.²² It was also found that non-catalytic thermal oxidation takes place in the presence of *t*-BuOOH, leading to 14% tetralin conversion.

Oxidation using *in situ* generated acylperoxy radicals

In situ generated acylperoxy radicals through O₂ and aldehyde were also considered as an alternative oxidant for tetralin oxidation over CrAPO-5H. Initially, the effect of reaction temperature in tetralin oxidation was investigated using O₂ in the presence of trimethylacetaldehyde. As shown in Fig. 6,

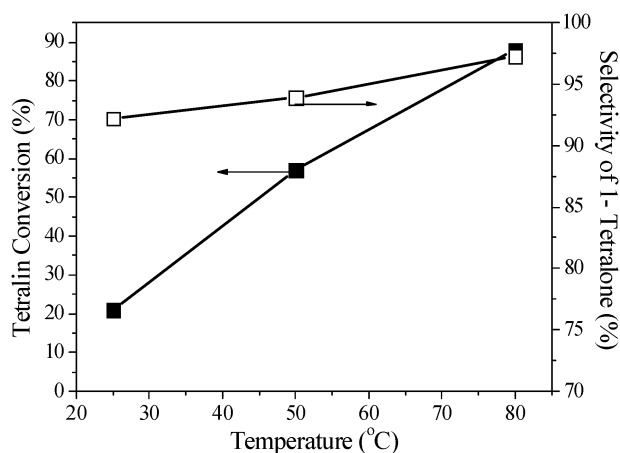


Fig. 6 Effect of temperature on the catalytic activity of Cr_{1.6}APO-5H using O₂/trimethylacetaldehyde (reaction conditions: 2 mmol tetralin, 4 mmol trimethylacetaldehyde, O₂ (1 atm), 10 mg catalyst, 10 ml acetonitrile, 8 h).

Table 3 Influence of Cr content in CrAPO-5H and aldehyde for *in situ* formation of acylperoxy radicals on tetralin oxidation^a

Catalyst	Aldehyde	Conversion (%)	Product selectivity ^b (%)	
			1	2
Cr _{1.6} APO-5H		22.0	84.1	13.5
Cr _{1.6} APO-5H		73.0	89.1	1.2
Cr _{1.6} APO-5H		88.0	97.3	0.4
Cr _{0.96} APO-5H		84.0	97.4	0.4
Cr _{0.48} APO-5H		80.0	95.8	0.5
Cr _{1.6} APO-5		77.0	90.4	5.4
No catalyst		21.0	90.8	0.3

^a Reaction conditions: 2 mmol tetralin, 4 mmol aldehyde, 10 ml acetonitrile, O₂ (1 atm), 10 mg catalyst, 80 °C and time 8 h.

^b 1-Tetralone and 1-tetralol are denoted as 1 and 2, respectively.

an increase in the temperature from 25 to 80 °C led to a drastic increase of conversion from 21 to 88% while the selectivity of 1-tetralone moderately increased from 92 to 97%. Reaction was then carried out using CrAPO-5H with different Cr contents at 80 °C. As listed in Table 3, the conversion increased from 80 to 88% with increased Cr loading from 0.5 to 1.6 mol% whilst the selectivity to 1-tetralone remained virtually constant. Therefore, the *in situ* generated acylperoxy radicals from O₂/trimethylacetaldehyde proved to be a more effective oxidant than *t*-BuOOH. A group of researchers also reported similar results in the oxidation of styrene using *in situ* generated acylperoxy radicals through an O₂/isobutyraldehyde and *t*-BuOOH oxidant.⁴⁴

The variation in concentration of oxidant is known to be an important factor affecting both the conversion and selectivity of a final product in oxidation reaction.^{45,46} In order to assess the comparison of a single-injection system and a continuous feeding system using *t*-BuOOH, tetralin oxidation over Cr_{1.6}APO-5H was carried out by continuous injection of oxidant (feeding rate 0.9 ml h⁻¹) to substrate in chlorobenzene at 80 °C. At the end of 8 h reaction, the latter produced both higher tetralin conversion (64%) and improved 1-tetralone selectivity (91.8%) over those (57% conversion and 86.2% selectivity) obtained for the former. Apparently, the efficiency

of *t*-BuOOH as an oxidant in tetralin oxidation can be improved by maintaining the *t*-BuOOH to tetralin ratio low by suppressing the oxidant decomposition. A similar trend for the oxidation of hydrocarbon upon variation of the concentration of peroxide was reported.^{45,46}

To study the influence of aldehyde type in an O₂/aldehyde system, tetralin oxidation was carried out using three different kinds of aldehyde, *viz.*, by substituting the α -hydrogen with a methyl group attached to the aldehyde group (Table 3). Tetralin conversion and selectivity to 1-tetralone were found to be strongly influenced by changing the aldehyde in the O₂/aldehyde system. The conversion increased in the following order: acetaldehyde < isobutyraldehyde < trimethylacetaldehyde, and the O₂/trimethylacetaldehyde system showed the highest activity. The results indicated that tetralin oxidation using O₂/aldehyde system proceeds much better in the presence of aldehyde containing high electron density of the carbon centre attached to aldehyde group. Again, Cr_{1.6}APO-5H exhibited superior catalytic performance to that of Cr_{1.6}APO-5 in the O₂/aldehyde system. Thermal oxidation was found to be promoted by changing the oxidant from *t*-BuOOH to O₂/trimethylacetaldehyde.

In order to study the influence of solvent, the oxidation of tetralin over Cr_{1.6}APO-5H was carried out in chlorobenzene and acetonitrile in the presence of two types of oxidant sources, such as *t*-BuOOH and *in situ* generated acylperoxy radicals, through trimethylacetaldehyde and O₂ at 80 °C. Chlorobenzene showed much higher conversion (57%) than acetonitrile (26%) when using *t*-BuOOH. Using O₂ in the presence of trimethylacetaldehyde as oxidant, chlorobenzene (45%) showed much lower conversion than acetonitrile (88%), under the identical reaction conditions. Similar trend on solvent-dependent activity was observed in oxidation of tetralin over a chromium(III) terephthalate, MIL-101.²⁶

Catalyst stability

To assess the stability of the chromium ions in CrAPO-5H during the tetralin oxidation reaction, catalyst recycling tests and hot filtering experiments (separation of catalyst at reaction temperature) were conducted at 80 °C using Cr_{1.6}APO-5H. At the end of each reaction cycle, the catalyst was recovered by filtration, washed with chlorobenzene for *t*-BuOOH or acetonitrile for trimethylacetaldehyde/O₂, calcined at 550 °C in air for 5 h to remove the adsorbed species, and reused. As shown in Fig. 7, tetralin conversions in the first catalyst recycle were only marginally affected, with a drop from 57 to 55% and 88 to 87% using *t*-BuOOH and in the presence of trimethylacetaldehyde and O₂, respectively. After the second recycle, conversion and selectivity were virtually constant irrespective of the number of cycles. The filtrates after the first run had 0.26 ppm (*t*-BuOOH) and 0.17 ppm (trimethylacetaldehyde and O₂) chromium, respectively.

Further experiments on the stability of the catalyst in tetralin oxidation were carried out using a hot filtering technique, and the results are shown in Fig. 8 and 9. For a *t*-BuOOH oxidant system (Fig. 8), when the catalysts were filtered-off after 30 min reaction, the reaction still proceeded but with a substantially lower final conversion than in the

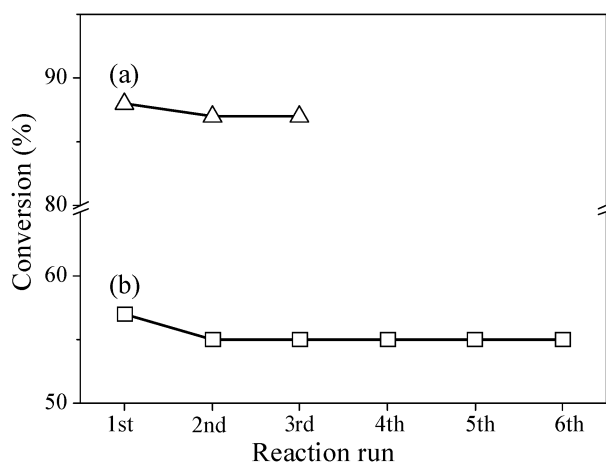


Fig. 7 Recycle test of tetralin oxidation over Cr_{1.6}APO-5H (80 °C, 8 h) using (a) O₂/trimethylacetaldehyde (Δ) and (b) *t*-BuOOH (\square) as oxidant.

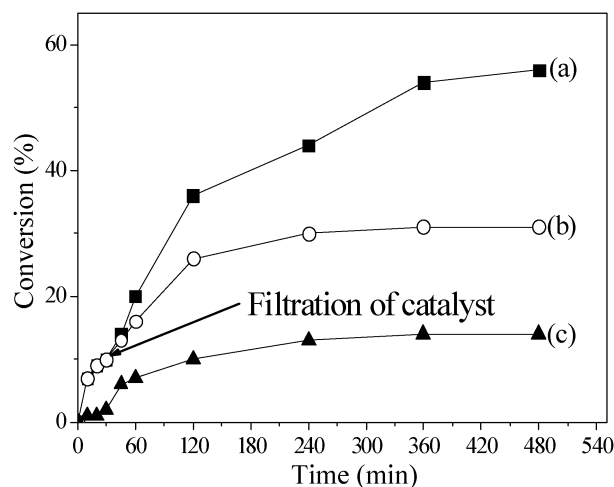


Fig. 8 Tetralin oxidation using *t*-BuOOH at 80 °C, catalyst amount 50 mg in chlorobenzene: (a) with Cr_{1.6}APO-5H catalyst, (b) filtrate (catalyst filtering off after 30 min reaction), (c) in the absence of catalyst (in the presence of *t*-BuOOH).

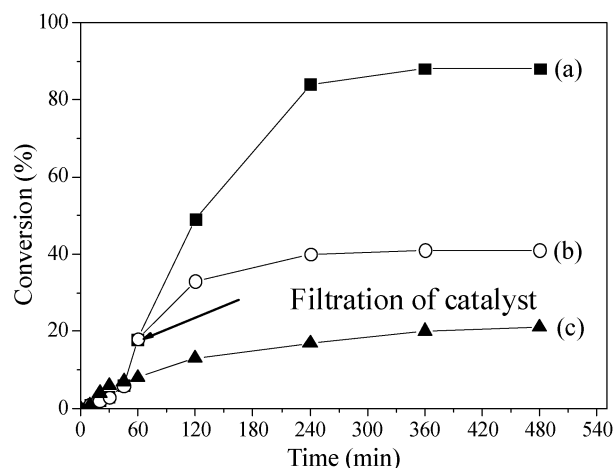


Fig. 9 Tetralin oxidation using O₂/trimethylacetaldehyde at 80 °C, catalyst amount 10 mg in acetonitrile: (a) with Cr_{1.6}APO-5H catalyst, (b) filtrate (catalyst filtering off after 60 min reaction), (c) in the absence of catalyst (in the presence of O₂ and trimethylacetaldehyde only).

Table 4 Catalytic activities of various catalysts in tetralin oxidation

Catalyst	Oxidant	Tetralin conversion (%)	1-Tetralone selectivity (%)	Ref.
Cr _{1.6} APO-5H	<i>t</i> -BuOOH	57.0	86.2	Present
Cr _{1.6} APO-5H	Trimethylacetaldehyde and O ₂	88.0	97.3	Present
CrMCM-41	<i>t</i> -BuOOH	92.5	95.0	20
CrZSM-5	<i>t</i> -BuOOH	—	85.0	24
CrAPO-5	<i>t</i> -BuOOH and O ₂	44.0	64.0	14
Fe/MgO	Acetaldehyde, <i>N</i> -hydroxyphthalimide and O ₂	99.0	52.0	9
OMS-2 (KMn ₈ O ₁₆)	<i>t</i> -BuOOH	70.9	70.1	11
MIL-101	<i>t</i> -BuOOH	68.0	85.5	26
MIL-101	Trimethylacetaldehyde and O ₂	66.0	93.0	26

presence of the catalyst. However, 1-tetralone selectivity in the filtrate (86%) remained virtually the same as that obtained in the presence of Cr_{1.6}APO-5H.

Similarly for the trimethylacetaldehyde/O₂ oxidant system (Fig. 9), reaction also proceeded in the filtrate with a similar trend after the catalyst was separated after 60 min reaction time. Again, 1-tetralone selectivity in the filtrate remained high at 95%. The higher tetralin conversion (by 9–10%) in the filtrate (b) compared with the one under the blank condition (c) appears to be mainly attributable to the thermal reaction caused by reaction intermediates remaining in the filtrate.¹³ A minor contribution from the trace amount of leached Cr, however, could not be ruled out.

To estimate the potential Cr contribution in the filtrate to the reaction, tetralin oxidation was also carried out in chlorobenzene using soluble pyridinium dichromate at a tetralin : *t*-BuOOH mole ratio of 1 : 2 at 80 °C. Conversion of tetralin gradually increased from 19 to 36% but selectivity of 1-tetralone remained low (42–48%) with varying Cr concentration from 1 to 100 ppm. Tetralin oxidation after hot catalyst filtration, however, shows a completely different trend in 1-tetralone selectivity (86–95%) as mentioned above. Therefore, the higher tetralin conversion and selectivity attained in the presence of the present catalyst seem to be attributed mostly to the framework Cr in the Cr_{1.6}APO-5H.

Comparison of performances against other catalytic systems

A comparison of our work against some earlier published data for the oxidation of tetralin was made and the findings are listed in Table 4. The comparison shows that the present CrAPO-5H is highly active in O₂ in combination with trimethylacetaldehyde as an oxidant in the oxidation of tetralin, and is found to produce 1-tetralone with higher selectivity compared to data previously reported for Cr-MCM-41²⁰ and CrAPO-5.¹⁴ As mentioned earlier, the origin of the high yield of 1-tetralone may be associated with continuous formation of the active *in situ* generated acylperoxy radicals in the trimethylacetaldehyde/O₂ system. The present catalyst CrAPO-5H with *t*-BuOOH as an oxidant also provided generally higher selectivity to 1-tetralone than did previously reported catalysts.^{9,11,14}

Conclusions

In this work, we synthesized a series of CrAPO-5 catalysts having a unique microporous–mesoporous hierarchical pore structure (CrAPO-5H) with varying Cr contents and tested the materials for the oxidation of tetralin using different oxidant

systems. Ammonium acetate-washed catalysts were reusable several times with retention of high catalytic activity and selectivity. CrAPO-5H was catalytically more efficient than conventional CrAPO-5 using either *t*-BuOOH or O₂/trimethylacetaldehyde oxidant systems. Furthermore, the use of *in situ* generated acylperoxy radicals *via* a trimethylacetaldehyde/O₂ oxidant system was found to be a more efficient method for the transformation of tetralin to 1-tetralone. In addition, the continuous feeding of oxidant resulted in superior catalytic performance than one-injection of oxidant. The sources of oxidant and the nature of solvents were found to play important roles on the yield and selectivity of the final product. Recycling, hot filtering, and blank experiments indicated that oxidation occurred over CrAPO-5H through mostly heterogeneous chromium centers and thermal autoxidation, but a contribution from leached Cr in solution could not be entirely excluded.

Experimental

Materials

Aluminium isopropoxide (Aldrich), Al(OH)₃ (Aldrich, 98%), orthophosphoric acid (85 wt%, Aldrich), chromium(III) acetate hydroxide (Aldrich), 3-(trimethoxysilyl)-propyl-hexadecyldimethylammonium chloride (Aldrich), tetralin (99%, Aldrich), trimethylacetaldehyde (96%, Aldrich), triethylamine (99.5%, Fluka), isobutyraldehyde (99.5%, Aldrich), acetaldehyde (99%, Aldrich), and *tert*-butyl hydroperoxide (5–6 M solution in decane, Aldrich) were purchased and used without further purification.

Catalyst preparation

CrAPO-5H catalysts were synthesized by adding 3-(trimethoxysilyl)propylhexadecyldimethylammonium chloride ([[(CH₃O)₃SiC₃H₆N(CH₃)₂C₁₆H₃₃]Cl, TPHAC) into the conventional synthesis composition of CrAPO-5. In a typical synthesis, aluminium isopropoxide {Al(O-*i*-Pr)₃}, phosphoric acid (Aldrich, 85%), triethylamine, chromium(III) acetate hydroxide, TPHAC (60% methanol solution), and distilled water were mixed to obtain the following gel composition. 1Al₂O₃ : 1 P₂O₅ : *x*Cr₂O₃ : 1.6 triethylamine : 100 H₂O : 0.1 TPHAC, where *x* = 0.5, 1.0, 2.0, and 4.0. The synthesis gels were transferred to a stainless steel autoclave and hydrothermally treated at 200 °C for 2 days. The solid products obtained were filtered, washed with distilled water, and calcined at 550 °C.

For comparison, a microporous CrAPO-5 sample was synthesized following the recipe reported by Chen and

Sheldon.¹⁴ Pure Al(OH)₃ (3.9 g) was slowly added to a solution of 4.9 g phosphoric acid (85 wt%) dispersed in 10 g water with stirring. An aqueous solution (8.0 g) of chromium(III) acetate hydroxide was then added to the above mixture dropwise with stirring for 2 h and triethylamine (2.5 g) was then added slowly to the mixture while stirring for a further 2 h. The gel-like mixture was sealed in a Teflon-lined stainless-steel autoclave and digested at 180 °C for 36 h. Upon cooling, the product was isolated by filtration, washed thoroughly with distilled water, and dried overnight at 60 °C. The material was heated in air to 550 °C at 5.0 °C min⁻¹ and calcined for 5 h.

Subsequently, chemical washing of the catalysts was carried out by treating the catalysts with a 3 M ammonium acetate solution. In a typical procedure, 100 mg of calcined catalyst was introduced to a 3 M ammonium acetate aqueous solution (30 ml), and stirred for 12 h at room temperature. The catalysts were filtered and then activated by the same procedure as earlier. Hereinafter, the sample prepared after ammonium acetate washing was denoted as Cr_nAPO-5H (or Cr_nAPO-5), where *n* stands for the actual Cr mol% of the catalyst.

Catalyst characterization

X-Ray powder diffraction patterns of the prepared catalysts were recorded on a Philips PW-1700 diffractometer using Ni-filtered CuKα ($\lambda = 1.54 \text{ \AA}$). BET surface areas were measured on a Micromeritics ASAP 2020 surface analyzer at -196 °C. Prior to the measurements, samples were degassed at 250 °C for 6 h. SEM micrographs were taken on a Hitachi S-4200. Chromium contents of the catalysts were measured by SEM-EDX. Metal contents in the filtrate in the hot filtering experiment and recycle runs were determined using inductively coupled plasma-MASS spectrometry (ICP-MS, Perkin-Elmer élan 6100). UV-Vis diffuse reflectance spectra were obtained on a Varian CARY 3E double-beam spectrophotometer using MgO as a reference at ambient temperature.

Tetralin oxidation

A tetralin oxidation reaction using *t*-BuOOH as an oxidant was carried out using a Chemistation PPS-2510 fitted with a condenser (Eyela). In a typical reaction, a mixture of 8 mmol tetralin, 5 ml chlorobenzene (solvent), and 0.05 g of catalyst was placed into a Chemistation glass reactor and heated to the desired temperature. Unless otherwise stated, we used CrAPO-5H containing 1.6 mol% Cr (Cr_{1.6}APO-5H) as the standard catalyst. The oxidant (*t*-BuOOH, 16 mmol) was then added through a septum to the reactant mixture and stirred at 600 rpm. Alternatively, *t*-BuOOH was added at a rate of 0.9 ml h⁻¹ via a syringe pump for continuous injection of the oxidant. Oxidation of tetralin was also carried out using O₂ at atmospheric pressure in a twin-necked round flask equipped with a condenser. In a typical run, 2 mmol of tetralin, 4 mmol aldehyde, 10 mL acetonitrile, and 0.01 g of catalyst were stirred while bubbling O₂ at atmospheric pressure and maintaining the desired reaction temperature. Tetralin conversion and product selectivity were measured using a GC (7890A GC System, 7683B series injector, Agilent

Technologies) fitted with a high performance HP-5 capillary column (30 m, 0.32 mm, 0.25 μm) and a FID.

Catalyst hot filtration experiments were carried out by separating the catalyst quickly from the reaction mixture after 30 min reaction while maintaining the reaction temperature (80 °C). The filtrate mixture was further stirred at 80 °C for an additional duration of up to 450 min.

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