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Selective Oxidation of Hydrocarbons with O_2 over Chromium Aluminophosphate-5 Molecular Sieve

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Chromium-substituted aluminophosphate-5 (CrAPO-5) is a heterogeneous, recyclable catalyst for the liquid phase autoxidation of hydrocarbons. CrAPO-5 catalyzed the autoxidation of cyclohexane at 115–130°C and 5 bar O_2, 20 bar air in the presence of a small amount of an alkyl hydroperoxide initiator, to afford cyclohexanone as the major product. Similarly, tetralin and indane were selectively oxidized to 1-tetralone and 1-indanone, respectively, at 100°C and 1 bar O_2. Ethylbenzene was selectively converted to acetophenone, in the presence of sodium-exchanged CrAPO-5, at 130°C and 1 bar O_2. The CrAPO-5 catalyst was recycled four times without loss of activity or selectivity in the decomposition of cyclohexyl hydroperoxide. Evidence is presented to support a mechanism involving initial free radical autoxidation of the hydrocarbons followed by selective CrAPO-5-catalyzed intramolecular, heterolytic decomposition of the secondary alkyl hydroperoxide intermediate to the corresponding ketone and water.

INTRODUCTION

Selective metal-catalyzed oxidations of hydrocarbons with molecular oxygen are of immense importance in chemicals manufacture (1). Among alkane oxidations, for example, the selective oxidation of cyclohexane to cyclohexanone has particular commercial significance since cyclohexanone is the key intermediate in the manufacture of nylon 6 and nylon 6,6 (2). 1-Tetralone is important commercially as the starting material for 1-naphthol manufacture (3). In the autoxidation of cyclohexane, most industrial processes involve the use of soluble cobalt or manganese catalysts at 150–180°C and afford a mixture of cyclohexanol, cyclohexanone, and dicarboxylic acids formed by further oxidation of the cyclohexanone and cyclohexanol (4). Since the cyclohexanone and cyclohexanol products are substantially more reactive than the cyclohexane reactant, high selectivities to the sum of cyclohexanone and cyclohexanol are observed only at low (<5%) cyclohexane conversions. Higher conversions (10–15%) can be achieved by carrying out the oxidation in the presence of stoichiometric amounts of boric acid which reacts with the cyclohexanol to give the borate ester (5). However, this process involves the recycling of large amounts of boric acid and the cyclohexanol product has to be dehydrogenated, in a separate step, to cyclohexanone. Moreover, the use of soluble metal catalysts in these systems often necessitates a tedious catalyst separation step. Consequently, the development of effective recyclable solid catalysts could offer advantages.

Two groups (6, 7) have recently reported the use of a cobalt-substituted aluminophosphate-5 (CoAPO-5) as a heterogeneous catalyst for the autoxidation of cyclohexane in acetic acid as solvent. The intermediate cyclohexanol is converted to the more stable cyclohexyl acetate. Hence, this system suffers from the inherent disadvantages of requiring acetic acid solvent and separate hydrolysis and dehydrogenation steps.

Recently, we reported that a chromium-substituted aluminophosphate-5 (CrAPO-5) is an active and very selective catalyst for the oxidation of secondary alcohols, using either molecular oxygen or *tert*-butyl hydroperoxide (TBHP) as oxidant (8) and for the decomposition of alkyl hydroperoxides (9, 10). We now report the use of CrAPO-5 as a selective, recyclable catalyst for the autoxidation of hydrocarbons to the corresponding ketones, in the absence of a solvent (11), conditions which more closely approximate those of industrial processes.

EXPERIMENTAL

Catalyst Preparation

CrAPO-5 was hydrothermally synthesized by a modified version of the published procedure (12). The gel composition was $0.025–0.05Cr_2O_3 : 0.93–0.9Al_2O_3 : P_2O_5 : Pr_3N : 50H_2O$. Typically, pseudoboehmite was hydrolyzed for 2 h at room temperature. A solution of $Cr_3(OH)_2(CH_3COO)_7$ in deionized water was combined with H_3PO_4(85%) and the resulting solution added to the alumina slurry at room temperature. After aging for 1 h

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at room temperature, the tri-*n*-propylamine was added dropwise followed by vigorous stirring at 0°C for another 2 h. Finally, the gel was charged in a Teflon-lined autoclave and allowed to crystallize for 24 h at 175°C. The CrAPO-5 crystals were filtered and washed several times with water until a clear liquid was obtained. The crystals were dried at 120°C for 4 h and then calcined at 500°C for 10 h.

Twofold ion exchange was made by placing 2 g of the calcined CrAPO-5 in 400 ml of 0.1 *M* NaCl aqueous solution (Na/Cr > 100), which was shaken at room temperature for 24 h and subsequently washed three times with water, to completely remove nonframework Cr species before use.

Catalyst Characterization

Synthesized and calcined samples were characterized by X-ray diffraction (XRD) using a Philips PW 1877 automated powder diffractometer with Cu*Kα* radiation, scanning electron microscopy (SEM) using a Jeol JSM-35 scanning microscope, and diffuse reflectance spectroscopy (DRS) using a Hitachi 150-20 UV-VIS spectrophotometer equipped with a diffuse reflectance unit. The unit cell volume was measured by XRD using a Guinier-de Wolff camera with wavelength of 1.54 Å (Cu*Kα*). Elemental analysis was performed using inductively coupled plasma-atomic emission spectrometry (ICP, Perkin-Elmer Plasma-II).

The acidic properties of calcined CrAPO-5 were studied by IR absorption spectroscopy. IR spectra were measured on a Bruker FTIR spectrometer (IFS 113v) equipped with a vacuum cell. Self-supporting discs with a thickness of 6 mg cm^{-2} were used. The measurements were carried out by co-adding 500 scans at room temperature with a resolution of 1 cm^{-1}. Activation of the samples was performed at 447°C in high vacuum for 1 h. After the sample had been cooled to room temperature the spectrum of the unloaded sample was taken, followed by contacting the sample with deuteriated acetonitrile at a pressure of 1.3 mbar for 30 min, then another spectrum was recorded. After this, the loading of the sample was reduced stepwise by lowering the equilibrium pressure of the deuteriated acetonitrile to 0.05 mbar and by desorption at room temperature for 15 min. The last two spectra were recorded after desorption for 60 min at 80 and 300°C, respectively.

Oxidation of Hydrocarbons with O_2

The autoxidation of cyclohexane was carried out in a 300-ml autoclave (Parr Instrument, USA) equipped with a heating jacket, stirrer, water cooled condenser, liquid separator, outlet for gas with needle valve, and sampling valve. Typically, 78.1 g (928 mmol) of cyclohexane containing 0.5 wt% cyclohexyl hydroperoxide (CHHP), 4.8 g (1.4 mmol Cr) of CrAPO-5, and 5.5 g of chlorobenzene (internal standard) were introduced into the reactor with a Teflon insert inside. The reactor was charged with 20 atm of air and 5 atm of O_2, heated to 115°C within 15 min with stirring and kept at this temperature for about 6 h, while O_2 was fed continuously to maintain a constant O_2 concentration. When the reaction was stopped, the catalyst could be separated by filtration.

The autoxidations of tetralin and indane were carried out in a 50-ml thermostated flask equipped with a condenser and a magnetic stirrer. Typically, 6.61 g (50 mmol) of tetralin, 1.2 g of *p*-dichlorobenzene (internal standard), and 2.5 g (0.72 mmol Cr) of CrAPO-5 were charged and O_2 was bubbled at a rate of 15 ml/min through the reaction mixture at 100°C. 1.54 g of TBHP (5 mmol) in chlorobenzene was added dropwise into the reaction mixture during the reaction with stirring at 1000 rpm. The reaction was continued at 100°C for 10 h. The autoxidation of ethylbenzene was carried out at 130°C for 6 h using 0.173 or 2.5 g (0.05 or 0.72 mmol Cr) of sodium exchanged CrAPO-5 as catalyst, and the other conditions are the same as given above.

Decomposition of Cyclohexyl Hydroperoxide and Oxidation of Cyclohexanol

The procedure of the decomposition of cyclohexyl hydroperoxide was reported elsewhere (10). The oxidation of cyclohexanol was carried out with the same setup as the decomposition. Typically, 0.29 g (2.9 mmol) of cyclohexanol, 0.94 g (2.9 mmol) of TBHP in chlorobenzene, 0.10 g of *n*-decane (internal standard), and 0.10 g (0.029 mmol Cr) of CrAPO-5 were charged in 12 ml of chlorobenzene (solvent), and the oxidation proceeded at 70°C for 5 h.

The quantitative analyses were carried out by gas chromatography (GC) with a capillary column (25 m × 0.32 mm CP Sil 5 CB) for the autoxidation of cyclohexane, and with a semicapillary column of (25 m × 0.53 mm, CP WAX 52 CB) for the other reactions. A reaction aliquot was diluted with twice its volume of acetone to dissolve carboxylic acids. After destroying remaining hydroperoxides by the addition of an excess of triphenylphosphine, the mixture was silylated with 200 μl of hexamethyldisilazane and 100 μl of trimethylchlorosilane for 30 min at room temperature. The concentrations of alkyl hydroperoxides were determined by iodometric titration. Typically, 1.0 g of a reaction mixture was diluted with 35 ml of chloroform/acetic acid (1 : 2 v/v). Saturated aqueous KI solution (25 ml) was added and the solution was allowed to stand for 30 min in the dark before adding 50 ml of deionized water and then titrating with 0.1 *M* sodium thiosulfate.

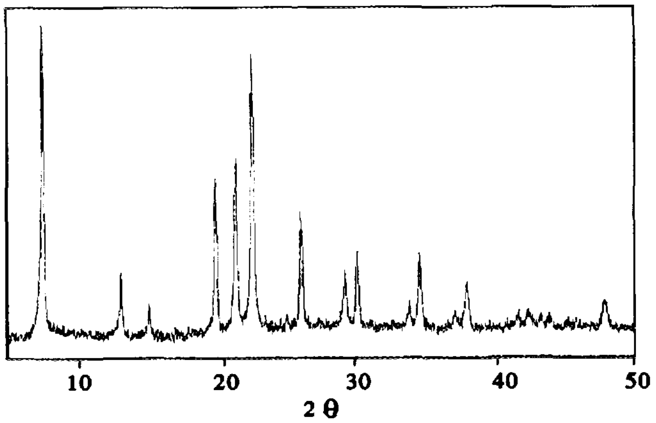


FIG. 1. XRD powder diffraction pattern of calcined CrAPO-5.

RESULTS AND DISCUSSION

Characterization of CrAPO-5

Figure 1 shows the typical XRD powder diffraction pattern of calcined CrAPO-5, which demonstrates that the product is pure and highly crystalline material with AFI structure, being in agreement with that in the literature (12). No phase related to chromium oxides or chromium clusters could be detected. SEM pictures show that as-synthesized and calcined products are uniform in size. When the crystallization was performed in a rotating autoclave this led to a decrease in particle size of CrAPO-5 from 50 (static) to 7 μm. The pore volumes of CrAPO-5 samples are 0.136 to 0.139 ml/g (determined by the BET method), comparable to that (0.138 ml/g) of $AlPO_4$-5 and close to the theoretical value of 0.140 ml/g, confirming that no impurities block the micropores of catalysts.

The DRS spectrum of calcined CrAPO-5 is presented in Fig. 2. In accordance with the literature (13, 14) the strong absorption bands around 270 and 340 nm are assigned to the two charge transfer transitions of Cr(VI). Weckhuysen and Schoonheydt (15) reported a quantitative method for determining Cr(III) and Cr(VI) by DRS and concluded that Cr(III) is almost quantitatively oxidized to Cr(VI) in the calcined CrAPO-5. Similar results were obtained with our calcined CrAPO-5.

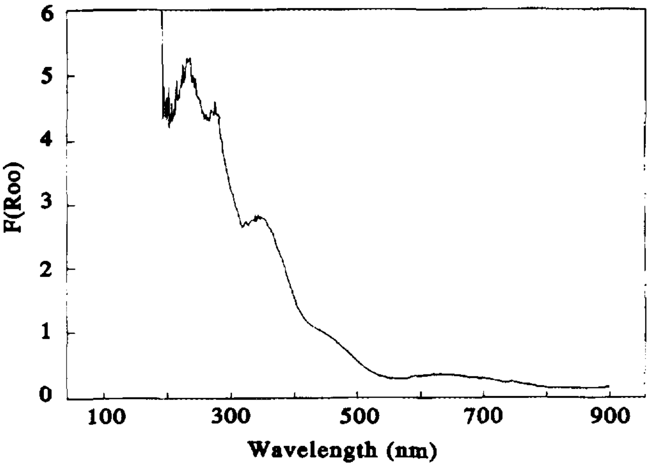


FIG. 2. DRS spectrum of calcined CrAPO-5.

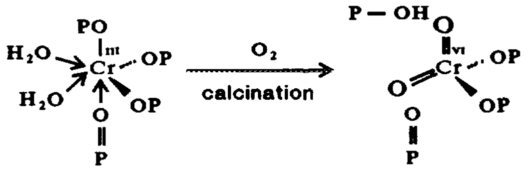


FIG. 3. Location of chromium in as-synthesized and calcined CrAPO-5.

It was reported that nonframework Cr(VI) species could be easily and almost quantitatively extracted from a calcined CrS-1 sample (14) or a calcined Cr-exchanged zeolite (16) by washing it with cold water. However, repeated ion exchange treatments of our calcined CrAPO-5 with NaCl aqueous solution did not cause any loss of the Cr(VI) from the calcined CrAPO-5. Furthermore, confirmation of the incorporation of Cr in the framework was further supported by the observed decrease of 0.26% in the unit cell volume of calcined CrAPO-5 containing 1.5% Cr when compared to the corresponding $AlPO_4$-5. During calcination most of the Cr is oxidized to the hexavalent state (DRS) which probably exists as a dioxochromium(VI) species formed by breaking Cr–O–P bonds. This actually creates defect sites in the CrAPO-5 framework and is most probably responsible for the decrease of unit cell volume.

The as-synthesized Cr(III)$AlPO_4$ is electronically neutral. We tentatively assume that, in the as-synthesized CrAPO-5, Cr(III) is most likely to be octahedrally coordinated (there are two extra water ligands) within the framework. During calcination it is presumed to afford dioxochromium(VI) which is still bonded to the internal aluminophosphate structure. In order to balance the charges Cr(VI) $AlPO_4$ must contain an acidic P–OH group in its microenvironment (see Fig. 3). The H of the P–OH group is most probably derived from decomposition of the tri-*n*-propylamine template (the amount occluded inside the as-synthesized CrAPO-5 is more than sufficient for providing the H) during calcination. This assumption was confirmed using DRS. The measurements performed on the as-synthesized CrAPO-5 were in agreement with Cr(III) in octahedral coordination within the $AlPO_4$-5 framework. When the sample was heated to 347°C to remove only water without oxidizing the Cr(III) species, the coordination of Cr(III) changed from octahedral to tetrahedral (17). After calcination in air the Cr(VI) was

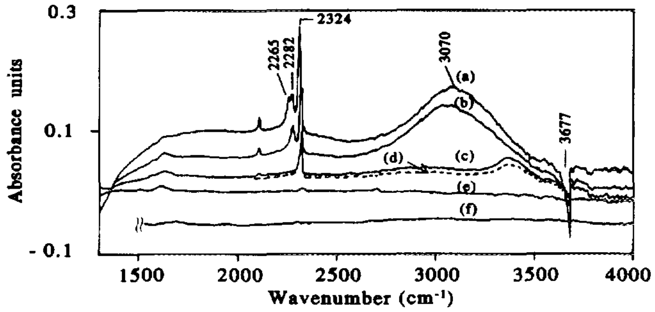


FIG. 4. IR difference spectra of CrAPO-5 and AlPO$_4$-5 loaded with d_3-acetonitrile. CrAPO-5: (a) Adsorption at 22°C for 30 min with a pressure of 1.3 mbar and (b) with 0.05 mbar; (c) desorption at 22°C for 15 min, (d) at 80°C for 60 min, and (e) at 300°C for 60 min. (f) AlPO$_4$-5 desorption at 22°C for 15 min.

tetrahedrally coordinated, which is consistent with the literature (13).

That substitution of Cr for Al in AlPO$_4$-5 increases the framework acidity was further supported by microcalorimetry measurements (18), which showed that after subtracting a small amount due to the blank sample (AlPO$_4$-5), 0.26 mmol/g catalyst of irreversible NH$_3$ was adsorbed by the calcined CrAPO-5, corresponding to 0.92 NH$_3$ per Cr atom. Thus, framework substitution of Al by Cr, after the calcination at 500°C, generates about one acidic site (P–OH) per Cr^{VI}. The presence of outer surface chromium oxides can be ruled out, since no characteristic adsorption was observed. Moreover, IR measurements using acetonitrile as a probe for the identification of different acid sites on CrAPO-5 confirmed that incorporation of Cr in the AlPO$_4$-5 framework created both strong Lewis acid sites (absorption band at 2324 cm^{-1}) and acidic P–OH groups (at ca. 3070 cm^{-1}). After a desorption treatment, the band at ca. 3070 cm^{-1} is still observed, which is strongly indicative of some acidic P–OH groups in the neighborhood of the Lewis acid sites (see Fig. 4). Moreover, a Cr(VI) species bound to the AlPO$_4$-5 framework is coordinatively unsaturated and should exhibit the characteristics of strong Lewis acid (19, 20).

Peeters *et al.* (21) reported a quantitative ^{31}P MAS NMR study of CrAPO-11. They found that substitution of Al by Cr had a significant effect on the framework, in which at least the first and the third coordination sphere (P) around the Cr nuclei became NMR invisible. In contrast, nonframework Cr did not seem to have such an effect. Similarly, Helliwell *et al.* (22) concluded from a single crystal study of as-synthesized CrAPO-14 that about 5% of Al at the octahedral coordinate site was substituted by Cr.

Oxidation of Cyclohexane with O_2

The results of the oxidation of cyclohexane with molecular oxygen catalyzed by CrAPO-5 at 115°C are presented in Fig. 5. A small amount (0.5%) of CHHP was added to the reaction mixture prior to reaction, as an initiator, and no induction time was observed. In practice, a small amount of the CHHP-containing product stream could be recycled to the oxidation reaction. The results in Fig. 5 reveal that CrAPO-5 predominantly produces cyclohexanone, which, as noted above, is an advantage for industrial processes.

Table 1 compares the results of the oxidation of cyclohexane with molecular oxygen at 115 and 130°C. Although a decrease in the selectivity for cyclohexanone and cyclohexanol with increasing conversion was observed at the higher reaction temperature, the ratios of cyclohexanone to cyclohexanol were almost constant, regardless of different temperatures and reaction time. This strongly suggests that the high selectivity for cyclohexanone is not caused by a consecutive oxidation of cyclohexanol. It was further observed that turnover numbers (note that the Cr is assumed to be atomically dispersed in CrAPO-5 since there is no indication from the characterization data that Cr oxides or clusters existed in CrAPO-5 samples) in the decomposition (10) were higher than that in the autoxidation of cyclohexane even at the lower temperature (70°C). This is consistent with rate-determining formation of CHHP followed by its rapid catalytic decomposition. A proposed reaction pathway is shown in Scheme 1.

Mechanism of Cyclohexanone Formation

Because a key function of the CrAPO-5 is to selectively catalyze the decomposition of CHHP into cyclohexanone, we investigated the mechanism of this reaction (Scheme 2). We previously reported (10) that CrAPO-5 was the most selective catalyst among various redox molecular sieves tested for the decomposition of CHHP to cyclohex-

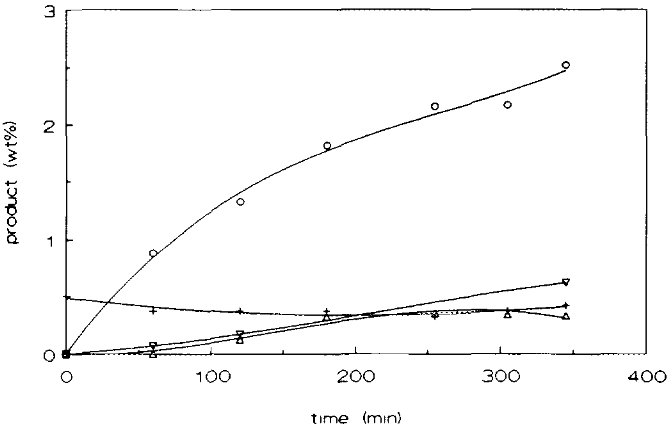


FIG. 5. Product distribution of CrAPO-5-catalyzed oxidation of cyclohexane with O$_2$ at 115°C. Conditions as given in Table 1. ○, cyclohexanone; Δ, cyclohexanol; ▽, others (see Table 1); and +, CHHP.

TABLE 1

Selective Oxidation of Cyclohexane with Molecular Oxygen over CrAPO-5[a]

T (°C)	Time (h)	Conversion (%)	Turnovers[b] (h^{-1})	Selectivity (%) Ketone[c]	Alcohol[d]	CHHP	Others[e]
130	1.4	3.4	14.2	71.0	8.0	12.4	8.6
130	5.5	10.5	11.9	48.1	5.4	6.4	40.1
115	5.8	3.8	4.0	65.6	8.6	9.6	16.2

[a] Reaction conditions: cyclohexane, 928 mmol; O_2, 5 atm; air, 20 atm; CHHP, 3.4 mmol; CrAPO-5, 1.4 mmol Cr.

[b] Moles of oxygenated products except CHHP over 1 mole of chromium in 1 h.

[c] Cyclohexanone.

[d] Cyclohexanol.

[e] A major product is adipic acid.

anone at 70°C, giving a cyclohexanone/cyclohexanol ratio of 7. The observed results with CrAPO-5 are strongly indicative of reaction occurring predominantly via a heterolytic pathway (reaction 1), since a homolytic pathway (Haber-Weiss mechanism, reaction 2) would afford cyclohexanol as the major product. However, CrAPO-5 is also an active catalyst for the oxidation of cyclohexanol and therefore an intermolecular reaction (reaction 3) of initially produced cyclohexanol with CHHP could not be *a priori* excluded. In order to distinguish between the intramolecular (reaction 1) and the intermolecular mechanism, we performed the oxidation of cyclohexanol with cyclohexenyl hydroperoxide or TBHP as oxidant; under the same reaction conditions and time, only about 6% cyclohexanone was formed, while the decomposition of CHHP gave cyclohexanone in 86% selectivity at 87% conversion (Table 2). From these results we conclude that the decomposition of CHHP mainly involves an intramolecular, heterolytic β-hydrogen elimination from an alkylperoxochromium(VI) intermediate without any change in the oxidation state of Cr (23).

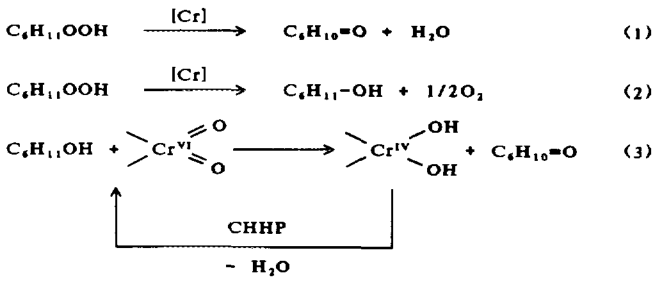
Oxidation of Alkylaromatics with O_2: Active Species of the Catalyst

Similarly, the alkylaromatic hydrocarbons tetralin and indane were oxidized with molecular oxygen at one atmosphere, using 10 mol% of TBHP as initiator. As shown in Table 3, the major products in both reactions are the corresponding ketones. The small amounts of alcohols formed probably result from a competing homolytic reaction pathway at 100°C. When tetralin hydroperoxide was decomposed by CrAPO-5 at 70°C, 1-tetralone was observed as the only product. It was also observed that the selectivity of 1-indanone increased with increasing ratio of Cr to indane. Surprisingly, in the autoxidation of ethylbenzene CrAPO-5 appeared to function as an inhibitor. When the autoxidation was carried out at 130°C for 6 h in the absence of the catalyst and solvent, a 99% selectivity of ethylbenzene hydroperoxide was obtained at a 20% conversion of ethylbenzene. In contrast, in the presence of CrAPO-5 only a 3% conversion was observed.

As can be seen from Table 4, when using CrAPO-5 as the catalyst for the autoxidation of ethylbenzene 1.5% of the ethylbenzene was converted to phenol, which was most probably produced by an acid-catalyzed decomposition of ethylbenzene hydroperoxide and is the cause of the inhibition of the autoxidation (24). This was confirmed by the observation that similar results were obtained with SAPO-5 (only acid sites available) as the catalyst. On the

$$
\begin{aligned}
&R^1R^2CH_2 \xrightarrow{\text{initiation}} R^1R^2CH\cdot \\
&R^1R^2CH\cdot + O_2 \longrightarrow R^1R^2CHOO\cdot \\
&R^1R^2CHOO\cdot + R^1R^2CH_2 \longrightarrow R^1R^2CHOOH + R^1R^2CH\cdot \\
&R^1R^2CHOOH + Cr^{VI}{=}O \longrightarrow Cr^{VI}{=}O + R^1R^2C{=}O + H_2O
\end{aligned}
$$

SCHEME 1. A proposed reaction pathway of the autoxidation of hydrocarbons catalyzed by CrAPO-5.



SCHEME 2. Possible reactions occurred in the selective decomposition of CHHP over CrAPO-5.

TABLE 2

Comparison between the Decomposition of CHHP[a] and the Oxidation of Cyclohexanol with Alkyl Hydroperoxide[b] over CrAPO-5

Subtrate	R-(OOH)	Yield (%)[c]
Cyclohexyl hydroperoxide	No	75
Cyclohexanol	Cyclohexenyl-	6
Cyclohexanol	*tert*-butyl-	6

[a] Reaction conditions: CHHP, 2.9 mmol; cyclohexane(solvent), 12 ml; CrAPO-5, 0.029 mmol Cr; temperature, 70°C; duration, 5 h.

[b] Reaction conditions: cyclohexanol, 2.9 mmol; R-(OOH), 2.9 mmol; chlorobenzene(solvent), 12 ml; CrAPO-5, 0.029 mmol Cr; temperature, 70°C; duration, 5 h.

[c] The yield of cyclohexanone based on the substrate (reactant) charged initially.

other hand, an increased conversion (13%) and selectivity to acetophenone (85%) were obtained when CrAPO-5 was ion exchanged with NaCl aqueous solution to reduce the acidity of CrAPO-5. Furthermore, a 72% selectivity of acetophenone at a 23% conversion could be achieved when using the sodium-exchanged CrAPO-5 as catalyst and increasing the molar ratio of ethylbenzene to chromium from 70 to 1000, indicating that a high catalyst concentration can also inhibit the autoxidation via scavenging of alkylperoxy radicals (25). Hence, it can be concluded that the active species of the catalyst is the framework-bound Cr(VI). An acid-catalyzed autoxidation can be ruled out, as the predominant pathway, since it would lead to the formation of phenol from the ethylbenzene autoxidation, and to the nonselective decomposition of the hydroperoxides formed from the autoxidations of cyclohexane, tetralin, and indane.

Accessibility and Stability of Chromium in CrAPO-5

The particle size of the CrAPO-5 samples used is about 50 μm. There was no difference in activity and selectivity between the catalyst with the particle size of 50 and 7 μm for the decomposition of CHHP, indicating that diffusion is not rate limiting. Furthermore, liquid-phase adsorption measurements (18) showed that 80% of initially charged ethylbenzene was adsorbed at 25°C within 0.5 h. In contrast, the autoxidation rate of ethylbenzene is much slower than the rate of ethylbenzene adsorption in CrAPO-5. As discussed above, the formation of alkyl hydroperoxides is rate-determining while the CrAPO-5 catalyzed decomposition step is fast, which further confirms the absence of diffusion effects on these autoxidations.

Evidence for the autoxidation essentially occurring inside the micropores of CrAPO-5 was provided by the observation that the decomposition of triphenylmethyl hydroperoxide hardly took place (1% conversion) at 70°C for 2 h since the hydroperoxide is too bulky to enter the catalyst. In contrast, the soluble Cr(III)acetylacetonate and the supported CrO_2Cl_2/silica–alumina were effective catalysts for the decomposition, giving conversions of 75 and 72%, respectively under the same reaction conditions (26).

CrAPO-5 was recovered by filtration and regenerated at 500°C for 5 h. Table 5 shows that the reused catalyst retained its activity and selectivity for the decomposition of CHHP over four cycles, except the second recycle in which the used catalyst was not recalcined. The recalcination is necessary presumably to remove trace amounts of dicarboxylic acids in the micropores of the CrAPO-5. It was shown that in the autoxidation of tetralin the CrAPO-5 could be recycled five times without loss of activity

TABLE 3

Selective Oxidation of Hydrocarbons with Molecular Oxygen over CrAPO-5[a]

Substrate	Substrate/Cr (Molar ratio)	Conversion (%)	Selectivity (%)		
			Ketone[b]	Alcohol[c]	Peroxide[d]
Indane	70	65	70	8	10
Indane	140	64	57	12	20
Indane	700	45	48	5	35
Tetralin	70	44	64	7	20
Ethylbenzene[e]	70	3	42	0	58

[a] Reaction conditions: substrate, 50 mmol; O_2, 15 ml/min; TBHP, 5 mmol; temperature, 100°C; duration, 10 h.

[b] 1-Indanone or 1-tetralone or acetophenone.

[c] 1-Indanol or 1-tetralol or α-methylbenzyl alcohol.

[d] Indane hydroperoxide or tetralin hydroperoxide or ethylbenzene hydroperoxide.

[e] At 130°C for 6 h.

TABLE 4

Selective Oxidation of Ethylbenzene with Molecular Oxygen over CrAPO-5[a]

Catalyst	Substrate/Cr (Molar ratio)	Conversion (%)	Selectivity (%)			
			Ketone[b]	Alcohol[c]	EBHP[d]	Phenol
No	—	20	1	0	99	0
SAPO-5[e]	—	3	38	0	62	1.2
CrAPO-5	70	3	42	0	58	1.5
Na–CrAPO-5[f]	70	13	85	6	9	0.5
Na–CrAPO-5	1000	23	72	8	20	0.1

[a] Reaction conditions: substrate, 50 mmol; O_2, 15 ml/min; TBHP, 5 mmol; temperature, 130°C; duration, 6 h.

[b] Acetophenone.

[c] α-Methylbenzyl alcohol.

[d] Ethylbenzene hydroperoxide.

[e] Containing 2% Si, 2.5 g was added.

[f] Sodium exchanged CrAPO-5.

and recalcination of the catalyst between cycles was not necessary (26). ICP elemental analysis showed that CrAPO-5 was quite stable during the catalyst recycling and no Cr could be detected in the reaction solutions.

CONCLUSION

CrAPO-5 is an active, selective, and recyclable heterogeneous catalyst for the liquid-phase oxidation of hydrocarbons with molecular oxygen in the presence of a small amount of alkyl hydroperoxide as initiator. This is particularly useful for the selective production of cyclohexanone from cyclohexane. The active catalytic species is chromium(VI) located within the CrAPO-5 framework and stable toward leaching under oxidation conditions. We suggest that the oxidations proceed via initial free radical autoxidation followed by an intramolecular, heterolytic decomposition of the formed alkyl hydroperoxide catalyzed by CrAPO-5.

TABLE 5

Recycles of CrAPO-5 in the Selective Decomposition of Cyclohexyl Hydroperoxide[a]

Recycles[b]	Conversion (%)	Selectivity (%)		Cr (wt%)[c]
		Cyclohexanone	Cyclohexanol	
1	87	86	13	1.63
2[d]	54	—	—	1.56
3	95	85	12	—
4	96	88	12	1.58

[a] Reaction conditions as given in Table 2.

[b] The catalyst was regenerated at 500°C for 5 h.

[c] ICP accuracy = ±3%.

[d] No regeneration treatment before this recycle.

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