Alumina- and Y-zeolite-catalyzed reaction of cyclohexanol with tert-butyl hydroperoxide

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Abstract. The use of γ -alumina and exchanged Y-zeolites as catalysts in the liquid-phase oxidation of cyclohexanol by tert-butyl hydroperoxide (tBHP) has been studied. With γ -alumina, cyclohexanone is formed, whereas the zeolites NaCeY and NaLaY give cyclohexyl formate as the main product. This compound is thought to originate from a zeolite-mediated rearrangement of tBHP to acetone and methanol, oxidation of methanol to formic acid and electrophilic addition of formic acid to cyclohexene (formed in situ from cyclohexanol).

Introduction

For the transformation of a secondary alcohol into the corresponding carbonyl compound, a large number of stoichiometric transition metal oxidants are available. However, from an economical and environmental point of view, there is a need for alternative catalytic oxidation processes. These should make use of readily available and non-polluting oxygen donors, such as *tert*-butyl hydroperoxide (tBHP) and hydrogen peroxide, in combination with a catalyst. In the past decade, several examples of such transition-metalcatalyzed alcohol oxidations have been reported¹⁻⁵.

Application of a heterogeneous catalyst is attractive with respect to the work-up procedure and recovery of the catalyst. Kanemoto et al.6 reported a heterogeneous catalytic analogue of Ce(IV) and Cr(VI) reagents using Ce(IV)- or Cr(VI)-impregnated Nafion-K ion-exchange resins and tBHP to oxidize secondary alcohols.

We have studied the potential of heterogeneous inorganic catalysts in the oxidation of a secondary alcohol by tBHP. The catalytic activities of a Ce-exchanged Y-zeolite (as an inorganic analogue of the Ce-Nafion resin) and y-alumina (known to be active in alcohol oxidation under Oppenauer conditions⁷) have been compared using cyclohexanol as the model secondary alcohol.

Experimental

Materials

Zeolite NaY was obtained from Union Carbide (type SK 40). NaY was exchanged at 293 K (24 h) with 0.033 M aqueous metal chloride solution to yield zeolites denoted as NaMY-70. The percentage of Na ions exchanged for metal ion M, as determined by X-ray fluorescence spectroscopy of the exchanged zeolite, was 70%. γ -Alumina (S_{BET} 200 m²/g) was obtained from Akzo Chemie (Amsterdam, The Netherlands). The catalysts were activated (16 h) in air (zeolites, 673 K) or N_2 (γ -alumina, 473–1073 K). tBHP was obtained as a 70% aqueous solution from Janssen

Chimica (Beerse, Belgium). Benzene was chosen as solvent since it

is not susceptible to oxidation by tBHP⁸. A 4.0 M anhydrous solution of tBHP in benzene was obtained by azeotropic distillation and was stored over zeolite KA⁹. Cyclohexyl formate was prepared according to the literature¹⁰. Other reagents and solvents were analytical-grade commercial products and were used without prior purification.

Adsorption experiments

The competitive adsorption of reactants and products onto zeolite NaCeY-70 was performed by adding a solution of the substrates to the calcined zeolite at 277 K. Adsorption was monitored by GC analysis (vide infra).

Reaction conditions and analysis

tBHP (10-40 mmole) and cyclohexanol (3.5 mmole) dissolved in benzene (25 ml) were added to the calcined catalyst (1.0-2.5 g) at 353 K with stirring under reflux. Samples were withdrawn at appropriate intervals and immediately analyzed by GC (50 m $\,$ capillary CP Si15; internal standard ethylbenzene). Qualitative analysis of formic acid was performed by HPLC (Biorad HPX-87H, 0.01 M trifluoroacetic acid, 333 K) of an aqueous extract of the reaction mixture. At the end of the reaction, any product remaining on the catalyst was desorbed by addition of methanol/ water (80:20 v/v, 4 ml).

Results and discussion

The oxidation of cyclohexanol in the presence of γ -alumina was performed using a tBHP/cyclohexanol ratio of 3:1. The zeolite-catalyzed reaction consumed more tBHP and was performed at an 11:1 ratio. Two types of catalytic activity can be observed and the results are summarized in Tables I and II. A general picture of the reactions observed is shown in Fig. 1.

Type I catalysts: rearrangement of tBHP

With NaCeY-70 as the catalyst, cyclohexanol was transformed into cyclohexanone and cyclohexyl formate as the major products (Table I). tBHP was not only reduced to



Fig. 1. Reactions of cyclohexanol (with tBHP) on γ -alumina, NaCeY, NaLaY and NaHY.

tert-butanol, but also rearranged to acetone and methanol. Di-*tert*-butyl peroxide and formic acid (HPLC) were also formed. Evolution of oxygen was not observed.

There was no involvement of the Ce(III)/Ce(IV) redox couple in the rearrangement of tBHP on NaCeY-70, since (i) the NaLaY-70-catalyzed oxidation resembles that of NaCeY while La(III) has no higher oxidation state and (ii) no Ce(IV) was detected in a tBHP-treated NaCe(III)Y-70 zeolite [Fe(II) titration of hydrolyzed zeolite]. With NaHY, formation of cyclohexyl formate was also observed. In contrast, non-exchanged NaY yielded cyclohexanone with moderate selectivity and no cyclohexyl formate was observed.

The adsorption strength of reactants and products was found to follow the sequence tBHP > cyclohexanol > cyclohexanone > cyclohexyl formate. This indicates that the reactants will continuously replace the products formed during the reaction.

The rearrangement of tBHP and the formation of cyclohexyl formate with NaCeY, NaLaY or NaHY is ascribed to strong Brönsted acid sites formed in these zeolites during calcination¹¹. The following sequence of steps, leading to the formation of cyclohexyl formate, is proposed:

- tBHP undergoes a zeolite-acid-catalyzed rearrangement to acetone and methanol (Fig. 2);
- methanol is oxidized (by the excess tBHP) to formic acid;
- cyclohexanol is dehydrated to cyclohexene;
- electrophilic addition of formic acid to cyclohexene gives cyclohexyl formate.

The overall reaction is shown in Fig. 3.

Acid-catalyzed rearrangement of tBHP has been previously reported and, in 96% H_2SO_4 , acetone and methyl hydrogen sulfate are the only reaction products¹². In acetonitrile with $HClO_4$, acetone, methanol and di-*tert*-butyl peroxide are formed¹³ and tBHP reacts with 58% H_2SO_4 to give 70% di-*tert*-butyl peroxide together with bis(*tert*-butylperoxy)methane [formaldehyde bis(*tert*-butylperoxyacetal)]¹⁴. A comparable, zeolite induced, rearrangement of cumene hydroperoxide has also been reported; phenol and acetone



Fig. 2. Zeolite-acid-catalyzed rearrangement of tBHP.

Table I Reaction of tBHP with cyclohexanol using zeolite catalysts (Type I)^a.

Catalyst	Cyclohexanol	tBHP	Selectivity ^b to	Selectivity ^b to	Other
	conversion	conversion	cyclohexanone	cyclohexyl formate	products ^c
	(%)	(%)	(%)	(%)	(%)
NaCeY-70	44	87	30	51	19
NaLaY-70	47	100	19	70	11
NaHY-70	20	49	35	10	55
NaY	32	17	67	0	33
NaCoY-70	39	100	28	0	72

^a tBHP (40 mmole) and cyclohexanol (3.5 mmole) in benzene (25 ml) were added to the catalyst (2.5 g, activated at 673 K, 16 h, air) at 353 K; reaction time 8 h. ^b Selectivity based on cyclohexanol converted. ^c Cyclohexanol-derived products, characterized as *tert*-butyl-and *tert*-butyssubstituted cyclohexanols and cyclohexanones and *tert*-butyl cyclohexyl ether.



Fig. 3. Overall equation for the reaction of cyclohexanol with tBHP to give cyclohexyl formate.

are formed on zeolite beta (Si/Al = 30) at 450 K¹⁵, or on NaCaY at 393 K¹⁶.

Since formaldehyde can be formed by oxidation of the methanol arising in the tBHP rearrangement¹⁴, further oxidation to formic acid should be possible. Indeed, we have found formic acid, methanol, acetone, *tert*-butanol and di-*tert*-butyl peroxide as decomposition products of tBHP on NaCeY.

Brönsted-acid-catalyzed¹⁷ dehydration of cyclohexanol to cyclohexene (in the absence of tBHP) was found to occur readily on NaCeY and NaLaY (80 and 100% conversion after 24 h, 100% selectivity to cyclohexene). In a separate experiment, the reaction of cyclohexanol or cyclohexene with formic acid with NaCeY as catalyst to yield cyclohexyl formate was shown to be quantitative and fast.

Comparison of NaCeY, NaLaY and NaHY with NaCoY provides further evidence for the heterolytic mechanism of formation of cyclohexyl formate on the Brönsted acid zeolites. With NaCoY, no cyclohexyl formate is formed. On this zeolite, tBHP is catalytically decomposed via a homolytic pathway involving Co(II)/Co(III) redox cycles (with formation of *tert*-butanol, water and oxygen¹⁸).

Thus, in contrast with the Ce-Nafion-resin-based system⁶, catalytic activity of NaCeY is dominated by its acidic character.

Type II catalysts: oxidation of cyclohexanol

With γ -alumina as the catalyst, selective oxidation of cyclohexanol to cyclohexanone occurred and tBHP was reduced to *tert*-butanol (Table II). Dehydrated zeolite KA was added in order to adsorb the water formed during the reaction and thus to prevent deactivation of the catalyst⁷. The water-deactivating effect is shown by the increased cyclohexanol conversion on γ -alumina upon KA addition and by the lower activity of γ -alumina in the presence of water (Table II, entries 3, 4 and 5). Zeolite KA itself was hardly active as a catalyst (entry 2). A reaction time exceeding 8 h gave additional formation of *tert*-butyl- and *tert*butoxy-substituted cyclohexanols and cyclohexanones.

An increased cyclohexanol conversion was obtained when the γ -alumina activation temperature increased from 473 to 1073 K (entries 7–10).

Oxidation of secondary alcohols catalyzed by γ -alumina (with trichloroacetaldehyde or benzaldehyde as the hydrogen acceptor) has been described by *Posner* et al.⁷. The reaction presumably proceeds according to a mechanism related to the Oppenauer oxidation. The oxidation of cyclohexanol by tBHP on γ -alumina may also involve an alkoxyaluminum intermediate with tBHP acting as the hydrogen acceptor. We have found that aluminum isopropylate is also catalytically active in the reaction of cyclohexanol with tBHP¹⁹. A tentative mechanism, involving dehydroxylated alumina as the catalytically active site, is shown in Fig. 4. A similar mechanism has been proposed for the transfer hydrogenation of ketones on γ -alumina^{20,21}.

The deactivation of the catalyst by water can be explained as adsorption of water on a dehydroxylated alumina surface site. This process is clearly reversible since regeneration of γ -alumina at 673 K restored its original activity (entry 6). Reuse of the catalyst is therefore possible.

Conclusions

- zeolites NaCeY and NaLaY transform cyclohexanol into cyclohexyl formate via acid-catalyzed rearrangement of tBHP;
- γ -alumina catalyzes the oxidation of cyclohexanol to cyclohexanone by tBHP, via a surface Oppenauer-type reaction.

Table II Reaction of tBHP with cyclohexanol using γ -alumina as the catalyst (Type II)^a.

Entry	Catalyst	Activation temperature (K)	Cyclohexanol conversion (%)	tBHP conversion (%)	Selectivity ^b to cyclohexanone (%)
1	-	_	3	3	>95
2	zeolite KA	673	4	7	> 95
3	γ -Al ₂ O ₃ + H ₂ O ^c	673	29	20	96
4	γ -Al ₂ O ₃	673	37	34	96
5	γ -Al ₂ O ₃ + KA	673	69	42	94
6	γ -Al ₂ O ₃ + KA ^d	673	58	38	94
7	γ -Al ₂ O ₃ + KA	473	62	40	96
8	$\gamma - Al_2O_3 + KA$	673	69	42	94
9	$\gamma - Al_2O_3 + KA$	873	68	50	95
10	$\gamma - Al_2O_3 + KA$	1073	79	65	92

^a tBHP (10.5 mmole) and cyclohexanol (3.5 mmole) in benzene (25 ml) were added to the catalyst (1.0 g γ -alumina activated at 473–1073 K, 16 h, N₂) and/or zeolite KA powder (1.0 g, activated at 673 K, 16 h, air) at 353 K; reaction time 8 h. ^b Selectivity based on cyclohexanol converted. ^c 50 µl water/g γ -alumina. ^d Reused catalyst (after activation at 673 K, 16 h, air).



Fig. 4. Formal representation of the γ -alumina-catalyzed oxidation of cyclohexanol by tBHP. (Bonds linking aluminium and oxygen are represented only for the sake of convenience.)

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