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Ion-Exchanged Y Zeolites as Catalysts for the Liquid Phase Autoxidation of Cyclohexane

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The effect of Zeolite Y in its acidic form or ion-exchanged with Na^+-, Ba^{2+}, Sr^{2+}, or Ca^{2+} cations on the autoxidation of cyclohexane was studied. Using hydrated ion-exchanged samples, a pronounced catalytic activity, with a reactivity order CaY > SrY > BaY > NaY, can be observed. On the other hand, in the presence of acidic and/or calcined samples, inhibition occurs. In the decomposition of organic hydroperoxides, like cyclohexyl hydroperoxide and *t*-butyl hydroperoxide, a product distribution typical of homolytic peroxide decomposition is observed when using ion-exchanged Y samples, with the same order of reactivity CaY > SrY > BaY > NaY. This strongly suggests a homolytic peroxide decomposition mechanism to be at the basis of the observed activity in autoxidation reactions, which is confirmed by kinetic analysis. The observed order of activity is indicative of a charge-transfer mechanism. Inhibition is rationalized in terms of heterolytic peroxide decomposition, in the case of acidic samples, and strong peroxide adsorption, followed by intrazeolitic decomposition, in the case of the calcined samples.

INTRODUCTION

The autoxidation of cyclohexane is a major bulk process for the production of cyclohexanol and cyclohexanone as intermediates in manufacturing nylon-6 or nylon-6,6. Recently, Frei and co-workers (1) and the present authors (2) have observed that cyclohexane when adsorbed on alkaline earth-exchanged zeolites is oxidized spontaneously to mainly cyclohexanone at moderate or low temperatures, far below the normal temperatures for free-radical chain autoxidation. This unusual catalytic activity has been ascribed to the stabilization of a substrate oxygen charge-transfer state by the intrazeolitic electrostatic field (1):

$$RH + O_2 \xrightarrow[\Delta T]{} \left[RH^{+\bullet} + {}^{-}O_2^{\bullet}\right] \longrightarrow R^{\bullet} + HOO^{\bullet}.$$

Nevertheless, a significant contribution of free radical chemistry cannot be excluded (2, 3), especially since a study by Bergk *et al.* suggests that Ca^{2+} exchanged faujasites may be capable of decomposing *t*-butyl hydroperoxide via a free-radical chain pathway (4). Earlier we have shown that an AlPO-11 molecular sieve has a distinct catalytic effect on cyclohexane autoxidation, apparently even when no transition metal ions where present in the system (5). The catalytic activity of such highly polar solids may be related to the reported catalytic activity of calcium and barium oxides and carbonates (6, 7) or even surfactants (8) in cumene autoxidation.

From the widely accepted reaction pathways for autoxidation (Scheme 1) (9– 11), it is clear that liquid phase autoxidation reactions may be catalyzed by enhancing primary chain initiation ($k_{in,1}$ [In]), for example by a direct reaction between oxygen and the substrate, as proposed by Frei and co-workers. However, in most cases, catalysis results from homolytic peroxide decomposition ($k_{in,2}$ [ROOH]), as in the case of classic transition metal catalysts.

The aim of the present study was to establish whether and how the IR-results on the dark thermal oxidation of zeolite adsorbed substrates can be expanded to a zeolite-based catalytic system for liquid-phase hydrocarbon autoxidation. Thus, we investigated the effect of acidic and alkaline earth-exchanged Y zeolites on the liquid phase autoxidation of cyclohexane. We focused on distinguishing between homolytic peroxide decomposition and primary chain initiation as mechanisms for catalytic activity. Data from a kinetic study, initiated reactions and test reactions for peroxide decomposition were combined in order to elucidate the reaction mechanism.

METHODS

Cyclohexane (Acros, 99.5+) autoxidation was studied in a stirred 300-ml stainless steel Parr high-pressure reactor, using 75 ml of cyclohexane and an initial room-temperature pressure of 1.0 MPa. Prior to each experiment, the reactor wall was passivated overnight using a saturated sodium pyrophospate (Acros, p.a.) solution. The reaction mixture was heated up and the temperature was maintained constant

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Initiation:

$$In_2 \xrightarrow[k_{i,1}]{} 2In^{\bullet}$$

$$ROOH \xrightarrow[k_{i,2}]{} RO^{\bullet} + {}^{\bullet}OH$$

Propagation:

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + RH \xrightarrow[k_p]{} ROOH + R^{\bullet}$$

Termination:

$$2ROO^{\bullet} \xrightarrow[k_t]{} NRP + O_2$$

SCHEME 1. General pathways in free radical chain oxidation. NRP = nonradical products.

at 420 ± 0.2 K using an Eurotherm 808 temperature controller. Please note that the gas mixture obtained in these conditions is potentially explosive and measures should be taken to protect personnel while carrying out similar experiments.

The decrease of pressure during reaction was monitored using a computer. The reaction was stopped automatically after a pressure drop equivalent to a cyclohexane conversion of approximately 3.5% was reached. Catalytic activities were evaluated by the time needed to reach this conversion. In reactions without any catalyst, this conversion was obtained very reproducibly after 310 ± 10 min. The pressure drop as a function of time was fitted to the exponential expression $P(t) = C - A \cdot \exp(B \cdot (t - t_0))$ using the program Origin 2.8 (Microcal) and the obtained kinetic factors A and B were recalculated to mM (A) and s^{-1} (B).

In zeolite catalyzed experiments, 0.5 g of calcined (500°C, overnight) or hydrated zeolite was used, and, in the case of hydrated samples, increasing amounts of water were added to the reaction mixture. In another set of experiments, 1 ml of an oxidation mixture, obtained using the above-described standard reaction conditions, was added to the reaction mixture as an initiator.

For peroxide decomposition experiments, 1.5 g of a 7.5 wt% solution of *t*-butyl hydroperoxide in benzene (obtained by extracting 70% *t*-BHP in water (Acros) and drying the resulting organic phase with Na_2SO_4), or 1.5 g of an cyclohexane autoxidation mixture (obtained by standard liquid-phase oxidation), and 0.1 g of various zeolites were stirred in glass bottles that were heated in an oil bath.

Products were analyzed by GC (HP 5890, Chrompack Cpsil-5, 50 m) and GC/MS (Fisons MD-800, J&W DB-5MS, 50 m); concentrations of cyclohexanol, cyclohexanone, and cyclohexyl hydroperoxide were calculated from a double injection, before and after reduction of the hydroperoxide using triphenyl phosphine, as described earlier (5). Oxygen efficiency for mono-functionalization was used as a measure for overall selectivity and calculated as oxygen taken up by formation of mono-functionalized products (cyclohexanol, cyclohexanone, and cyclohexyl hydroperoxide), divided by the total amount of oxygen taken up, derived from the pressure drop during reaction.

Zeolite samples were prepared by triple ion-exchange under reflux of a NaY sample (PQ) in an excess of 0.1 *N* solution of the chloride salt of Ca^{2+}, Sr^{2+}, Ba^{2+}, Na^{+}, and NH_4^{+}. H-USY (PQ) was used as such.

RESULTS

Catalyst Characterization

D.R.I.F.T. spectra of *in situ* calcined (500°C) BaY, but especially SrY and CaY showed formation of an absorption band around 3630 cm^{-1}, indicative of the formation of Brønsted acid sites and in good agreement with literature spectra (12, 13).

^{27}Al MAS NMR gave no indication for the formation of extra-framework aluminum, even after calcination of the NaY, BaY, SrY, and CaY samples at slightly higher temperature (550°C).

Cyclohexane Oxidation

Figures 1a and 1b summarize results for cyclohexane autoxidation in the presence of CaY, SrY, BaY, and NaY. The most striking feature of these reactions was that, when using calcined samples, a pronounced inhibition of the reaction was observed, whereas with hydrated samples catalysis occurred and an optimum in the activity was reached when an excess of 0.5-g water was added to the reaction mixture. It can be calculated that this optimum corresponds to the amount of water that evaporates when heating up the reaction mixture to the reaction temperature, thus resulting in a hydrated sample under reaction conditions. In this case, a clear order of activity CaY > SrY > BaY > NaY was observed.

When using calcined samples, it was noted that samples became pale to dark brown after reaction, indicating the formation of side-products. The main IR feature of such spent catalysts was a very intense carbonyl stretching vibration, indicating a mixture of ketone, acids, and esters that may be termed "oxidative coke" in the zeolite pore system. The hydrated samples retained their original white color during reaction.

When using H-USY, the inhibition, accompanied by a dark coloring of the catalyst, became even more pronounced, even when a hydrated sample was used (Table 1). For ammonium-exchanged Y samples, the effect of the zeolite was a function of the pretreatment, with inhibition at moderate temperatures of calcination and catalysis at higher pretreatment temperatures. With all these samples, excessive side-product formation occurred, as is evident

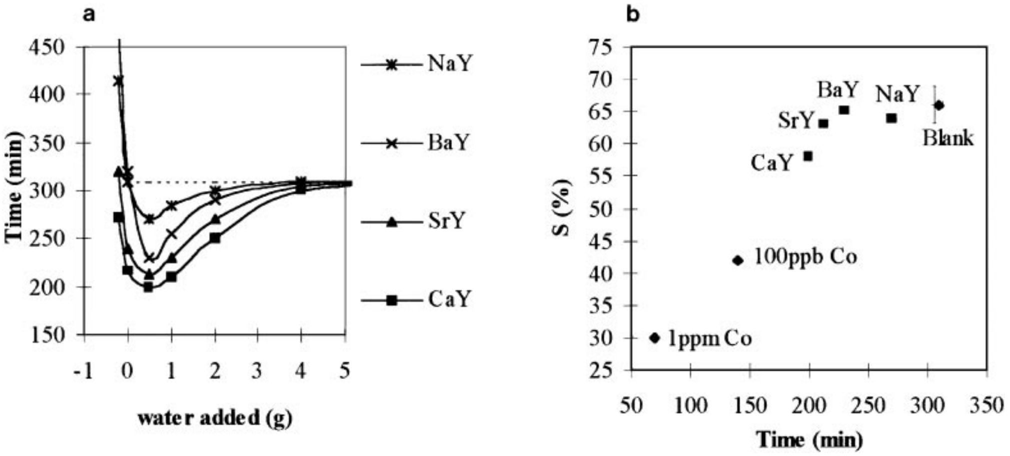


FIG. 1. Autoxidation of cyclohexane in the presence of Y zeolites. (a) Time needed to reach a conversion of 3.5% (0.33 MPa pressure drop) as a function of amount of water added to the reaction mixture, 0 denotes hydrated samples, calcined samples are represented as −0.2 g water. (b) Selectivity for cyclohexyl hydroperoxide as a function of the time needed to reach a conversion of 3.5% (0.33 MPa pressure drop) for hydrated Y zeolites with 0.5 g water added to the reaction mixture.

from the low oxygen efficiency for mono-functionalization, and the cyclohexanol/cyclohexanone ratio was increased significantly.

Kinetic Analysis

The pressure drop, as a measure of the oxygen uptake during autoxidation, was fitted to the simplified rate expression $P(t) = C - A \cdot \exp(B \cdot (t - t_0))$.

We have shown earlier that in this simplified kinetic model, the addition of a catalyst for homolytic peroxide decomposition results in an increase in B, accompanied by a decrease in A, whereas the addition of an initiator results in an increase in A (14). Hence, this model should allow distinguishing between primary chain initiation through a zeolite-stabilized charge-transfer (increase in A) and homolytic peroxide decomposition (decrease in A, increase in B) as the mechanism for autoxidation catalysis by zeolite samples.

TABLE 1

Autoxidation of Cyclohexane at 145°C in the Presence of Acid Y Zeolites

Sample	Pretreatment	$T_{3.5}$ (min)	S_{cHHP} (%)	E_{monof} (%)	ol/one
None		310	63	84	1.91
CaY	Hydrated + 0.5 g water	200	58	80	1.88
NH_4-Y	Calcined 500°C	340	53	54	2.10
	Calcined 600°C	365	49	47	2.10
	Calcined 650°C	240	52	46	2.78
	Calcined 700°C	270	53	45	2.82
	Calcined 700°C rehydrated + 0.5 g water	+300	54	36	2.82
H-USY	Calcined 500°C	+4500[a]	/	/	/
H-USY	Hydrated + 0.5 g water	+400[a]	/	/	/

Note. Time required to reach an oxygen uptake corresponding to 0.33 MPa pressure drop, selectivity for cyclohexyl hydroperoxide, oxygen efficiency for monofunctionalization, and alcohol/ketone ratio. Data for CaY (hydrated + 0.5 g water) are included for comparison.

[a] At this stage, virtually no conversion was observed. After opening the reactor, a dark brown slurry containing the zeolite was present at the bottom of the reactor.

The data represented in Fig. 2 are clearly indicative of homolytic peroxide decomposition.

The data in Table 2 demonstrate how the inhibition by calcined NaY and BaY results from a period of induction ($t_0 \gg 0$), rather than from a decrease in reaction rate constants.

Effect of Initiator

Another means of distinguishing whether homolytic peroxide decomposition plays a role in catalyzing the autoxidation reaction is the addition of peroxide as an initiator. When peroxide decomposition would be uncatalyzed, the

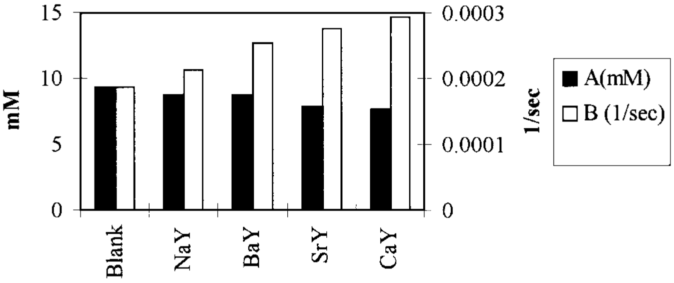


FIG. 2. Kinetic analysis of zeolite catalyzed cyclohexane autoxidation. Kinetic parameters A and B obtained by fitting the experimental pressure curves from experiments in Fig. 1 (hydrated + 0.5 g water added) to the equation $P(t) = C - A \cdot \exp(B \cdot (t - t_0))$.

TABLE 2

Autoxidation of Cyclohexane in the Presence of NaY and BaY

Sample		t_0 (min)	A (mM)	B (sec^{-1})
NaY	Calcined 500°C	184	8.2	0.00024
	Hydrated + 0.5 g water	2	8.8	0.00021
BaY	Calcined 500°C	278	7.8	0.00031
	Hydrated + 0.5 g water	−3	8.8	0.00025

Note. Results from fitting pressure curves in the corresponding experiments in Fig. 1 to the expression $P(t) = C - A \cdot \exp(B \cdot (t - t_0))$.

catalyst and the initiator should operate independent of one another, and the overall reaction observed would be the direct sum of the reaction with the catalyst and without the initiator and the reaction with initiator and without the catalyst. On the other hand, when the catalyst enhances peroxide decomposition, the combined effect of the peroxidic initiator and the catalyst would exceed by far the sum of their independent actions. The latter was observed when adding cyclohexyl hydroperoxide as an initiator at 130°C (Fig. 3). As observed in the reactions without the initiator, the order of activity was CaY > SrY > BaY > NaY. We obtained similar results when using *t*-butyl hydroperoxide as an initiator at 100°C.

Peroxide Decomposition

Figure 4 shows the decomposition of cyclohexyl hydroperoxide over cation-exchanged Y zeolites. Again, the order of reactivity CaY > SrY > BaY > NaY is apparent. The product mixture, a 2 : 1 mixture of cyclohexanol and cyclohexanone with little by-products is typical of homolytic peroxide decomposition.

Similarly, decomposition of *t*-butyl hydroperoxide yields a mixture of acetone, *t*-butanol, and di-*t*-butyl peroxide (Fig. 5) that typifies homolytic peroxide decomposition, and the same order of reactivity is observed.

On the other hand, when acidic samples were used (Table 3), a complicated mixture of products, largely other than cyclohexanol and cyclohexanone, was produced. In the case of H-USY, the amount of cyclohexanone detected after reaction was even lower than in the starting oxidation mixture, resulting in an apparently negative selectivity for cyclohexanone. In GC/MS-analysis, most products formed exhibited m/z peaks typical of cyclohexyl esters, but only cyclohexyl formate and cyclohexyl acetate could be positively identified. Furthermore, trace amounts of 2-cyclohexylidenecyclohexanone were detected.

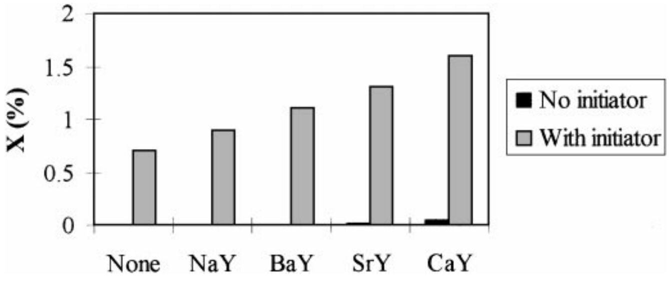


FIG. 3. Zeolite catalyzed autoxidation of cyclohexane with and without initiator. Conversion at 130°C, 5 h, in the presence of 5-ml oxidation mixture as initiator and various hydrated cation exchanged Y zeolites.

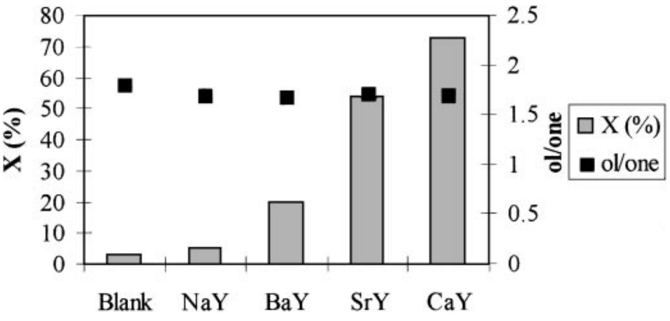


FIG. 4. Decomposition of cyclohexyl hydroperoxide by Y zeolites. 1.5-g oxidation mixture, 0.1-g zeolite, 383 K, 24 h.

DISCUSSION

Mechanism of Catalytic Activity

The results presented clearly indicate that the catalytic activity of zeolites in autoxidation reactions results from an enhanced homolytic peroxide decomposition. Peroxide decomposition experiments and autoxidation experiments using initiator, clearly demonstrate that the zeolite samples are capable of catalyzing homolytic peroxide decomposition. The kinetic analysis suggests this to be the only catalytic effect exerted by the catalyst, and no evidence for primary chain initiation playing an important role in the catalysis can be found.

It is less clear what the exact mechanism and the active site for the catalysis are. Brønsted acid sites are clearly not involved, as they give rise to inhibition, rather than catalysis. The activity of the NH_4Y-zeolite after calcination at higher

TABLE 3

Decomposition of Cyclohexyl Hydroperoxide by Acid Zeolites

Sample	Conversion (%)	$S_{alcohol}$ (%)	S_{ketone} (%)	R (%)
NH_4-Y	65	23	1	76
H-US-Y	100	22	−5	83
NH_4-Beta	93	22	0	78

Note. Conversion of cyclohexyl hydroperoxide, selectivity for cyclohexanol and cyclohexanone (calculated by subtracting initial from final concentrations), and other products (R, calculated from a mass balance). Zeolite samples were precalcined at 500°C.

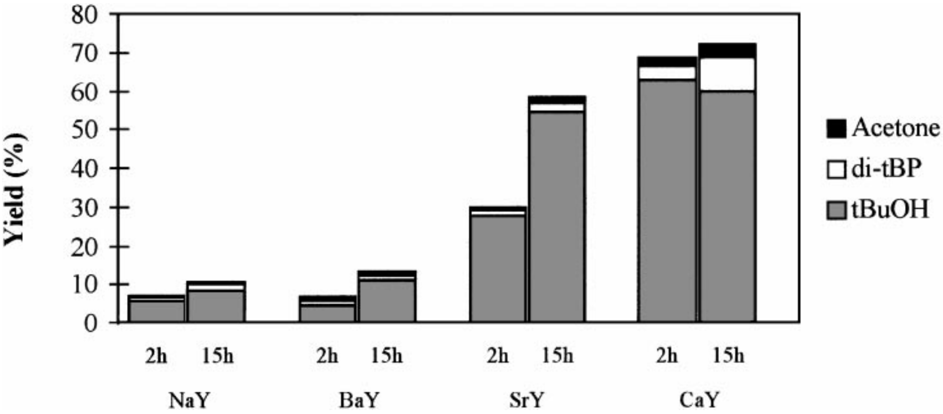


FIG. 5. Decomposition of *t*-butyl hydroperoxide by Y zeolites. 1.5-g *t*BHP solution in benzene (7.5 wt%), 0.1-g zeolite, 343 K, 2 h, and 15 h.

temperatures suggests that Lewis acid sites, associated with extra-framework aluminum, may play a role.

Using ion-exchanged samples, a clear order of reactivity, CaY > SrY > BaY > NaY, is observed in autoxidation reactions, with or without initiator and in peroxide decomposition experiments. Earlier, we observed the same order of reactivity in the oxidation of zeolite-adsorbed cyclohexane, monitored by *in situ* infrared spectroscopy (2). The consistent observation of this cation effect in four types of experiments, the dramatically different behavior of acid samples, and the absence of any evidence for extra-framework aluminum in the NMR-data, strongly suggest that the catalytic activity is associated with the presence of the cations themselves, rather than with the presence of other species like transition metal impurities or Brønsted or Lewis acid sites.

Inspired by the work of Frei *et al.*, it may be suggested that the observed order of reactivity reflects the electrostatic field generated by the cations. Indeed, the field that is generated by the presence of such (unshielded) cations in the zeolitic matrix can be expected to be higher as the charge of the cation becomes larger and its size becomes smaller.

The electrostatic field generated by the cations might catalyze reactions of adsorbed molecules by polarizing bonds or enhancing electron transfer reactions. Csányi and Jáky recently have proposed the catalytic effect of surfactants they observed in autoxidation reactions to be caused by a polarization of the peroxidic O−O bond, which would facilitate homolysis (8). However, it is somewhat unclear how such a polarization would enhance homolytic cleavage, a reaction that by definition does not require any charge separation. Therefore, we prefer an electron-transfer reaction between two hydroperoxide molecules, enhanced by polar interactions with the zeolite surface. Rearrangement of the resulting charge-transfer state subsequently would lead to the formation of an alkyloxy radical, an alkylperoxy radical, and water (Scheme 2). This is the same overall result as in the well-known Haber–Weiss mechanism for homolytic peroxide decomposition with transition metal catalysts.

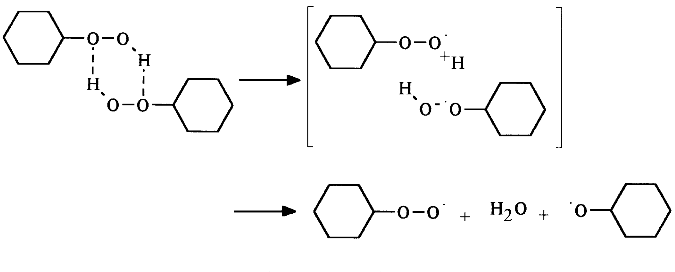
In such a scheme, the cation formally acts as a Lewis acid, activating the electron-accepting hydroperoxide molecule. This also would explain the catalytic activity of acid samples after calcination at high temperatures, apparently associated with Lewis acid sites.

Finally, it should be clear that, in order to circumvent inhibition, the zeolite is strongly deactivated, as the presence of water dipoles around the cations will inevitably reduce the electrostatic field. This, at least partly, explains the somewhat disappointing results in liquid-phase oxidation, when compared to the related IR experiments (1–3).

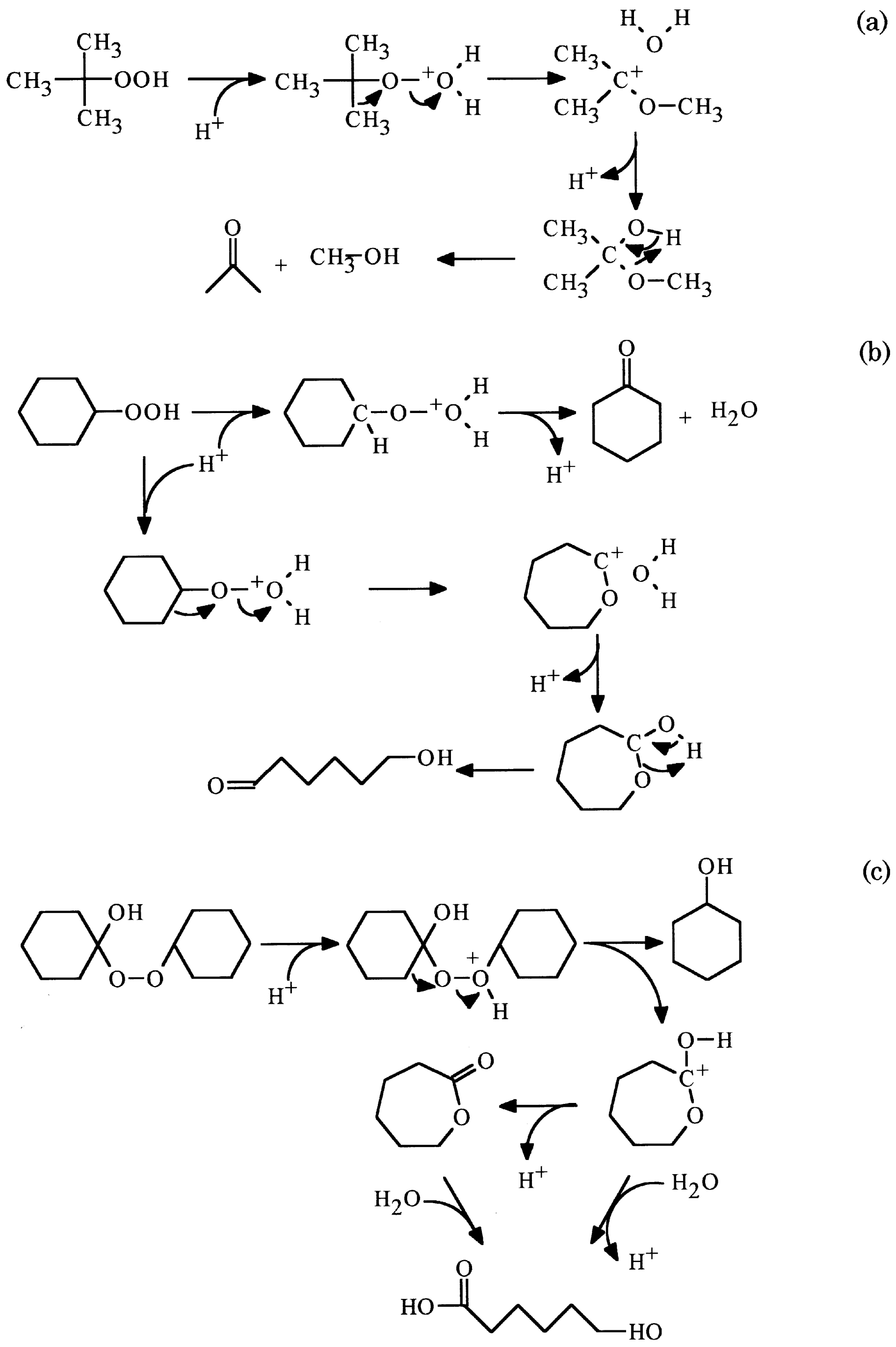
Mechanism of Inhibition

The inhibition observed using calcined and/or acidic samples shows a kinetic behavior that is reminiscent of the effect of free radical inhibitors.

The results of peroxide decomposition using acid zeolites clearly suggest that Brønsted acid sites convert the peroxide through an essentially nonradical mechanism, resulting in a complicated mixture of esters. The formation of esters may be related to the formation of cyclohexyl formate as the main product in the reaction of *t*-BHP with cyclohexanol over acidic Y zeolites (15). This was explained by an acid Hock-like rearrangement, yielding methanol and acetone



SCHEME 2. Charge-transfer pathway for the homolytic decomposition of cyclohexyl hydroperoxide.



SCHEME 3. Hock-like rearrangements of hydroperoxides: (a) rearrangement of *t*-butyl hydroperoxide to acetone and methanol (15); (b) rearrangements proposed for cyclohexyl hydroperoxide (16); (c) rearrangement proposed for the perhemiketal of cyclohexyl hydroperoxide and cyclohexanone.

(Scheme 3a), with subsequent oxidation of methanol to formic acid. The latter reacts with cyclohexanol to form the ester. In analogy with this reaction scheme, a Hock-like rearrangement of cyclohexyl hydroperoxide may be proposed, to yield the 6-hydroxy-capraldehyde (Scheme 3b), from which through further oxidation a whole series of acids can be formed that can form esters with cyclohexanol. The formation of 2-cyclohexylidene cyclohexanone (the acid-catalyzed aldol condensation product of cyclohexanone) at least partly explains the apparent consumption of cyclohexanone in some reactions. Alternatively, an acid catalyzed Hock-like rearrangement of the perhemiketal (10) of cyclohexyl hydroperoxide and cyclohexanone may be proposed (Scheme 3c).

Such a heterolytic conversion of hydroperoxide accounts for the dramatic inhibition that is observed using a H-US-Y zeolite: peroxides are continuously being adsorbed in the zeolite and converted without free radical production, so that no free radical chains can be started. The other results in Table 5 are to be interpreted as the combined effect of Brønsted acid sites, structural collapse (a Y zeolite with high Al content is not stable in its acid form), and Lewis acid sites.

As upon calcination of alkaline earth-exchanged Y zeolites acid sites are being formed; it is tempting to attribute the inhibition observed with these samples to the same mechanism. However, this does not hold upon closer examination of the data. Peroxide decomposition experiments clearly indicate homolytic peroxide decomposition to be dominating. Moreover, adding water to an acid-catalyzed autoxidation experiment did not eliminate inhibition, as it did when using ion-exchanged samples.

This inhibition can be related to the adsorption capacity of the molecular sieve; only when the zeolite pore system has been filled up with reaction products, can the reaction proceed unhindered. This process of filling up the pore system with oxidation products can be observed visually, as the catalyst turns from white to dark brown. This phenomenon may be bypassed by the use of an excess of water as a molecule competing for sorption: the inhibition disappears and catalysis occurs. The optimum in catalytic activity corresponds to a situation in which the zeolite inner pores are filled up with water, leaving the outer pores available for catalysis. Further increasing the amount of water added ultimately results in the formation of a separate water phase containing the zeolite. Catalysis is no longer observed.

Csányi *et al.* have described a catalytic effect of water on initiated liquid-phase oxidation of hydrocarbons, and they obtained a similar dependency on the amount of water present (17). Therefore, the inhibition may be ascribed to removal of water impurities from the reaction mixture by adsorption in the calcined samples. However, we failed to observe a similar inhibition when using calcined zeolite A samples and we could not establish a distinct catalytic effect of water in the reference experiments.

Therefore, we prefer to rationalize these results in terms of strong absorption of small amounts of hydroperoxide in the molecular sieve in an early stage of the reaction. In a typical liquid phase autooxidation, the decomposition of the initially formed hydroperoxide initiates free radical chain reactions. However, when the hydroperoxides are adsorbed into the zeolite pore system and subsequently decomposed, confinement of the radicals to the zeolite pores may result in rapid radical recombination, preventing radical chains of sufficient length to be started. This may result in a net consumption of hydroperoxide, which leads to inhibition.

Still, it is most intriguing that in our liquid phase system inhibition is observed, while in related IR experiments with zeolite adsorbed cyclohexane the formation of oxidation products readily occurs, even at much lower temperatures (1–3). We believe this may be related to the high loading of cyclohexane in the zeolite (in direct contact with the liquid phase) when compared to the IR experiments. This should result in a lower mobility (18) of cyclohexane and intermediates in the zeolite pores, which may lead to shorter chain lengths (eventually lower than 1), thus causing inhibition.

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