

Cyclohexane oxidation over rare earth exchanged zeolite Y

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Abstract

Rare earth exchanged zeolites Y (REY) were prepared from HY with Si:Al ratios of 2.6, 12.5 and 28 by solid-state ion exchange with CeCl_3 , NdCl_3 , SmCl_3 , EuCl_3 or YbCl_3 . The resulting REY were used as catalysts for the liquid-phase oxidation of cyclohexane with *tert*-butyl hydroperoxide. Cyclohexene, *n*-hexanal, cyclohexanone and cyclohexanol are the principal products formed. The activity of the catalysts depends on the Si:Al ratio: $12.5 > 2.6 > 28$, on the rare earth cations: $\text{Ce} \gg \text{Yb} > \text{Sm} > \text{Eu} > \text{Nd}$, and on the temperature. Using CeY with a Si:Al ratio of 12.5, at 50, 70 and 90°C, cyclohexane conversions of 4.7, 7.3 and 10% and turnover numbers of 236, 366 and 505, respectively, are observed after 24 h. However, at 90°C large amounts of carboxylic acids are formed. Leaching experiments with CeY show that most of the products are formed in a heterogeneously catalysed reaction. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Rare earth metal oxides are known to exhibit strong redox properties and to catalyse, in the presence of oxygen, the oxidation of hydrocarbons, such as *n*-butane, propylene and benzene, to carbon dioxide and water [1,2]. Recently the selective liquid-phase oxidation of cyclohexane to cyclohexanol and cyclohexanone catalysed by SmCl_3 was reported [3]. Also Ce(IV) exchanged cation exchange resin was used as catalyst for the oxidation of alcohols to the corresponding carbonyl compounds [4]. Al-

though these results demonstrate the suitability of rare earth cations as catalysts for the oxidation of hydrocarbons, no attention has been given to the redox properties of rare earth cation exchanged zeolites, which have been very well studied as acid catalysts in petrochemical processes [5]. Recently, we communicated first results of the application of REY (Si:Al = 3) as catalysts for the liquid-phase oxidation [6] and could demonstrate that REYs are active catalysts for the oxidation of cyclohexane with *tert*-butyl hydroperoxide (TBHP). Here we will describe in more detail the influence of the rare earth cation, the Si:Al ratio of the parent zeolite and of the reaction temperature on the activity and selectivity of the REY catalyst. Also a proposed mechanism for the cyclohexane oxidation over REY will be discussed.

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2. Experimental

2.1. Synthesis of the catalysts

The catalysts were prepared from acid zeolite Y (HY) with Si:Al ratios of 2.6, 12.5 and 28 by solid-state ion exchange [7] with $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, respectively. The HY was mixed with the rare earth chloride (RECl_3) in a molar ratio $\text{Al}:\text{RECl}_3 = 3:1$. The homogenised mixture was placed in a reaction tube, which was sealed, evacuated to 0.1 mmHg and heated to 520°C for 6 h. After cooling to room temperature, the solid REY was separated, carefully washed with an excess of water and dried at 120°C for 12 h.

2.2. Catalyst characterisation

The REY catalysts were characterised by X-ray diffraction (XRD) using a Shimadzu XD-3A diffractometer with Cu K α radiation. Infrared spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer from KBr wavers containing the zeolite. The metal contents were determined with a Spectrace TX-500 X-ray fluorescence spectrometer, using calibration curves prepared from mixtures of SiO_2 and the respective rare earth oxides.

2.3. Catalytic reaction

The oxidation of cyclohexane was carried out in a suspension of 200 mg of the REY, dried at 80°C under vacuum, in 15.6 g of cyclohexane. A solution of 10 mmol of TBHP (86% in cyclohexane) was added and the reaction mixture was refluxed for 24 h at 70°C under an atmosphere of air. The CeY zeolite with Si:Al = 12.5 was also used as catalyst at 50 and 90°C. After filtering off the solid catalyst, the reaction products were quantified by gas chromatography on a 10% Carbowax 20M on Chromosorb WAW 80/100 (2.5 m \times 3.2 mm i.d.) column coupled to a flame ionization detector,

using an internal standard and appropriate calibration curves. In two additional experiments at 70°C the CeY (Si:Al = 12.5) catalyst was removed from the reaction mixture after 1 and 4 h, and the homogeneous reaction solution was submitted to the reaction conditions. All results presented in the tables and figures were corrected by the amounts of oxidation products obtained in blank experiments carried out under the same conditions described above but using the parent HY as catalyst.

3. Results and discussions

All peaks observed in the XRD patterns of the REY can be assigned to the FAU structure and the unit cell parameters a_0 , calculated by linear regression, do not vary with respect to the parent HY. The absence of a broad reflection between 20 and 25° (2θ), which would indicate the presence of amorphous silica, demonstrates that the FAU structure remains intact after the solid-state ion exchange. The decreased intensity of the reflections observed in the patterns of the REY may be attributed to an enhanced adsorption of X-rays in the presence of the rare earth cations, rather than to a decreased crystallinity, and can be taken as a first indication for the successful ion exchange. The FTIR spectra reveal that the intensity ratios between the bands around 1000, 710 and 460 cm^{-1} , attributed to vibrations of the internal tetrahedra linkages (structure insensitive) [8] and the bands around 1130, 780 and 570 cm^{-1} , attributed to the vibrations of the external linkages (structure sensitive) [8], do not differ between the parent HY and the REY, thus confirming that the FAU structure remains intact after the solid-state ion exchange.

The results of the elemental analyses are given in Table 1. It can be seen that for the zeolite Y with a high aluminium content (Si:Al = 2.6) the exchange degree after one ion exchange reaches only approximately 25%. However, a higher exchange degree can be achieved

Table 1
Elemental analysis of the rare earth exchanged zeolite Y

	Si:Al = 2.6			Si:Al = 12.5			Si:Al = 28		
	metal content (wt.%)		exchange degree (%)	metal content (wt.%)		exchange degree (%)	metal content (wt.%)		exchange degree (%)
	observed	calculated		observed	calculated		observed	calculated	
Ce	4.3	17.7	24	2.6	5.4	48	1.5	2.6	58
Ce ^a	11.5	17.7	65	—	—	—	—	—	—
Nd	4.5	18.2	25	2.8	5.6	50	—	—	—
Sm	4.4	18.8	23	3.6	5.8	62	—	—	—
Eu	4.3	19.0	23	2.1	5.9	36	—	—	—
Yb	4.6	21.0	22	4.0	6.6	61	—	—	—

^aExchanged twice.

by repeating the ion exchange. For the silicon rich zeolites Y (Si:Al = 12.5 and 28) exchange degrees of approximately 50% are already achieved after the first ion exchange.

The results of the oxidation of cyclohexane at 70°C catalysed by REY and HY are given in Table 2. It can be seen that the cyclohexane conversion over HY is very low (0.1%), while the rare earth exchanged zeolites are very active catalysts for the oxidation of alkanes in the liquid phase. The cyclohexane conversion of 7.3%, which is obtained after 24 h with CeY (Si:Al = 12.5) as catalyst, is significantly higher than that obtained in the industrial process (ca. 4%) [9] and corresponds to a turnover number of 366. However, the REY catalysts produce cyclohexene (ene) and *n*-hexanal (al) as the principal products and less of the desired cyclo-

hexanone (one) and cyclohexanol (ol). The results given in Table 2 demonstrate, further, that the activity of the REY catalysts depends on their aluminium content and decrease in the following order of the Si:Al ratio: 12.5 > 2.6 > 28.

The different activities of the REY catalysts with different Si:Al ratios might be explained by their different hydrophobicities. As shown by Berke et al. [10] the aluminium content of zeolite Y strongly influences the adsorption properties. To characterise the adsorption properties they define the ratio of adsorbed toluene and adsorbed water (wt.:%wt.%) from a gaseous mixture of these components as the hydrophobicity index (HI). For NaY zeolites with Si:Al ratios of 2.5, 8 and 35 they found HI equal to 0.2, 1.1 and 14.8, respectively [10]. This

Table 2
Results of the oxidation of cyclohexane with TBHP catalysed by REY^a

	Si:Al = 2.6					Si:Al = 12.5					Si:Al = 28				
	conversion (%)	products ^b (mmol)				conversion (%)	products ^b (mmol)				conversion (%)	products ^b (mmol)			
		ene	al	one	ol		ene	al	one	ol		ene	al	one	ol
H	—	—	—	—	—	0.1	0.0	0.0	0.14	0.10	—	—	—	—	—
Ce	1.7	1.16	0.52	0.77	0.60	7.3	3.87	5.88	2.15	1.68	1.0	0.80	0.51	0.34	0.26
Ce ^c	5.4	3.13	3.15	2.09	1.73	—	—	—	—	—	—	—	—	—	—
Nd	0.7	0.76	0.30	0.18	0.11	1.3	0.88	0.85	0.43	0.29	—	—	—	—	—
Sm	0.6	0.65	0.28	0.12	0.05	2.2	2.35	0.65	0.58	0.53	—	—	—	—	—
Eu	0.7	0.56	0.52	0.17	0.12	1.9	1.74	0.66	0.60	0.58	—	—	—	—	—
Yb	1.3	0.99	1.05	0.32	0.11	2.3	2.25	0.48	0.95	0.54	—	—	—	—	—

^a10 mmol TBHP; 187 mmol C₆H₁₂; 200 mg of catalyst; 70°C, 24 h.

^bThe amounts of oxidation products obtained in blank experiments without REY are already subtracted.

^cExchanged twice.

ene = cyclohexene, al = *n*-hexanal; one = cyclohexanone; ol = cyclohexanol.

demonstrates that zeolite Y, with an intermediate content of aluminium, adsorbs the hydrophobic toluene and the hydrophilic water in approximately equal amounts. A high activity of redox zeolite as catalysts for the liquid phase oxidation of alkanes requires that the hydrophobic substrate (e.g., cyclohexane) and the hydrophilic oxidant (e.g., TBHP) are adsorbed in equal amounts, which is probably possible for the zeolite Y with Si:Al = 12.5, while for zeolite Y with Si:Al = 2.6 (HI \approx 0.2), the adsorption of the hydrophobic substrate is hampered and, for zeolite Y with Si:Al = 28 (HI \approx 14), the adsorption of the hydrophilic oxidant is more difficult, thus resulting in a reduced activity of these catalysts. However, also the CeY with Si:Al = 2.6 and an exchange degree of 65% shows a remarkable good cyclohexane conversion of 5.4%.

For the REY catalysts with a Si:Al ratio of 12.5 the activity at 70°C decreases in the following order: CeY \gg YbY > SmY > EuY > NdY. For the CeY (Si:Al = 12.5) catalyst, the time dependence of cyclohexane conversion and the product distribution are given in Fig. 1. It can be seen that the catalyst is still active after 24 h. The observed peroxide efficiency (mol oxidised products:mol TBHP consumed) which

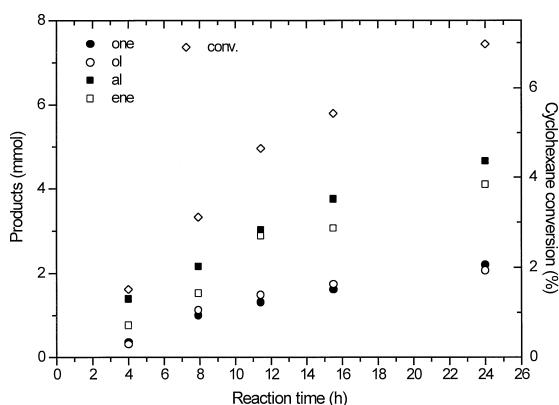


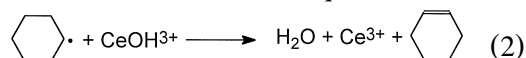
Fig. 1. Time dependence and product distribution from cyclohexane oxidation catalysed by CeY (10 mmol TBHP; 187 mmol C₆H₁₂; 200 mg of catalyst; Si:Al = 12.5, 70°C; 24 h; the amounts of oxidation products obtained in blank experiments are already subtracted).

is around 130% indicates the participation of molecular oxygen in the reaction. Reactions performed under an inert atmosphere produced much less oxidation products, confirming that molecular oxygen takes part in the reaction.

We therefore propose a reaction mechanism for the REY catalysed cyclohexane oxidation as depicted in Fig. 2. It is assumed that the rare earth cation in REY is oxidised by decomposing TBHP, thus forming *tert*-butoxy radicals, as illustrated in the following equation [11]:



These radicals abstract hydrogen from cyclohexane forming cyclohexyl radicals which react with molecular oxygen from air. The cyclohexylperoxy radicals thus formed can suffer a bimolecular Russell termination [12] to form cyclohexanone (one) and cyclohexanol (ol) or abstract a hydrogen from cyclohexane to form cyclohexyl hydroperoxide, whose formation was confirmed by capillary gas chromatography [13]. Hydroxy radical abstraction from cyclohexyl hydroperoxide by REY forms cyclohexyloxy radicals which are in equilibrium with the open-chain isomer [14], thus forming the observed *n*-hexanal (al). The cyclohexyl radicals may also suffer dehydrogenation to cyclohexene (ene) by reduction of the Ce(IV) formed by the decomposition of the TBHP, thus regenerating the REY as illustrated in the equation:



The cyclohexane conversion, turnover number, peroxide efficiency and the products observed at 50, 70 and 90°C, respectively, are summarised in Table 3. It can be seen that the activity and the efficiency increase with the temperature. However, at 90°C the yield of *n*-hexanal (al) is strongly reduced and a large amount of carboxylic acids, such as hexanoic acid and adipic acid, are formed by overoxidation of the aldehyde.

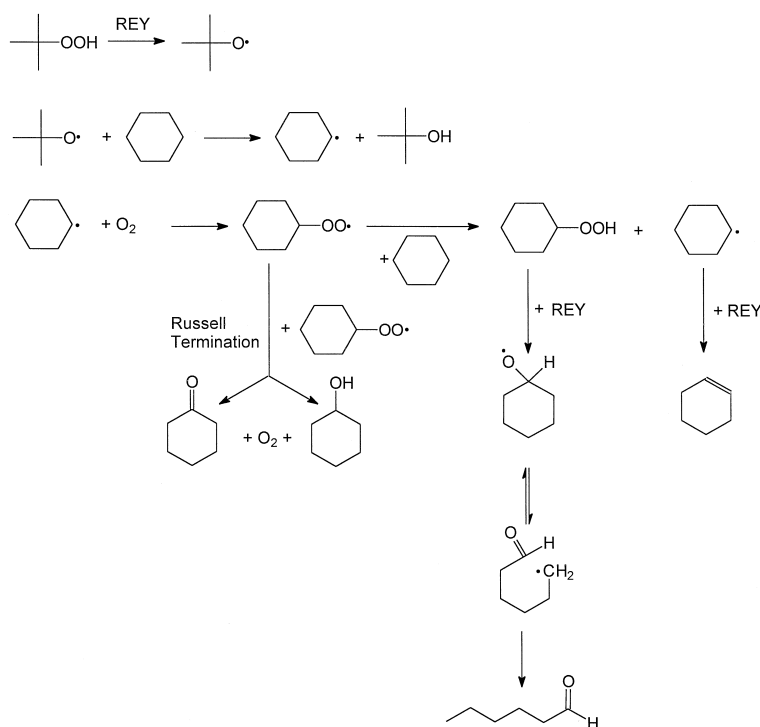


Fig. 2. Proposed reaction mechanism for the oxidation of cyclohexane catalysed by REY.

Analysis by X-ray fluorescence of the used CeY shows that no detectable leaching of the Ce had occurred during the reaction. Furthermore the catalyst can be recycled without significant loss of activity. However, it was recently demonstrated that a quantity of leached metal too small to be detected by elemental analysis could be responsible for the observed activity

[15]. We therefore performed two experiments at 70°C in which the CeY was separated from the reaction mixture after 1 and 4 h of reaction time, respectively, and the reactions were continued in the absence of the solid catalyst. As shown in Fig. 3, the homogeneous reaction solution shows very low activity, and only negligible amounts of cyclohexanone (one) and cy-

Table 3
Temperature dependence of the oxidation of cyclohexane catalysed by CeY^a

Temperature (°C)	Cyclohexane conversion (%)	Turnover number	Peroxide efficiency ^b (%)	Products ^c (mmol)			
				ene	al	one	ol
50	4.7	236	88	3.22	3.31	1.06	1.17
70	7.3	366	136	3.87	5.88	2.15	1.68
90 ^d	10.0 ^e	505 ^e	187	6.82	1.08 ^d	1.98	2.86

^a 10 mmol TBHP; 187 mmol C₆H₁₂; 200 mg of catalyst; Si:Al = 12.5, 24 h.

^b Mol cyclohexane converted:mol TBHP consumed.

^c The amounts of oxidation products obtained in blank experiments are already subtracted.

^d Approximately 6 mmol of carboxylic acids are formed by overoxidation.

^e The carboxylic acids formed are already considered.

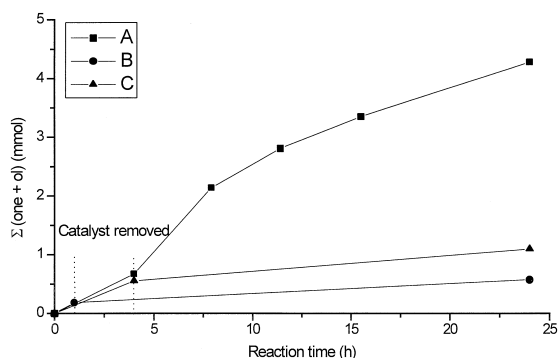


Fig. 3. Formation of cyclohexanone (one) and cyclohexanol (ol) catalysed by CeY (A) and after removal of the catalyst at 1 h (B) and 4 h (C); (10 mmol TBHP; 187 mmol C_6H_{12} ; 200 mg of catalyst; Si:Al = 12.5, 70°C; 24 h; the amounts of oxidation products obtained in blank experiments are already subtracted).

clohexanol (ol) are formed after the removal of the catalyst. This result clearly demonstrates that the reaction is catalysed by CeY in heterogeneous phase.

4. Conclusions

Rare earth exchanged zeolites Y are active catalysts for the oxidation of cyclohexane with TBHP, forming, besides cyclohexanone and cyclohexanol, *n*-hexanal and cyclohexene as the main products. The activity strongly depends on the Si:Al ratio of the zeolite, on the rare earth cation and on the temperature. The highest activity is obtained for CeY with a Si:Al ratio = 12.5 at 90°C. However, at this temperature large amounts of carboxylic acids are formed by overoxidation of *n*-hexanal. The reaction probably proceeds via formation of *tert*-butoxy radicals catalysed by CeY. CeY is also active in the catalytic decomposition of the cyclohexyl hydroperoxide formed, which gives *n*-hexanal, and in hydrogen abstraction from intermediate cyclohexyl radicals to form cyclohexene.

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