

Amorphous silicates containing cerium: selective catalysts for the oxidation of cyclohexane

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Abstract

Cerium containing silicates have been synthesized by different procedures and characterized by X-ray diffraction, X-ray fluorescence and N₂-physorption. The silicates are efficient catalysts for the selective oxidation of cyclohexane with *tert*-butyl hydroperoxide under mild conditions. Cyclohexane conversions higher than 12% can be obtained, using acetone as solvent and the only products formed are cyclohexanone, cyclohexanol and cyclohexyl hydroperoxide. Peroxide efficiencies exceed 100% and indicate that molecular oxygen is the ultimate oxidant. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The development of heterogeneous catalysts for the selective oxidation of hydrocarbons is a current challenge and has been studied extensively in recent years. Due to environmental and economic concerns, the development of highly efficient catalytic processes, which minimize the formation of side products and residues, is quite desirable. An interesting approach is supporting catalytically active metals on molecular sieves or related systems, thus enhancing the selectivity because of the well-defined porous system [1]. Titanium containing molecular sieves, especially titanium silicalite 1 (TS-1), have been successfully applied as heterogeneous oxidation catalysts in the liquid phase [2,3]. Furthermore, various transition metals, e.g. Sn, Zr, Cr, Fe, Mn and Cu, have been incorporated into zeolites, silicalites, SAPO's and AIPO's and used in

oxidation reactions [1,4–7]. However, the use of these materials as oxidation catalysts is restricted because of relatively low activity or of metal leaching from the molecular sieves [8–10]. On the other hand, rare earth exchanged zeolite Y has been studied in cyclohexane oxidation and showed considerable selectivity and activity [11,12]. In this paper, we wish to report the synthesis of amorphous silicates containing cerium and the application of these new materials as catalysts in the oxidation of cyclohexane.

2. Experimental

Three different methods were used for the synthesis of the catalysts: (i) sol–gel encapsulated cerium (CSG) was obtained by an acid catalyzed sol–gel process following the procedure described by Klein et al. [13]. 1.12 g of CeCl₃·7H₂O were dissolved in a mixture of 33 ml of tetraethoxysilane and 26 ml of ethanol and 6.6 ml of 8 mol/l HCl were added slowly. The reaction mixture was allowed to stand at room temperature to

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remove the volatiles by slow evaporation. The gel was first dried at 323 K, then at 373, 423, 473 and 523 K for 24 h each; (ii) silicate supported cerium (CSP) was prepared by dissolving 200 mg of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (Aldrich) in a suspension of 500 mg of silica (Aerosil 200) in 100 ml of water, followed by controlled solvent evaporation at 343 K under magnetic stirring. The material was calcined at 773 K for 8 h under a flow of synthetic air; (iii) hydrothermal synthesis was used to prepare a cerium containing silicate (CHT) from 200 mg of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, 500 mg of silica (Aerosil 200) and 62 mg of sodium metasilicate. 10 ml of a 25% solution of tetramethylammonium hydroxide (TMAOH, Aldrich) in water and 2.3 g of cetyltrimethylammonium bromide (CTMABr, Sigma) in water were added to obtain a gel with the following final molar composition: 1.0 SiO_2 : 0.11 Na_2O : 0.88 TMAOH: 0.21 CTMABr: 125 H_2O : 0.018 Ce. The gel was heated under reflux for 16 h, filtered and the solid was washed with hot water until chloride ions were no longer present in the washings (tested with a AgNO_3 solution). The solid was then dried at 373 K and finally calcined at 813 K for 1 h under a flow of nitrogen and subsequently for 8 h under a flow of synthetic air (600 ml/h).

The materials were characterized by powder X-ray diffraction (XRD) using a Shimadzu XD-3A diffractometer. Metal contents of the silicates were determined by X-ray fluorescence analysis (XRF) on a Spectrace TX-5000 instrument using calibration curves prepared from mixtures of SiO_2 (Aldrich) and Ce_2O_3 (Merck). Physisorption isotherms were measured at 77 K on a Micromeritics ASAP 2010 instrument with nitrogen as probe molecule.

In a typical experiment for cyclohexane oxidation, 90–250 mg of the catalyst, dried immediately before the reaction at 393 K for 12 h, were suspended in a mixture of 185 mmol (15.6 g) of cyclohexane (Merck), 10 mmol of H_2O_2 (45% in cyclohexane) or *tert*-butyl hydroperoxide (TBHP, 90% in cyclohexane) and 40 ml of solvent (acetonitrile, acetone or methanol). The reaction mixture was heated under reflux at an oil bath temperature of 343 K for 24 h under air at atmospheric pressure with magnetic stirring. The catalyst was removed and gas chromatography coupled to mass spectrometry (GC–MS, HP5970–HP5890, Carbowax 20 M capillary column) was used to identify the reaction products, which were quantified by gas chromatography (GC, HP5890) on a 10% Carbowax 20 M on

Chromosorb WAW 80/100 (2.5 mm \times 3.2 mm i.d.) column coupled to a flame ionization detector, using an internal standard (cyclooctane, Fluka) and calibration curves.

Peroxide concentrations of the reaction mixtures were determined after the catalytic reaction by iodometric titration. Cyclohexyl hydroperoxide (CHHP) contents were determined by decomposition with PPh_3 and quantification of the additionally formed cyclohexanol by GC [14].

In a series of leaching experiments with CHT, the catalyst was removed by filtration at reaction temperature before completion of the reaction and the filtrate was immediately allowed to react further in the absence of the catalyst. The reaction mixture before and after filtration was analyzed by GC, taking samples at different reaction times. In another experiment, 200 mg of the CHT catalyst were treated with a mixture of 10 mmol of TBHP and 40 ml of acetone under reaction conditions. After 24 h, the catalyst was filtered off, 185 mmol of cyclohexane were added to the filtrate and the mixture was subjected to reaction conditions for another 24 h. Recycling tests with repeated use of CHT were carried out. The catalyst was removed from the reaction mixture after 24 h by filtration, washed with cyclohexane, dried at 373 K for 24 h and subjected to the next catalytic cycle.

3. Results and discussion

Powder X-ray diffraction revealed that all synthesized materials are amorphous silicates. X-ray fluorescence analysis showed Ce contents of 5.9 wt.% for CSG, 2.7 wt.% for CSP and 4.8 wt.% for CHT. From N_2 -physorption isotherms average pore diameters of about 3.3 nm and surface areas around 170 m^2/g were calculated for CSG and CSP, whereas an average pore diameter of 2.8 nm and a surface area of about 322 m^2/g were determined for CHT. The pore size distributions were very narrow with a maximum deviation of less than 10%.

The results of cyclohexane oxidation using TBHP as oxidant are summarized in Table 1 (the amounts of oxidation products obtained in blank experiments, under the same conditions, are already subtracted). The catalytic activities of CSG and CSP are similar and cyclohexane conversions of around 1.5% with

Table 1
Cyclohexane oxidation with TBHP catalyzed by amorphous Ce containing silicates^a

Catalyst (mg)	Cyclohexanone (mmol)	Cyclohexanol (mmol)	Conversion (%)	TON ^b
CSG (241)	2.11	0.63	1.48	27
CSP (258)	2.15	0.75	1.56	58
CHT (178)	3.34	1.03	2.36	72
CeY-12.5 ^c (248)	2.15 ^c	1.68 ^c	1.98 ^d	83 ^d

^a Reaction conditions: 185 mmol cyclohexane; 10 mmol TBHP (90% in cyclohexane); 343 K; 24 h.

^b Turnover number mol (cyclohexanone + cyclohexanol)/mol metal.

^c Data obtained from [12].

^d Values considering only cyclohexanone and cyclohexanol.

cyclohexanone as the main product were obtained. A considerably higher conversion of 2.36% was observed using CHT. In contrast to reactions with cerium exchanged zeolite Y [11], where cyclohexene and *n*-hexanal are the main products, the amorphous silicates exhibit high selectivities for cyclohexanone and cyclohexanol. Besides these products, only cyclohexyl hydroperoxide (CHHP) was detected in the reaction mixtures. Using cerium exchanged zeolite Y, the cyclohexanone:cyclohexanol ratio was approximately 1.3, whereas for CHT cyclohexanone formation is favored and a ratio of 3.3 was observed. However, when cyclohexanol was submitted to reaction conditions in the presence of CHT, rapid cyclohexanone formation was observed with conversions higher than 30%, thus confirming that part of the cyclohexanone is obtained by over-oxidation of initially formed cyclohexanol.

For reactions with CHT and H₂O₂ instead of TBHP, a drastic reduction in cyclohexane conversion was observed. Using a mixture of 45% aqueous H₂O₂ and cyclohexane (tri-phase system), 0.6 mmol of cyclohexanone and cyclohexanol were formed, whereas only 0.3 mmol were obtained with 30% aqueous H₂O₂. However, when reactions with TBHP were carried out with solvent (acetone, acetonitrile, methanol), a

considerable increase in cyclohexane conversion was observed (Table 2). Cyclohexane conversions increase in the order: methanol < acetonitrile < acetone. Using acetone as solvent, an approximately five-fold increase in cyclohexane conversion (12.7%) was observed, compared to the system without solvent. The good results obtained in acetone can be rationalized, taking into account that acetone and hydroperoxides can react with each other to form dimethyldioxirane which is a powerful oxidant for organic compounds [15]. Although, in the presence of *tert*-butanol there should be only trace amounts of dimethyldioxirane in the reaction mixture, a similar effect using acetone was already observed in the cyclohexane oxidation with H₂O₂ in the presence of TS-1 [16]. Furthermore, efficient removal of the oxidation products from the active sites of the catalyst by the polar solvent is assumed. The material balance (cyclohexanone + cyclohexanol + CHHP + unreacted cyclohexane/initial amount of cyclohexane) was always better than 98% and no other products were detected.

Additional reactions with CSG, CSP and CHT were carried out in acetone and the total peroxide and CHHP content of the reaction mixtures after 24 h were determined. The results are summarized in Table 3 and it

Table 2
Effect of solvents on the activity and selectivity of cyclohexane oxidation with TBHP catalyzed by CHT^a

Solvent	CHT (mg)	Cyclohexanone (mmol)	Cyclohexanol (mmol)	Conversion (%)	TON
Cyclohexane	178	3.34	1.03	2.36	72
Acetone	101	18.73	4.82	12.73	680
Acetonitrile	109	14.58	3.91	9.99	497
Methanol	93	11.33	2.84	7.64	442

^a Reaction conditions: 185 mmol cyclohexane; 10 mmol TBHP (90% in cyclohexane); 40 ml of solvent; 343 K; 24 h.

Table 3
Analysis of total peroxide and CHHP contents after cyclohexane oxidation reactions catalyzed by Ce containing silicates^a

Catalyst	Total peroxide content (mmol)	CHHP content (mmol)
CSG	12.72	6.51
CSP	15.34	7.56
CHT	6.77	4.29

^a Reaction conditions similar to Table 1.

can be seen that in reactions with CSG and CSP, the final total peroxide contents are higher than the initial amount of TBHP added to the reaction mixture. This is in agreement with the observation that the oxidations continue after 24 h. For CHT, the total peroxide content is reduced after 24 h, thus explaining why the production of cyclohexanone and cyclohexanol is slowing down (Fig. 1). In all three reaction mixtures, a considerable amount of cyclohexyl hydroperoxide was detected (Table 3). TBHP consumption, determined as the difference between total peroxide and CHHP content, is about 38% for CSG and 23% for CSP, whereas approximately 75% is consumed when using CHT as

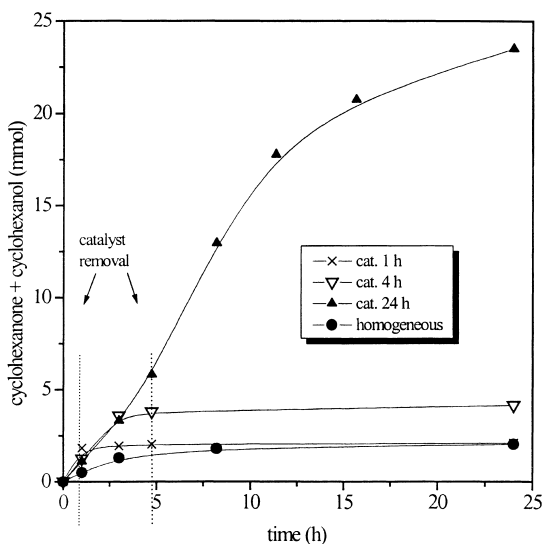


Fig. 1. Oxidation of cyclohexane catalyzed by $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ in homogeneous phase and by CHT without and with removal of the catalyst after 1 and 4 h. Reaction conditions: 185 mmol cyclohexane; 10 mmol TBHP (90% in cyclohexane); 101 mg of CHT or 26 mg of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$; 40 ml of acetone; 343 K; total reaction times: 24 h.

catalyst. These results demonstrate that CSG and CSP are less active in the decomposition of TBHP as well as CHHP, thus explaining the lower conversion of cyclohexane.

As already shown in the cyclohexane oxidation with TBHP in the presence of soluble Fe(III) or Cu(II) catalysts [17] or of Ce exchanged zeolite Y [12], the reaction is initiated by the homolytic cleavage of the TBHP to form *tert*-butoxy radicals which abstract a hydrogen from cyclohexane. The cyclohexyl radical thus formed reacts with molecular oxygen to form a cyclohexylperoxy radical. We could confirm this by performing a reaction under an inert atmosphere, where the amount of oxygenated products was reduced to approximately 30% and dicyclohexyl was formed as a by-product. The cyclohexylperoxy radicals can then undergo bimolecular Russell termination [18] to form cyclohexanone and cyclohexanol or abstract a hydrogen from cyclohexane to form cyclohexyl hydroperoxide, as discussed in our previous paper [12]. The abstraction of hydrogen from cyclohexane by the cyclohexylperoxy radical explains why we get as much as 23.5 mmol of oxygenated products from only 10 mmol of TBHP (Table 2). This efficiency with respect to the oxidant is similar to what we observed for the same reaction catalyzed by soluble Cu(II) catalysts [17]. We were, however, not able to run the reaction catalytically with respect to TBHP. As already observed for Ce exchanged zeolite Y [19], reduction of the amount of TBHP to 4 mmol results in an approximate three-fold reduction of oxygenated products, showing that the cyclohexylperoxy radical is not sufficiently reactive at 343 K to maintain the radical chain process.

To investigate whether the reactions are catalyzed in the homogeneous or the heterogeneous phase, CHT was suspended in a mixture of acetone and TBHP and heated under reflux for 24 h. After removal of the catalyst by filtration, cyclohexane was added and the mixture was allowed to react in the absence of the catalyst. The reaction mixture was analyzed after 24 h and only negligible amounts (<0.2 mmol) of cyclohexanone and cyclohexanol, similar to the quantities found in blank experiments, were observed. Furthermore, X-ray fluorescence analysis of the used catalyst showed that there was no detectable leaching of Ce from the catalyst. In catalyst filtration experiments, the catalyst (CHT) was separated by filtration after reaction times of 1 and 4 h, respectively, and the reaction

mixtures were analyzed before and after removal of the catalyst. As shown in Fig. 1, the catalytic reactions stopped immediately after removal of the catalyst. A final conversion of only 1.3% was obtained in the reaction with catalyst removal after 4 h, in contrast to a final conversion of 12.7% for the reaction with the catalyst present during 24 h. These tests indicate that the reactions with CHT are catalyzed by the heterogeneous catalyst. Furthermore, reactions with $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ in the homogeneous phase gave only negligible conversions, thus showing that, even if there is slight leaching of cerium, this would not result in any additional conversion of cyclohexane. Recycling experiments showed that CHT can be recycled at least three times without detectable loss of activity.

4. Conclusions

The results show that cerium containing amorphous silicates are active catalysts for the oxidation of cyclohexane with TBHP. Although, the materials do not present well-defined porous systems, remarkably high activities and selectivities can be attained. Depending on the preparation mode and the solvent used in the catalytic reaction, conversions can exceed 10% and cyclohexanone, cyclohexanol and cyclohexyl hydroperoxide are the only products obtained. Peroxide efficiencies higher than 100% show that molecular oxygen is the ultimate oxidant. Best results are obtained in acetone with mesoporous CHT, which shows no metal leaching and can be used repeatedly. These new materials and especially CHT can be considered as promising catalysts for hydrocarbon oxidation.

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