

# Epoxidation of alkenes with hydrogen peroxide catalyzed by $\text{ReO}_4\text{--SiO}_2\cdot\text{Al}_2\text{O}_3$ and $\text{ReO}_4\text{--Al}_2\text{O}_3$

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## Abstract

Rhenium oxides supported on zeolite Y, mixed silica–alumina and pure alumina were prepared by impregnation of the supports with  $\text{Re}_2\text{O}_7$  or  $\text{NH}_4\text{ReO}_4$ . The materials are active catalysts in the epoxidation of cyclooctene and cyclohexene with anhydrous  $\text{H}_2\text{O}_2$  in EtOAc. Catalyst stabilities with regard to metal leaching are closely correlated with the alumina content of the support and almost no leaching was observed with  $\text{ReO}_4^-$  supported on pure alumina. Stable catalysts  $\text{ReO}_4\text{--Al}_2\text{O}_3$  with  $\text{ReO}_4^-$  contents up to 12 wt.% can be prepared. Higher contents result in extensive metal leaching and catalysis in the homogeneous phase. The catalyst  $\text{ReO}_4(12 \text{ wt.}\%)\text{--Al}_2\text{O}_3$  was re-used in three catalytic runs, without loss of activity. Selectivities for cyclooctene epoxide were around 96%, whereas cyclohexanediol was obtained as the only product in cyclohexene epoxidation. Adding pyridine to the reaction mixtures, the selectivity for cyclohexene epoxide increased from 0 to 67%, however, a significant decrease in conversion was observed. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Epoxidation; Rhenium; Hydrogen peroxide; Alumina; Cyclooctene; Cyclohexene

## 1. Introduction

Catalytic epoxidation of alkenes to form epoxides is a versatile reaction from a synthetic point of view. Epoxides can be easily converted into polyethers, diols and aminoalcohols [1]. Each of these classes of compounds has widespread application in bulk chemistry, fine chemistry and the pharmaceutical industry. Several methods have been developed for the production of epoxides from alkenes. These include stoichiometric reactions with peracids or aqueous

chlorine (to form chlorohydrins that can be ring closed to epoxides) and metal catalyzed reactions with alkyl hydroperoxides or hydrogen peroxide.

Hydrogen peroxide gives a clean and environmentally friendly reaction since the starting material is safe and inexpensive and only water is formed as a by-product. Reactions with  $\text{H}_2\text{O}_2$  generally require a catalyst. In spite of a large number of research efforts during the last decades, only a few useful catalytic systems for epoxidation with  $\text{H}_2\text{O}_2$  have been developed. These include tungsten [2–5], manganese [6–8] and rhenium [9–17] based systems. Systems based on rhenium are of particular interest since rhenium has, unlike most other transition metals, a very low activity

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for unproductive hydrogen peroxide decomposition. This side reaction can severely limit the applicability of the method.

The most efficient catalyst based on rhenium is the well known methyltrioxorhenium ( $\text{CH}_3\text{ReO}_3$ , MTO). First discovered by Herrmann and coworkers [9,10], this catalyst is active but only moderately selective in epoxidation with anhydrous hydrogen peroxide. The low selectivity is related to the high Lewis acidity of MTO, catalyzing the ring opening of the epoxide to diol and related oxidation products. A major improvement was achieved by Sharpless and coworkers [11,12] and later by Herrmann's group [13]. Large amounts of heterocyclic N-bases significantly improve selectivity for epoxide and also allow the use of aqueous hydrogen peroxide. MTO is now an established and highly active catalyst [11–16] for the selective epoxidation of a wide range of alkenes.

The only disadvantage of MTO is its difficult, hazardous and environmentally unfriendly synthesis, involving organotin reagents [17]. Catalysts based on inorganic rhenium compounds are much more readily available, since no organometallic synthesis is required. In this paper, we describe the catalytic activity of inorganic rhenium compounds ( $\text{Re}_2\text{O}_7$  and  $\text{ReO}_4^-$ ) supported on zeolite Y (Wessalith<sup>®</sup>), mixed silica–alumina and pure alumina in epoxidation with anhydrous  $\text{H}_2\text{O}_2$ . Besides evaluating the activity and selectivity, the stability of the catalysts with regard to leaching and recycling is investigated.

## 2. Experimental

### 2.1. Synthesis of the catalysts

The catalyst  $\text{Re}_2\text{O}_7$ (3 wt.%)–Wessalith<sup>®</sup> was obtained by heating of Wessalith<sup>®</sup> (Degussa, Si/Al > 100, pore volume of  $0.3\text{ cm}^3/\text{g}$ , surface area of  $700\text{ m}^2/\text{g}$ ) at 773 K for 20 h and subsequent sublimation of  $\text{Re}_2\text{O}_7$  under vacuum (0.01 mmHg) at 463 K [18]. The catalysts  $\text{ReO}_4$ (3 wt.%)– $\text{SiO}_2\cdot\text{Al}_2\text{O}_3$  (13 wt.%),  $\text{ReO}_4$ (3 wt.%)– $\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ (24 wt.%) and  $\text{ReO}_4$ (3 wt.%)– $\text{Al}_2\text{O}_3$  were prepared by impregnation of the respective supports ( $\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ , Strem, 13 wt.%  $\text{Al}_2\text{O}_3$ , pore volume of  $0.78\text{ cm}^3/\text{g}$ , surface area of  $337\text{ m}^2/\text{g}$ ;  $\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ , Akzo, 24.3 wt.%

$\text{Al}_2\text{O}_3$ , pore volume of  $0.91\text{ cm}^3/\text{g}$ , surface area of  $374\text{ m}^2/\text{g}$ ;  $\text{Al}_2\text{O}_3$ , Fluka, for chromatography, pH = 7) with aqueous solutions of  $\text{NH}_4\text{ReO}_4$  following procedures described in the literature [19–22]. Catalysts with higher rhenium contents  $\text{ReO}_4$ (12 wt.%)– $\text{Al}_2\text{O}_3$ ,  $\text{ReO}_4$ (15 wt.%)– $\text{Al}_2\text{O}_3$  and  $\text{ReO}_4$ (18 wt.%)– $\text{Al}_2\text{O}_3$  were obtained by repeated impregnation of alumina, using the same procedure. The impregnated materials were calcined immediately before use in the catalytic reactions at 773 K for 15 h under a flow of dry air (60 ml/min).

### 2.2. Catalytic epoxidations

Anhydrous solutions of hydrogen peroxide in ethyl acetate (EtOAc) were prepared by removal of the water from aqueous  $\text{H}_2\text{O}_2$  (Peróxidos do Brasil, 60%) under Dean–Stark conditions. The catalytic reactions were carried out without precautions against moisture and oxygen. A mixture of 25 mmol of cyclooctene (Aldrich, 95%), 25 mmol of  $\text{H}_2\text{O}_2$  (23.8% in EtOAc), 25 ml EtOAc and 7 mmol of *n*-decane (Aldrich, 99%), used as internal standard for gas chromatography (GC), was kept under reflux for 1 h. The catalytic reactions were started, adding 400 mg (nearly  $50\text{ }\mu\text{mol Re}$ ) of  $\text{Re}_2\text{O}_7$ (3 wt.%)–Wessalith<sup>®</sup>,  $\text{ReO}_4$ (3 wt.%)– $\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ (13 wt.%),  $\text{ReO}_4$ (3 wt.%)– $\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ (24 wt.%) or  $\text{ReO}_4$ (3 wt.%)– $\text{Al}_2\text{O}_3$ . Epoxidation of cyclohexene (Aldrich, 99%) was carried out, using the same reaction conditions as described for cyclooctene epoxidation and 1 mmol of *n*-heptane (Aldrich, 99%) as GC standard. To start the catalytic reactions 100 mg ( $50\text{ }\mu\text{mol Re}$ ) of  $\text{ReO}_4$ (12 wt.%)– $\text{Al}_2\text{O}_3$ , 83 mg ( $50\text{ }\mu\text{mol Re}$ ) of  $\text{ReO}_4$ (15 wt.%)– $\text{Al}_2\text{O}_3$  or 69 mg ( $50\text{ }\mu\text{mol Re}$ ) of  $\text{ReO}_4$ (18 wt.%)– $\text{Al}_2\text{O}_3$  were added. Blank experiments, reacting the olefin with  $\text{H}_2\text{O}_2$  under the same reaction conditions in the absence of Re, but in the presence of the different supports, were also performed.

The course of the reactions was monitored by taking aliquots from the reaction mixtures at different reaction times. The samples were analyzed using a Hewlett Packard HP 5890 Series II gas chromatograph equipped with a HP Ultra 2 capillary column and a FID detector. Products were quantified using calibration curves obtained with standard solutions. Unknown products were separated and identified

by GC–MS using a HP 5970 Series mass selective detector.  $\text{H}_2\text{O}_2$  consumption was determined after the reactions by iodometric titration.

### 2.3. Leaching and recycling tests

In a series of leaching experiments the catalyst was added to a solution of 25 mmol of  $\text{H}_2\text{O}_2$  (23.8% in EtOAc) in 25 ml of EtOAc and the suspension was heated under reflux for 1 h. The catalyst was removed from the reaction mixture by filtration of the hot suspension and the alkene as well as the internal GC standard were added to the filtrate. The reaction mixture was subsequently allowed to react in the absence of the solid catalyst. Recycling tests with repeated use of  $\text{ReO}_4(12 \text{ wt.}\%)\text{-Al}_2\text{O}_3$  were carried out with cyclohexene as substrate. The catalyst was removed from the reaction mixture after 5 h by filtration, washed with EtOAc, dried at 373 K for 24 h, calcined at 773 K for 12 h and subjected to the next catalytic run. Re contents of the catalysts were determined by ICP-AES.

## 3. Results and discussion

### 3.1. Epoxidation of cyclooctene

Reaction profiles for the epoxidation of cyclooctene with different types of supported rhenium catalysts are given in Fig. 1. Anhydrous  $\text{H}_2\text{O}_2$  (solutions of  $\text{H}_2\text{O}_2$  in EtOAc) was used as oxidant, since the presence of water deactivates the catalytic system. EtOAc was chosen because of the good solubility of the oxidant in this solvent and its inertness with regard to the catalyst. Cyclooctene conversions around 60% after 5 h were obtained, using  $\text{Re}_2\text{O}_7$  supported on Wessalith<sup>®</sup> or  $\text{ReO}_4^-$  supported on silica with an alumina content of 13 wt.%. Using the catalyst with higher alumina content,  $\text{ReO}_4(3 \text{ wt.}\%)\text{-SiO}_2\cdot\text{Al}_2\text{O}_3(24 \text{ wt.}\%)$ , or  $\text{ReO}_4^-$  supported on pure alumina  $\text{ReO}_4(3 \text{ wt.}\%)\text{-Al}_2\text{O}_3$ , cyclooctene conversions around 40% were observed. The selectivity for epoxide after 5 h was 96% or higher with the exception of the reaction catalyzed by  $\text{Re}_2\text{O}_7(3 \text{ wt.}\%)\text{-Wessalith}^{\text{®}}$ , which gave an epoxide selectivity of 93%. The consumption of  $\text{H}_2\text{O}_2$  was between 60 and 80%, depending on the support used,

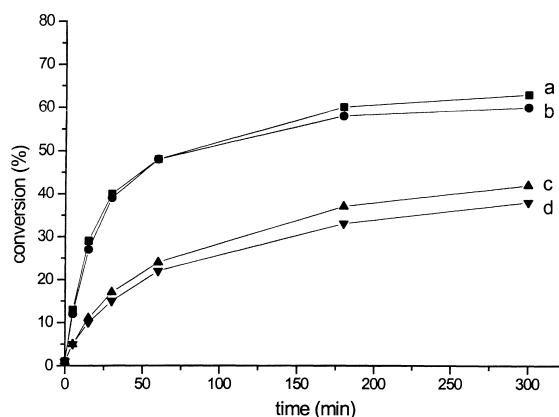


Fig. 1. Epoxidation of cyclooctene catalyzed by (a)  $\text{Re}_2\text{O}_7(3 \text{ wt.}\%)\text{-Wessalith}^{\text{®}}$ ; (b)  $\text{ReO}_4(3 \text{ wt.}\%)\text{-SiO}_2\cdot\text{Al}_2\text{O}_3(13 \text{ wt.}\%)$ ; (c)  $\text{ReO}_4(3 \text{ wt.}\%)\text{-SiO}_2\cdot\text{Al}_2\text{O}_3(24 \text{ wt.}\%)$  and (d)  $\text{ReO}_4(3 \text{ wt.}\%)\text{-Al}_2\text{O}_3$ . Reaction conditions: 25 mmol of cyclooctene, 25 mmol of  $\text{H}_2\text{O}_2$  (23.8% in EtOAc), 25 ml EtOAc, 7 mmol of *n*-decane and 400 mg (50  $\mu\text{mol}$  Re) of catalyst; 363 K.

which shows that some of the  $\text{H}_2\text{O}_2$  is used up in an unproductive decomposition.

In a series of leaching experiments the catalysts were suspended in  $\text{H}_2\text{O}_2/\text{EtOAc}$  and heated under reflux for 1 h. After removal of the solids by filtration, cyclooctene was added to the filtrate and the mixtures were immediately allowed to react in the absence of the solid catalyst. The reaction mixture was analyzed by GC and reaction profiles for the different catalysts are given in Fig. 2. Using  $\text{Re}_2\text{O}_7(3 \text{ wt.}\%)\text{-Wessalith}^{\text{®}}$ , it can be seen that the reaction after removal of the solid catalyst (Fig. 2) took the same course as the reaction with the catalyst present (Fig. 1). This indicates that the reaction takes place in the homogeneous phase and is catalyzed by species leached from  $\text{Re}_2\text{O}_7(3 \text{ wt.}\%)\text{-Wessalith}^{\text{®}}$ . This is probably also the reason for the above mentioned lower epoxide selectivity compared to the other catalysts. Reactions with  $\text{Re}_2\text{O}_7$  in homogeneous phase under the same reaction conditions gave remarkably high cyclooctene conversions of about 80% with epoxide selectivities of about 82%, thus confirming the catalytic activity and selectivity of soluble Re species. Catalytic reactions with  $\text{ReO}_4(3 \text{ wt.}\%)\text{-SiO}_2\cdot\text{Al}_2\text{O}_3(13 \text{ wt.}\%)$  were also considerably due to metal leaching and catalysis in the homogeneous phase. In the leaching test, a cyclooctene conversion of 33% after 5 h

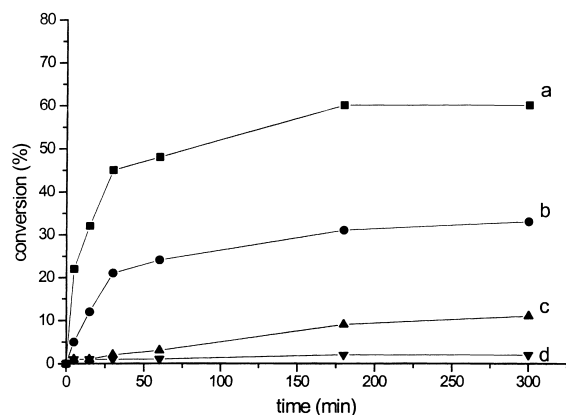


Fig. 2. Epoxidation of cyclooctene: leaching tests using (a)  $\text{Re}_2\text{O}_7$  (3 wt.%)–Wessalith<sup>®</sup>; (b)  $\text{ReO}_4$ (3 wt.%)– $\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ (13 wt.%); (c)  $\text{ReO}_4$ (3 wt.%)– $\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ (24 wt.%) and (d)  $\text{ReO}_4$ (3 wt.%)– $\text{Al}_2\text{O}_3$ . Reaction conditions: 25 mmol of cyclooctene, 25 mmol of  $\text{H}_2\text{O}_2$  (23.8 wt.% in EtOAc), 25 ml EtOAc, 7 mmol of *n*-decane and 400 mg (50  $\mu\text{mol}$  Re) of catalyst; 363 K.

was observed, whereas a conversion of 60% was obtained with the solid catalyst present during 5 h. The catalyst with higher alumina content in the support  $\text{ReO}_4$ (3 wt.%)– $\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ (24 wt.%) gave a cyclooctene conversion of 11% in the leaching test versus 42% in the standard reaction. Using the catalyst based on pure alumina  $\text{ReO}_4$ (3 wt.%)– $\text{Al}_2\text{O}_3$ , a negligible conversion of only 2% was observed in the leaching test, whereas the standard reaction gave a cyclooctene conversion of 38%. The low conversion of 2% is probably due to non catalytic reactions between cyclooctene and the oxidant. These results clearly show that leaching of catalytically active species is correlated with the alumina content of the support. With increasing alumina content leaching decreases and reactions with  $\text{ReO}_4$ (3 wt.%)– $\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ (24 wt.%) and, particularly,  $\text{ReO}_4$ (3 wt.%)– $\text{Al}_2\text{O}_3$  are mainly due to catalysis in the heterogeneous phase. These results are in agreement with temperature-programmed reduction (TPR) studies performed by Wachs and coworkers [23], which show for rhenium oxide supported on  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  a higher Re–O–Al bond strength compared to Re–O–Si bond strength.

### 3.2. Epoxidation of cyclohexene

Blank experiments showed that  $\text{Al}_2\text{O}_3$  itself is active in epoxidation [24]. Thus, considerable amount

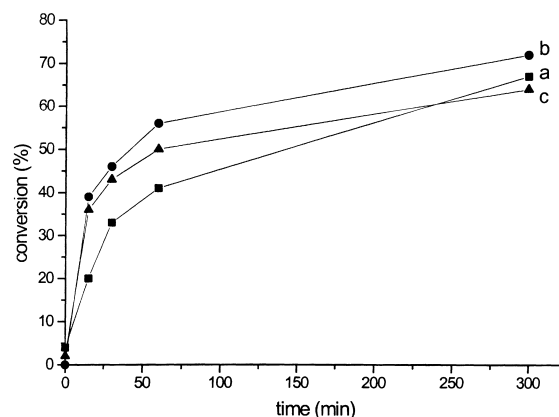


Fig. 3. Conversion of cyclohexene catalyzed by (a)  $\text{ReO}_4$  (12 wt.%)– $\text{Al}_2\text{O}_3$ ; (b)  $\text{ReO}_4$ (15 wt.%)– $\text{Al}_2\text{O}_3$  and (c)  $\text{ReO}_4$  (18 wt.%)– $\text{Al}_2\text{O}_3$ . Reaction conditions: 25 mmol of cyclohexene, 25 mmol of  $\text{H}_2\text{O}_2$  (23.8% in EtOAc), 25 ml EtOAc, 1 mmol of *n*-heptane and 100 mg (50  $\mu\text{mol}$  Re) of  $\text{ReO}_4$ (12 wt.%)– $\text{Al}_2\text{O}_3$ , 83 mg (50  $\mu\text{mol}$  Re) of  $\text{ReO}_4$ (15 wt.%)– $\text{Al}_2\text{O}_3$  or 69 mg (50  $\mu\text{mol}$  Re) of  $\text{ReO}_4$ (18 wt.%)– $\text{Al}_2\text{O}_3$ ; 363 K.

of the epoxide was formed just in the presence of the support. In order to reduce the participation of the support in the catalytic reaction,  $\text{Al}_2\text{O}_3$  catalysts with higher Re contents of 12, 15 and 18 wt.% were synthesized. The activity of  $\text{ReO}_4$ (12 wt.%)– $\text{Al}_2\text{O}_3$ ,  $\text{ReO}_4$ (15 wt.%)– $\text{Al}_2\text{O}_3$  and  $\text{ReO}_4$ (18 wt.%)– $\text{Al}_2\text{O}_3$  was tested in the epoxidation of cyclohexene and the results are shown in Fig. 3. Cyclohexene conversions were between 60 and 70% for all catalysts and were considerably higher than cyclooctene conversion obtained with  $\text{ReO}_4$ (3 wt.%)– $\text{Al}_2\text{O}_3$  (Fig. 1). However, the epoxide selectivity was very low in all reactions. Using  $\text{ReO}_4$ (12 wt.%)– $\text{Al}_2\text{O}_3$  and  $\text{ReO}_4$ (15 wt.%)– $\text{Al}_2\text{O}_3$ , the epoxide selectivity after 15 min was 12 and 3%, respectively. After 5 h cyclohexanediol was the only product observed. For  $\text{ReO}_4$ (18 wt.%)– $\text{Al}_2\text{O}_3$  no epoxide could be observed, even at the beginning of the reaction. Diol formation is a well known problem in Re catalyzed epoxidations [10] and is attributed to the acidic properties of the Re centers [25], which catalyze ring opening of the epoxide. The formation of acetic acid from the solvent EtOAc can be excluded, since the pHs of the reaction mixtures do not change during the reactions.

Leaching tests as described before were carried out and revealed that the catalytic reactions with  $\text{ReO}_4$ (15 wt.%)– $\text{Al}_2\text{O}_3$  and  $\text{ReO}_4$ (18 wt.%)– $\text{Al}_2\text{O}_3$

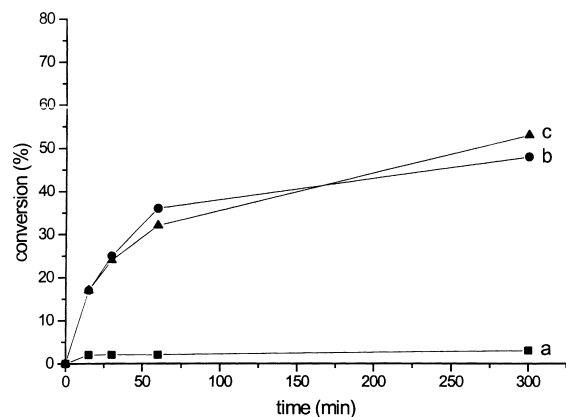


Fig. 4. Conversion of cyclohexene: leaching tests using (a)  $\text{ReO}_4(12 \text{ wt.}\%)\text{-Al}_2\text{O}_3$ ; (b)  $\text{ReO}_4(15 \text{ wt.}\%)\text{-Al}_2\text{O}_3$  and (c)  $\text{ReO}_4(18 \text{ wt.}\%)\text{-Al}_2\text{O}_3$ . Reaction conditions: 25 mmol of cyclohexene, 25 mmol of  $\text{H}_2\text{O}_2$  (23.8% in EtOAc), 25 ml EtOAc, 1 mmol of *n*-heptane and 100 mg (50  $\mu\text{mol}$  Re) of  $\text{ReO}_4(12 \text{ wt.}\%)\text{-Al}_2\text{O}_3$ , 83 mg (50  $\mu\text{mol}$  Re) of  $\text{ReO}_4(15 \text{ wt.}\%)\text{-Al}_2\text{O}_3$  or 69 mg (50  $\mu\text{mol}$  Re) of  $\text{ReO}_4(18 \text{ wt.}\%)\text{-Al}_2\text{O}_3$ ; 363 K.

were mainly due to catalysis in the homogeneous phase (Fig. 4). Cyclohexene conversions in the leaching experiments were around 50% for both catalysts, whereas almost no conversion was observed with  $\text{ReO}_4(12 \text{ wt.}\%)\text{-Al}_2\text{O}_3$ . These results are correlated with epoxide selectivities as increasing conversions in the leaching tests are accompanied by decreasing epoxide selectivities, indicating that the catalytically active species favors the formation of the diol in homogeneous phase. Reactions with  $\text{Re}_2\text{O}_7$  in the homogeneous phase gave 100% cyclohexene conversion after 1 h and cyclohexanediol was the only product obtained. Extensive metal leaching from the catalysts with  $\text{ReO}_4^-$  contents higher than 12 wt.% can be explained, considering detailed IR studies of alumina catalysts with different  $\text{ReO}_4^-$  loadings [26], which showed that  $\text{ReO}_4^-$  reacts preferably with basic surface OH groups up to a  $\text{ReO}_4^-$  loading of 12 wt.%. Higher loadings imply reactions with neutral and acidic OH groups, which result in weakly bound Re species susceptible to leaching.

The best results with regard to activity, selectivity and catalyst stability were obtained with  $\text{ReO}_4(12 \text{ wt.}\%)\text{-Al}_2\text{O}_3$ . Silica containing supports as well as  $\text{ReO}_4^-$  loadings higher than 12 wt.% resulted in considerable metal leaching. To avoid diol formation

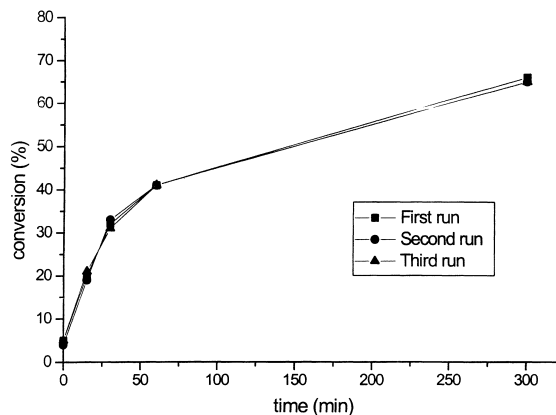


Fig. 5. Conversion of cyclohexene after repeated use of  $\text{ReO}_4(12 \text{ wt.}\%)\text{-Al}_2\text{O}_3$ . Reaction conditions: 25 mmol of cyclohexene, 25 mmol of  $\text{H}_2\text{O}_2$  (23.8% in EtOAc), 25 ml EtOAc, 1 mmol of *n*-heptane and 100 mg (50  $\mu\text{mol}$  Re) of catalyst; 363 K.

and to promote epoxide yield, reactions in the presence of pyridine were carried out. From epoxidations catalyzed by  $\text{CH}_3\text{ReO}_3$  in the homogeneous phase it is well known that the addition of large amounts of heterocyclic N-bases improve catalyst activity as well as epoxide selectivity [11–16]. Using a Re/pyridine ratio of 1:23 in the  $\text{ReO}_4(12 \text{ wt.}\%)\text{-Al}_2\text{O}_3$ -catalyzed epoxidation of cyclohexene, an epoxide selectivity of 67% after 5 h was obtained in contrast to 0% in the reaction without pyridine. However, the activity of the catalytic system decreases and cyclohexene conversions drop from 67 to 20% in the presence of the base. Reactions with lower amounts of pyridine (Re/pyridine ratios of 1:2, 1:4, 1:6 and 1:8, respectively) also gave conversions of around 20%. Similar conversions are obtained with pure  $\text{Al}_2\text{O}_3$ , showing that pyridine deactivates the catalytically active Re centers on the surface of alumina.

Catalyst recycling experiments were carried out with the repeated use of  $\text{ReO}_4(12 \text{ wt.}\%)\text{-Al}_2\text{O}_3$  in the epoxidation of cyclohexene. The results of three consecutive catalytic runs are shown in Fig. 5. It can be seen that the reactions take the same course without any decrease in conversion, indicating that  $\text{ReO}_4(12 \text{ wt.}\%)\text{-Al}_2\text{O}_3$  is stable with regard to metal leaching and can be re-used in at least three reactions. Furthermore, ICP-AES analysis of the used catalyst showed that there was no measurable leaching of Re from the catalyst.

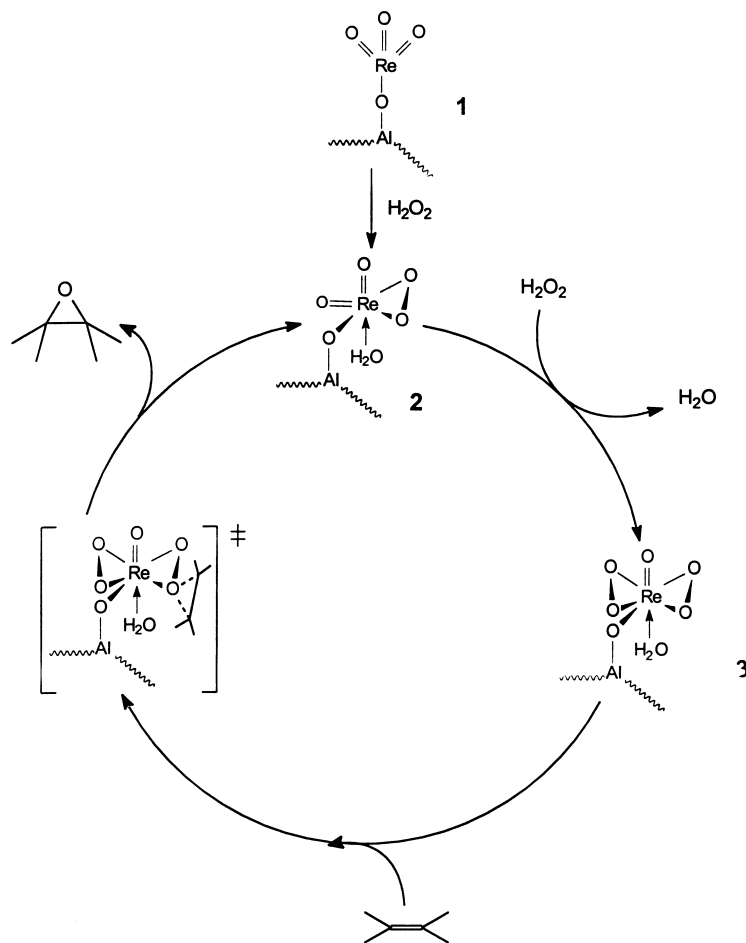


Fig. 6. Proposed mechanism for the Re-catalyzed epoxidation of alkenes at the surface of alumina.

From IR and Raman spectroscopic investigations on metathesis catalysts, prepared by impregnation of alumina with ammonium perrhenate, it is known that tetrahedral  $\text{ReO}_4^-$  species are attached to alumina surfaces by covalent Al–O–Re bonds [23,27–29]. Based on these results and the mechanism described by Espenson and coworker [30] for epoxidations catalyzed by  $\text{CH}_3\text{ReO}_3$  in the homogeneous phase, we propose the mechanism depicted in Fig. 6 for heterogeneously catalyzed epoxidations with  $\text{ReO}_4^-/\text{Al}_2\text{O}_3$  catalysts. Reaction of surface–Al–O– $\text{ReO}_3^-$  (1) with  $\text{H}_2\text{O}_2$  gives the peroxo species 2, which reacts with further  $\text{H}_2\text{O}_2$  to form complex 3. Oxygen transfer from 3 to the olefin yields the epoxide and complex 2.

#### 4. Conclusion

Rhenium oxides supported on mixed silica–alumina and alumina are active catalysts for the epoxidation of olefins with anhydrous  $\text{H}_2\text{O}_2$ . Stable and truly heterogeneous catalysts are formed with alumina as support and with Re loadings up to 12 wt.%. As alumina also shows activity in catalytic epoxidations, the most productive catalyst is obtained with a  $\text{ReO}_4^-$  loading of 12 wt.% on alumina. Selectivities for cyclooctene epoxide are high, however, cyclohexene epoxide suffers ring opening, promoted by the acidic Re centers and cyclohexane diol is obtained as the main oxidation product. Nitrogen bases improve epoxide selec-

tivity but reduce cyclohexene conversion significantly, as they block the active sites of the catalyst. The  $\text{ReO}_4(12 \text{ wt.}\%)\text{-Al}_2\text{O}_3$  catalyst can be re-used and is stable for at least three catalytic cycles. The crucial advantage of the system  $\text{ReO}_4\text{-Al}_2\text{O}_3$  is its easy preparation mode by simple impregnation of  $\text{Al}_2\text{O}_3$  with  $\text{NH}_4\text{ReO}_4$ . Considering that the reaction conditions are not yet optimized, we conclude that this material is a promising heterogeneous epoxidation catalyst.

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