

Oxidation of Cyclohexane by Hydrogen Peroxide over Ammonium 12-molybdophosphate

Ahmed Aouissi¹

1. Chemistry Department, College of Science, King Saud University. Riyadh. KSA

E-mail : aouissed@yahoo.fr

Abstract : The Keggin-type heteropolymolybdate $(\text{NH}_3)_4\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$, was prepared and characterized by means of IR and TG and then used as catalyst in the liquid phase oxidation of cyclohexane with hydrogen peroxide. Catalytic tests were carried out in liquid phase at 343K, under atmospheric pressure and using acetic acid as solvent. The effects of reaction time and catalyst amount on the conversion and the products selectivities were examined. It was found that the principal products of the reaction were cyclohexanone (K), cyclohexanol (A). Above 91% selectivity towards ketone-alcohol (K-A) oil products was achieved at conversion that exceed 5%. The higher selectivity of cyclohexanol at the beginning of the reaction, then its decrease, linked to a distinct increase in cyclohexanone concentration suggests that cyclohexanol might be a primary product from the cyclohexane oxidation.

Keywords : cyclohexane oxidation; heteropoly compound; hydrogen peroxide; cyclohexanone; cyclohexanol.

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Introduction.

The catalytic conversion of saturated hydrocarbons into oxygenated compounds (ketones, acids, aldehydes and alcohols) has been extensively investigated over the last decades, because the products are valuable intermediates for organic synthesis [1–4]. Among alkane oxidations, the partial oxidation of cyclohexane is of great interest. In fact, the oxidation products, viz., cyclohexanol and cyclohexanone are important intermediates in the production of polyamide fibers and plastics, such as Nylon-6 and Nylon-6,6 [5, 6]. More than 106 tonne of cyclohexanone and cyclohexanol (K-A oil) are produced worldwide per annum [7]. Homogeneous catalysis using soluble transition metal salts (such as cobalt naphthenate) is the only technology, which had actually been developed until now. In this process the cyclohexane conversion is kept low (3–8% with selectivities between 70 and 80% for the cyclohexanone / cyclohexanol mixture [8]). The low selectivity for the desired product is due to the fact that the products are more reactive than the inert C–H bonds in the alkanes as the cyclohexanol and cyclohexanone formed are more susceptible for further oxidation. However, reactions in homogeneous medium are often not efficient because the organic ligands of the transition metal complexes

used as catalysts can be degraded. Moreover, it is very difficult to separate the catalysts from reaction mixture in the homogeneous system. However, the characteristics of these soluble homogeneous catalysts often pose a serious obstacle to their practical utility because of various problems like easy deactivation and difficulty in regeneration of the catalysts, and tedious procedures needed for the separation of the catalyst and products. Increasing environmental concerns in recent years, as well as great demands for these products call for a more effective catalytic process [9,10]. However, due to the importance of the large-scale oxidation of cyclohexane to cyclohexanol and cyclohexanone, this process continues to be a challenge [11–15]. In this regard, several heterogeneous catalysts have been proposed, to overcome the problem of separating the catalyst from the products during homogeneous catalysis and the disposal of solid/liquid waste, researchers have developed many heterogeneous catalysts for this reaction. Generally, these catalysts are metal cations incorporated in inorganic matrices such as silica, alumina, zirconia, active carbon, zeolites [16] or aluminophosphates [17]. Many porous metal-containing molecular sieves with various structures have been synthesized and used as catalysts such as MeAPO, MeS-1 and MeMCM-41

(Me = Co, Mn, V, Cr, Fe, Ti, etc.) [18]. Unfortunately, further investigations [19] revealed that unavoidable leaching of metal from the framework with the use of acetic acid contributed to the observed results. In addition to the typical problem of leaching of the active metal ions from the matrix, it was found that the small pore opening of these microporous molecular sieve catalysts restricts their application in processes dealing with bulky molecules, the large size and charge difference between active metal and silicon have led to the formation of metal oxide clusters inside the mesopores of the framework structure [20–22].

An interesting approach is using HPA. This has attracted great interest as catalysts for its ability to catalyze various types of oxidative reactions. In fact they were used in the oxidation of alkane epoxidation of alkenes and the hydroxylation of alkanes [23–26]. In the present work, we report the catalytic activity of the dodecamolybdo-phosphate ammonium salt $(\text{NH}_3)_4\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$ on the oxidation of cyclohexane with aqueous hydrogen peroxide. The use of the latter in the oxidation of organic substrates is considered to be very attractive, since diluted aqueous H_2O_2 is cheap, environmentally clean and easy to handle [27,28].

Experimental

Preparation of the Catalysts

The $(\text{NH}_3)_4\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$ was prepared using the following procedure: the compound is precipitated by adding slowly the stoichiometric required amount of ortho-phosphoric acid (H_3PO_4 85%) and perchloric acid (HClO_4 70%) to an aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$. The Keggin-type anion $\text{PMo}_{12}\text{O}_{40}^{3-}$ is formed in solution at acid conditions, and the insoluble ammonium 12-molybdophosphate salt is immediately precipitated.

Catalyst Characterization

The purity and the Keggin structure of the sample were characterized by means of IR and thermogravimetry (TGA). IR spectra were recorded with an infrared spectrometer GENESIS II- FTIR ($4000\text{--}400\text{ cm}^{-1}$) as KBr pellets. TGA were carried out in flow of argon in a thermogravimeter (PERKIN-ELMER, TGA). Samples around 5–10 mg of ammonium 12 molybdophosphate salt was heated at 5 K per minute up to 793 K. The XRD powder patterns

were recorded on a Rigaku diffractometer Ultima IV using monochromatized Cu-K α radiation.

Catalytic measurements

Catalytic tests were carried out in a 200 ml pyrex flask surmounted by a condenser. The standard procedure is as follow : 5 ml of cyclohexane, 10ml of hydrogen peroxide (30% in aqueous solution) and 5ml of acetic acid were charged into the flask and it was heated to the desired temperature then 0.125g of ammonium 12-molybdophosphate was poured in the flask. After the required time, the liquid phase was cooled, sampled, and analyzed with a gas phase chromatography (PYE UNICAM PU 4500) equipped with a flame ionization, a catharometer detectors and a capillary column (HP-PLOT Q length 30m ID 0.53 mm). ^1H NMR spectra were recorded on a Bruker Avance 400 MHz spectrophotometer using 5mm NMR tubes.

Results and Discussion

Characterization of catalysts.

Infrared spectra

The Keggin type heteropolyanions have strong characteristic absorption bands in the range of $1100\text{--}700\text{ cm}^{-1}$. The IR spectra of the samples are shown in Fig. 1. They have been assigned according to Ref [29, 30]. The main characteristic features of the Keggin structure are observed at $1080\text{--}1060\text{ cm}^{-1}$ ($\nu_{\text{as}} \text{P-O}_a$), at $990\text{--}960\text{ cm}^{-1}$ ($\nu_{\text{as}} \text{Mo-O}_d$), at $900\text{--}870\text{ cm}^{-1}$ ($\nu_a \text{Mo-O}_d\text{-Mo}$), and at $810\text{--}760\text{ cm}^{-1}$ ($\nu_{\text{as}} \text{Mo-O}_c\text{-Mo}$). Besides the above characteristic frequencies of the heteropolyanion, there is a broad band at 3212 cm^{-1} , and a sharp band at 1414 cm^{-1} , which are the feature absorption of NH_4^+ group, this indicates the formation of $(\text{NH}_3)_4\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$ [29].

It can be seen from the Fig 1 that sample (a) and (b) have similar absorption bands of Keggin-type which indicates that the structure of the ammonium salt was not destroyed after the reaction. The great practical interest is the non destruction of the catalyst used in the reaction and its easy separation from the reaction mixture.

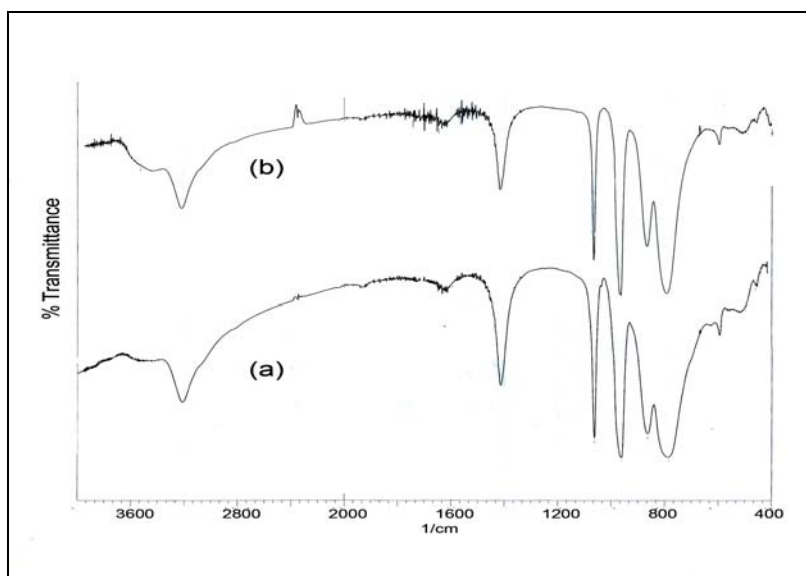


Figure 1 : IR spectra of $(\text{NH}_3)_4\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$: a) before reaction b) after reaction.

Thermogravimetric analysis

Fig 2 illustrates the thermogravimetric (TG) curve of $(\text{NH}_3)_4\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$. The number of ammonium cations and water molecules in the heteropoly compounds can be determined by thermogravimetric analysis by the loss of weight as soon as the temperature is increased. The TG curve shows that there are two steps of mass loss. The first

is the loss of hydration water (≈ 4 -hydrates), followed by a plateau corresponding to the anhydrous acid is observed between 140 and 270°C and the second is the loss of the ammonium cations ($\approx 3 \text{NH}_4^+$). With a further increase of the temperature, above 450-500°C only mixtures of oxides are characterized (typical by IR). The TG curves (Fig 2) are consistent with published results [16].

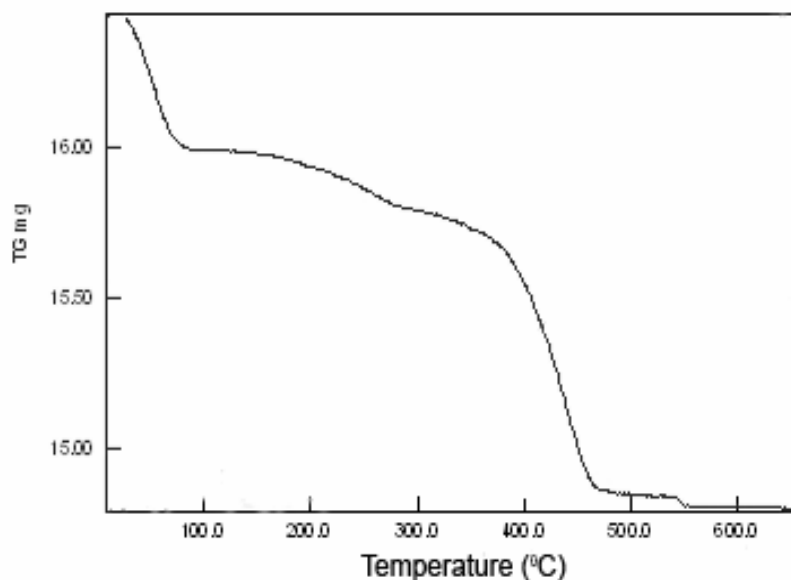


Figure 2 : Thermogravimetric curve of $(\text{NH}_3)_4\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$ (heating rate of 5 °C /min in N_2).

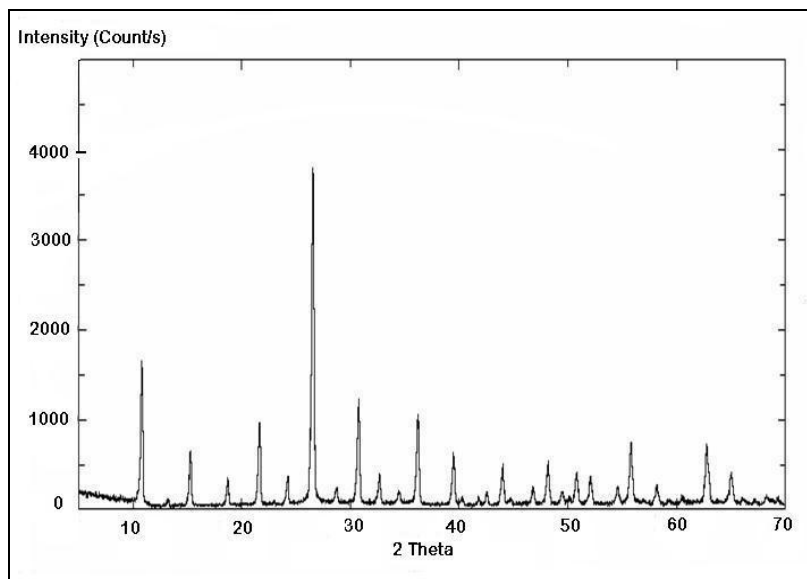


Figure 3 : XRD diagram of $(\text{NH}_3)_4\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$.

X-ray diffraction pattern of the sample (Fig 6), shows the diffraction lines typical of $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ (JCPDS 09-0412), with a cubic structure.

Catalytic reactivity

The main products observed during the oxidation of cyclohexane in the liquid phase at 343K with H_2O_2 catalyzed by ammonium 12-molybdophosphate were cyclohexanol and cyclohexanone and some minor products such as cyclohexene, hexanal and hexanoic

acid. This result is in agreement with that published in the literature [31-32]. Since cyclohexyl hydroperoxide (CHHP) decomposes during chromatographic analysis, the reaction products were also analyzed by ^1H NMR to check its formation. It can be seen from the Fig 4, that the peaks observed can be assigned to cyclohexane, cyclohexanone, cyclohexanol. A negligible trace of acid sometimes observed whereas the s corresponding to the cyclohexyl hydroperoxide not observed in the ^1H NMR spectrum.

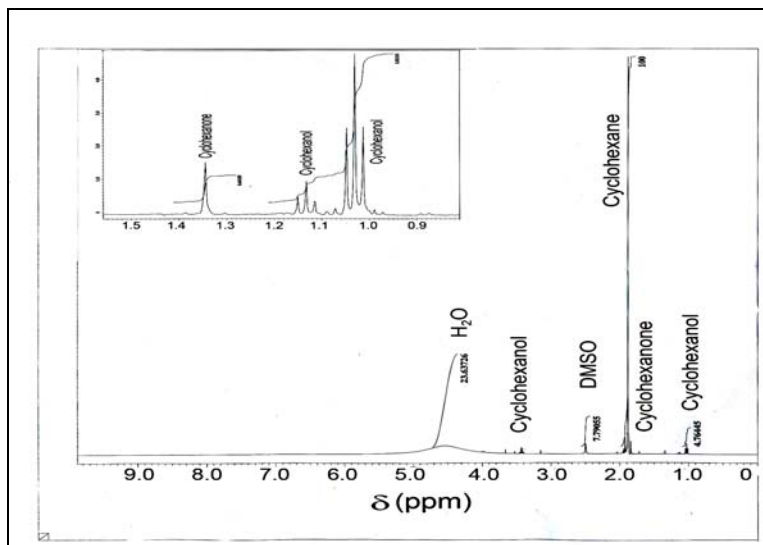


Figure 4 : ^1H NMR spectrum of the reaction mixture after 5h at 343K catalyzed by $(\text{NH}_3)_4\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$.

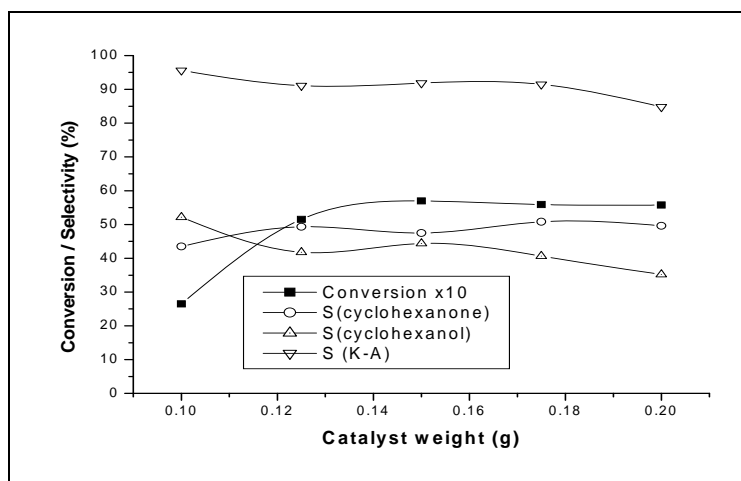


Figure 5 : Effect of catalyst weight on the conversion and selectivity over $(\text{NH}_3)_4\text{PMo}_{12}\text{O}_{40}$ (reaction conditions: volume ratio : cyclohexane / H_2O_2 = 1/2; T = 343 K).

Effect of the amount of catalyst on cyclohexane oxidation

The effect of the amount of catalyst on cyclohexane reaction over $(\text{NH}_3)_4\text{PMo}_{12}\text{O}_{40} \cdot 4\text{H}_2\text{O}$ was investigated and depicted in Fig 5. A slightly increase in cyclohexane conversion and in cyclohexanone selectivity were observed when the amount of the catalyst was increased up to 0.125 g. Beyond this amount, the conversion of cyclohexane and selectivity of cyclohexanone only increased a little. Inversely the selectivity of cyclohexanol and K-A, decreased up to 0.125g thereafter they only decreased a little. However a further increase in the amount of catalyst resulted in slight decrease in the conversion and in the K-A total selectivity which may be due to the decomposition of H_2O_2 at higher amount of catalyst. These results are in agreement with those obtained by W. Yao et al. [33], where it was observed that only small amount of catalyst (Ce-MCM-41) is active in the oxidation of cyclohexane. It was also observed that a further increase in the reaction temperature resulted in slight decrease in the conversion probably owing to a quicker decomposition of H_2O_2 at higher temperature.

3.2.2. Effect of reaction time on cyclohexane oxidation.

As 0.125g of the catalyst was observed as the suitable amount for the oxidation of cyclohexane, it was employed to investigate the progress of the reaction with time under the typical reaction condition. The effect of reaction time on cyclohexane

conversion and products distributions is shown in Fig 6. It can be seen from the figure that the cyclohexane conversion as well as the selectivity of cyclohexanone steadily increased with increasing reaction time whereas the selectivity of cyclohexanol decreased with the reaction time. It can also be noticed from this figure that, at the initial stages, the cyclohexanol was observed as a principal product then it decreased rapidly in favor of cyclohexanone. As for the total selectivity to K-A oil, it can be noticed that is maintained to approximately 100% for 3h thereafter it steadily decreased to the value of 91%.

The decrease in cyclohexanol selectivity is linked to a distinct increase in cyclohexanone concentration, thus suggesting over oxidation of cyclohexanol. The high initial rate of cyclohexanol formation suggests that the latter is a primary oxidation product of cyclohexane. Further oxidation of the cyclohexanol proceeds much more rapidly than that of cyclohexane, explaining the rapid leveling off of the selectivity as a function of reaction time. Fig 7 depicts the effect of reaction time on cyclohexanone to cyclohexanol (K/A) ratio. Similar to the conversion, the ratio of (K/A) increased with increasing reaction time. It varied respectively from (0.053) to (1.18) when the reaction time varied from 30 min to 5h. This result is in agreement with that published in the literature where it was mentioned that the formation of the cyclohexanone could be attributed to secondary oxidation of cyclohexanol [34-35].

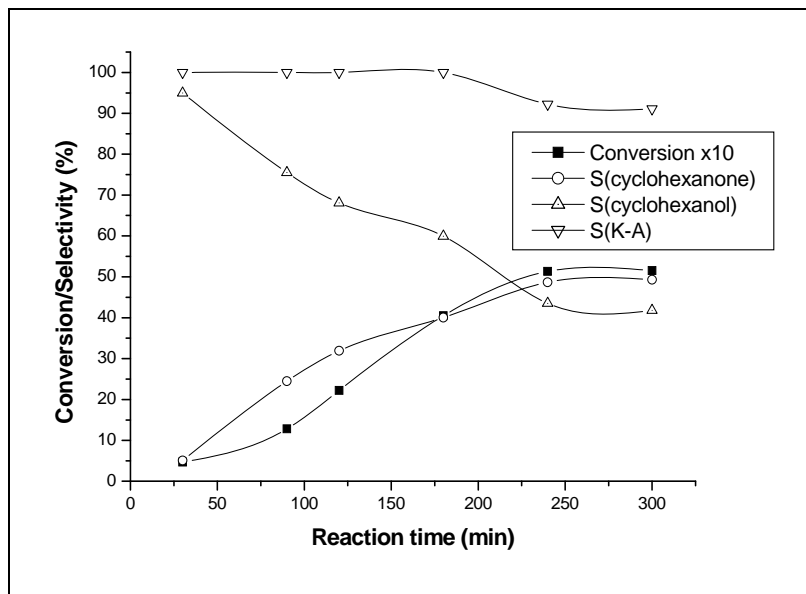


Figure 6 : Effect of reaction time on the conversion and the selectivity over $(\text{NH}_3)_4\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$ (reaction conditions: volume ratio : cyclohexane / $\text{H}_2\text{O}_2 = 1/2$; $T = 343 \text{ K}$; catalyst weight = 0.125g).

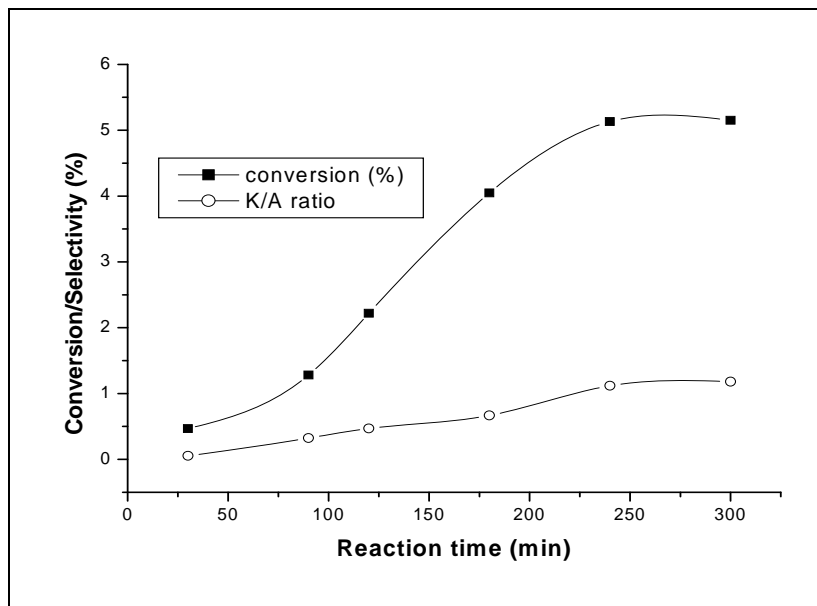


Figure 7 : Effect of reaction time on the cyclohexanone / cyclohexanol (K/A) ratio over $(\text{NH}_3)_4\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$ (reaction conditions: volume ratio : cyclohexane / $\text{H}_2\text{O}_2 = 1/2$; $T = 343 \text{ K}$; catalyst weight = 0.125g).

Conclusion

$(\text{NH}_3)_4\text{PMo}_{12}\text{O}_{40}\cdot 4\text{H}_2\text{O}$ having keggin structure is an active and selective catalyst for the oxidation of cyclohexane to cyclohexanol and cyclohexanone

under mild conditions without adding any initiator. Cyclohexanol might be the primary product which is further oxidized to cyclohexanone. Above 91% selectivity towards K-A oil products was achieved at

conversion that exceed 5%. Higher amounts of catalysts would cause the decomposition of hydrogen peroxide and result in a relatively low activity. Therefore only small amount of catalyst is active in the oxidation of cyclohexane. The catalyst can be separated from the reaction mixtures just by filtering. Its keggin structure was preserved after reaction, therefore it can be reused.

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