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Journal of Photochemistry and Photobiology A: Chemistry 188 (2007) 279–286
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Photocatalyzed oxidation of cyclohexane with heterogenized decatungstate

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Received 21 September 2006; received in revised form 14 November 2006; accepted 13 December 2006
Available online 16 December 2006

Abstract

The application of heterogeneous catalysis to the oxidation of alkanes in mild conditions still remains a challenge although in the last decade many interesting approaches were proposed and examined delivering numerous significant results. Following our interest in C–H bond activation by photocatalysis with sodium decatungstate research on the possibility of its heterogenization on ion-exchange organic resins and a carbon material was undertaken. The photocatalytic activity of obtained heterogenized decatungstate for cyclohexane oxidation with molecular oxygen was examined. It was found that the highest activity was observed for decatungstate supported on an ion-exchange resin. The decatungstate concentration and loading effect on the reaction progress and selectivity was investigated. Catalyst loading on the support, contrary to catalyst concentration in the irradiated solution, determined the oxidation selectivity, i.e. the formation of cyclohexanone, cyclohexanol and cyclohexyl hydroperoxide. The lower loading of decatungstate promoted cyclohexanone production whereas the catalysts of high decatungstate loading favoured cyclohexyl hydroperoxide generation.

Keywords: Supported catalyst; Decatungstate; Photocatalytic oxidation; Cyclohexane

1. Introduction

The development of mild and selective methods for the functionalization of carbon–hydrogen bonds to carbon–oxygen functional groups continues to be a challenging area of investigation [1]. The oxidation of cyclohexane to cyclohexanol and cyclohexanone, intermediate products in the synthesis of, e.g. synthetic fibbers and fine chemicals, is an example of this transformation. The reaction remains in the centre of interest of many research groups [2–4] as it is one of the least efficient of all major industrial chemical processes. Catalysis for the partial oxidation of alkanes was also identified as a highly attractive and compelling investigation field by the leading researchers at the forum on future directions in catalysis [5]. The new technology is yet to be developed for reducing the process burden on the environment.

The low efficiency and selectivity of C–H bonds oxygenation on the one hand and the benefits that can be gained from heterogeneous photocatalysis on the other hand have motivated the search for solid catalysts that could be used for the photocatalyzed oxidation of small hydrocarbons. Heterogeneous catalysis may be achieved by employing a catalyst naturally occurring in solid state or a catalyst immobilized on various supports. Heterogenization of active (photo)catalyst may lead to substantially different catalytic activities and selectivities.

One of the most commonly and widely investigated solid photocatalysts, also towards oxygenation of hydrocarbons, is titanium oxide [6–8]. Selective photooxidation of cyclohexane by TiO_2 has been briefly reviewed and thoroughly studied by Du et al. recently [9]. The photocatalysis over TiO_2 yielded mainly cyclohexanone if only photolysis was prevented. The surface hydroxyl groups on the semiconductor oxide were found to be an important factor in controlling the catalyst activity and the reaction rate. The competitive adsorption effect on product formation and selectivity was examined using various solvents [10]. Non-polar solvents were reported to enhance deep oxidation. Photon flux and wave effects examined by Brusa and Grela [8] delivered an insight into the origin of the selectivity changes.

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1010-6030/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.jphotochem.2006.12.023

Besides titanium oxide various supported catalysts were tested for photooxidation of cyclohexane. High selectivity to partial oxidation compounds (cyclohexanol and cyclohexanone) was achieved using alumina supported vanadium oxide [11,12]. The catalysts obtained in the immobilization process of $n(Bu_4N)_4W_{10}O_{32}$ and $Na_4W_{10}O_{32}$ on mesoporous and amorphous silicas by impregnation was demonstrated to be successful in oxidizing cyclohexane and cyclododecane. The mesoporous-silica supported catalyst promoted the process with higher chemoselectivity defined as a ketone/alcohol ratio. The heterogenized catalysts were stable and as efficient as decatungstate in homogenous phase [13,14]. Polystyrene-bound Mn(TPyP) was used for oxidation of various alkanes with sodium periodate under ultrasonic irradiation. The system allowed their conversion to the corresponding alcohols and ketones [15]. Highly selective oxidation of cyclohexane to cyclohexanone with molecular oxygen was achieved using Cr–Si binary oxide prepared by sol–gel method under visible light irradiation [16].

It is well documented that polyoxometalates, well known of their photocatalytic properties [17], are also effective photocatalysts for the oxidation of a C–H bond in hydrocarbons. One of the most promising catalysts is decatungstate $W_{10}O_{32}{}^{4-}$, which application was widely studied over the last few years. Both the mechanistic aspects of reactions [14,18–21] and the synthetic [22,23] and environmental [24,25] application possibilities were examined. A few attempts at heterogenizing decatungstate on various materials for divers photocatalytic purposes were made. Decatungstate immobilization on silica by impregnation [13,14,26], the catalyst incorporation into the network of silica formed via sol–gel technique [27,28] and into polymeric membrane [25] were reported and the photocatalytic activity of the obtained heterogeneous catalysts was demonstrated.

The aim of this paper is to investigate the possibility of decatungstate immobilization by ion-exchange onto organic ion-exchange resins: poly(4-vinylpyridine), cross-linked, methyl chloride quaternary salt, poly(4-vinylpyridinium tribromide) and poly(4-vinylpyridinium *p*-toluenesulfonate), which has not been examined yet, as well as its heterogenization on a carbon material (Ambersorb®). The photocatalytic properties, activity and selectivity, of so-obtained supported decatungstate are tested for the partial oxidation of cyclohexane. Decatungstate loading and catalyst concentration effects are investigated.

2. Experimental

2.1. Materials

Sodium decatungstate $Na_4W_{10}O_{32}$ was synthesised and characterised according to a literature method [29].

The following materials were used as supports for decatungstate: ion exchangers poly(4-vinylpyridine), cross-linked, methyl chloride quaternary salt—material A, poly(4-vinylpyridinium tribromide)—B and poly(4-vinylpyridinium *p*-toluenesulfonate)—C, a carbon material Ambersorb® 348F—material D, all purchased from Aldrich Chemical Company (Milwaukee, WI, USA).

Acetonitrile, propanol-2, both HPLC grade and cyclohexane, which was purified by distillation before use, were purchased from SDS (Peypin, France). Analytical grade thymol and triethylphosphine were purchased from Fluka (Sigma–Aldrich Chemie, Lyon, France).

2.2. Methods

2.2.1. Preparation of supported catalysts

Sodium decatungstate was dissolved in deionised water acidified with $HClO_4$ (pH 2.35) and added to powders of organic polymers obtained by fine grinding of materials A, B and C and to carbon material D. A solution to support material ratio was kept at 20:1 (v/w). Mixtures were stirred gently for 3 h. In the case of carbon material, water was removed in vacuum at 50 °C. Suspensions of organic polymer powders were filtered. Then catalysts were dried under vacuum overnight.

All obtained catalysts were washed three times with acetonitrile and the UV–vis spectrophotometry method was used to control the quantity of decatungstate desorbed from the support.

The catalysts were analyzed for carbon, hydrogen, oxygen and tungsten content by microanalysis (CNRS, Vernaison, France).

2.2.2. Adsorption experiments

Batch adsorption dynamic and equilibrium studies were performed using 2 mL of solution and 100 mg of dry polymer. For the adsorption dynamic experiments, the concentration of decatungstate ions was 50 g dm^{-3}. For the adsorption equilibrium experiments, the concentration of decatungstate ions was varied between 50 and 190 g dm^{-3}. The suspensions were stirred at room temperature. For the adsorption dynamic experiments, the aliquots of solution were collected every 90 min. All supernatants were analyzed for decatungstate content by UV-spectrophotometric method. The amount of adsorbed catalyst was calculated by mass balance end expressed in mg per g of dry support.

Adsorption dynamic and equilibrium data were fitted to the pseudo-first-order kinetic model and Langmuir adsorption isotherm model by GOSA software (BIO-LOG, 22, rue Valade 31000 TOULOUSE, FRANCE; http://www.bio-log.biz).

2.2.3. Irradiation

The samples were prepared by introducing the appropriate amount of decatungstate catalyst to 5% (v/v) solution of cyclohexane in acetonitrile, sonicated for 30 min, transferred into a photochemical reactor and saturated with dioxygen for 15 min before irradiation. A 200 mL cylindrical reactor with a flat bottom for magnetic stirring, equipped with a deep-in pyrex cold water cut-off filter ($\lambda > 280$ nm, reactor optical path length 1 cm) and a preheated Hanovia 125 W medium-pressure Hg arc lamp, was used for photochemical reactions. During irradiation dioxygen was introduced into the reaction tube at constant speed. Samples of photolyte were collected in 15 min intervals for 3 h and their aliquots immediately centrifuged and subjected to GC analysis. The total hydroperoxide concentrations were measured by iodometric titration.

To control decatungstate presence in photolytes, the samples collected after 3 h of the irradiation were centrifuged, concentrated and their UV–vis spectra were registered.

To examine the possibility of re-use of decatungstate/A, the cyclohexane/acetonitrile solution was irradiated in the presence of this catalyst for 6 h and then filtered. The catalyst was rinsed with acetonitrile three times, dried under vacuum overnight and introduced to the fresh solution of cyclohexane in acetonitrile. The suspension was irradiated for 6 h. In both cases samples were collected after 3 and 6 h of irradiation and GC analyses were carried out. The presence of decatungstate anion in the solution was controlled after 6 h of irradiation by UV–vis measurements.

2.2.4. GC analysis

The quantitative GC analyses were performed on a Varian CP 3800 instrument equipped with a DB-WAX fused silica capillary column (25 m × 0.25 mm i.d.), an autosampler and a flame ionization detector. Nitrogen was used as the carrier gas. The column temperature was kept at 50 °C for 2 min and then increased to 200 °C at a rate of 10 °C min^{-1}. The analyses were carried out in the presence of thymol as an internal standard. The method coefficient of variation did not exceed 5%.

To determine cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide content in the photolyte its aliquots were analyzed by GC before and after the treatment of the sample with triethylphosphine [30,31]. When it is not indicated otherwise the cyclohexanol and cyclohexanone concentrations discussed are the GC measured amounts of the compounds after a sample reduction with triethylphosphine.

3. Results and discussion

3.1. Effect of support on the cyclohexane oxidation

The ion-exchange immobilization of $W_{10}O_{32}{}^{4-}$ on powders of organic polymers resulted in stable heterogeneous catalysts: decatungstate/A, decatungstate/B and decatungstate/C, which did not release $W_{10}O_{32}{}^{4-}$ to the solution during washing steps and the irradiation. The concentrated aliquots of the photolytes were analyzed by UV–vis spectrometry and the characteristic absorption band of decatungstate at 323 nm was not observed. In contrast to this, decatungstate/D even after prolonged washing with acetonitrile still lost approximately 3–5% of $W_{10}O_{32}{}^{4-}$ to the irradiated solution. Moreover significant desorption of $W_{10}O_{32}{}^{4-}$ was observed from carbon material during washing steps leading to the removal of about 20–30% of the introduced catalyst.

The activity of the obtained heterogeneous catalysts was investigated towards the photooxidation of cyclohexane in acetonitrile (5%, v/v solution). Fig. 1 presents the curves of turnover numbers calculated as millimols of oxidized products (cyclohexanol and cyclohexanone) per millimol of $W_{10}O_{32}{}^{4-}$ when decatungstate/A, decatungstate/B, decatungstate/C and decatungstate/D were used as photocatalysts. The highest turnover values during 3 h of UV irradiation were observed for decatungstate/A. The turnover numbers for decatungstate/A were about 50% greater than these for decatungstate/B at the beginning of irradiation and about two times higher after 3 h. The change of the concavity of the curve relevant to decatungstate/B with time was observed. The different initial concavity with respect to the other curves was also apparent. Further study is needed to identify the source and nature of the differences. In the case of cyclohexane photocatalytic oxidation with decatungstate/C significantly lower turnovers were measured during the whole period of irradiation. The significant differences in the results might be attributed to the spatial conditions or the different ability of support to adsorb/desorb substrates and/or products from/to the solution. Yet, it is most likely that inhibited reoxidation of decatungstate/C is responsible for low turnover of cyclohexane oxidation. The catalyst remained blue even when the oxygen flow was increased; the blue colour of the catalyst is associated with the reduced form of decatungstate anion $HW_{10}O_{32}{}^{4-}$.

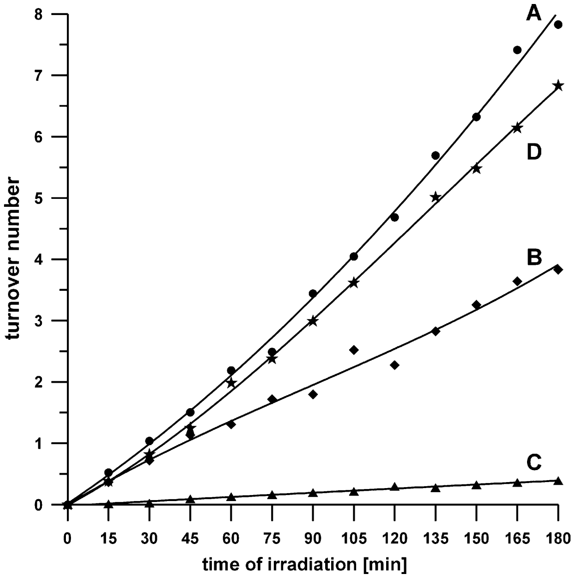

Fig. 1. The turnover numbers, calculated as millimols of oxidized products (cyclohexanol and cyclohexanone) per millimol of decatungstate $W_{10}O_{32}{}^{4-}$, observed during irradiations of 5% (v/v) cyclohexane/acetonitrile solution in the presence of (A) decatungstate/A, (B) decatungstate/B, (C) decatungstate/C and (D) decatungstate/D. The concentrations of decatungstate in irradiated mixture was 2×10^{-4} mol dm^{-3}.

The turnover numbers calculated for cyclohexane oxidation with decatungstate/D are close to those for decatungstate/A. One may say that they resulted from the fact that the surface of carbon materials was especially prompt to adsorb cyclohexane enhancing and facilitating its oxidation. However, it should be taken into account that this catalyst released $W_{10}O_{32}{}^{4-}$ into the solution (3–5%) hence homogeneous catalysis was likely to have been involved and take a part in the process as well. Moreover, when the time of irradiation was increased the destruction of material D structure was observed (the solution became darker) leading to the change of light conditions and making re-use of the catalyst impossible.

In the light of the obtained results it appears that the nature and strength of interaction/bond between decatungstate and the support should be considered carefully. It is as an important factor responsible for ensuring the catalyst stability, preventing its leaching, providing adequate ad-/de-sorption condition for reagents and products as well as guaranteeing fast catalyst reoxidation, which determine the progress of photocatalytic process and the catalyst usefulness. The catalyst prepared by immobilization of decatungstate on material A showed the most favourable properties for cyclohexane photooxidation. It both yielded the highest turnover numbers and did not release decatungstate to the solution. The heterogenization of decatungstate on material A and the catalytic efficiency and selectivity of the obtained catalyst were further examined in more details.

3.2. Catalyst heterogenization process

Two essential evaluation parameters for decatungstate heterogenization process are the mechanism and the adsorption rate.

3.2.1. Adsorption kinetics

Adsorption kinetics depends on the adsorbate–adsorbent interaction and system condition. Solute uptake rate determines the residence time required for completing the heterogenization reaction. The rate of decatungstate adsorption onto support A was determined by taking supernatant aliquots at various time intervals and measuring anion concentrations. Results are shown in Fig. 2. The amount of adsorbed decatungstate increases over time. The sorption of decatungstate by polymer A support, which is a strong anion exchanger, is fitted well by the pseudo-first-order kinetic equation ($R^2 = 0.999$):

$$q_t = q_e(1 - e^{-kt}),$$

where q_t and q_e are the amounts of decatungstate adsorbed at time t and at equilibrium (in mg g^{-1}), respectively, and k is the adsorption rate constant (in min^{-1}). Fig. 2 besides data points presents the simulation of the pseudo-first-order equation for the experimental kinetic data. In the pseudo-first-order kinetic reactions reaction rate do not depend on adsorbate concentration but only on the number of occupied adsorption centrums.

3.2.2. Adsorption isotherm

In an attempt to determine the adsorption capacity of the polymer support for decatungstate anions the empirical correlation of Langmuir:

$$q_e = \frac{q_m k c_e}{1 + k c_e},$$

in its linearized form:

$$\frac{c_e}{q_e} = \frac{1}{q_m k} + \frac{c_e}{q_m},$$

where q_m is adsorption capacity (mg g^{-1}), k is adsorption constant (L mg^{-1}), and c_e is the equilibrium concentration (mg L^{-1}) was used to fit data. The linearized equilibrium isotherm of decatungstate sorption onto polymer A support is shown in Fig. 3. As can be seen from the figure within the concentration range studied the adsorption equilibrium data are modelled well with the Langmuir equation ($R^2 = 0.98$). The adsorption capacity for decatungstate anions calculated from Langmuir isotherm $q_m = 1976.03$ mg g^{-1} corresponds well to the exchange capacity of the support, which is 3.4 mequiv. g^{-1}. An ion-exchange material A used as support for decatungstate has a measured CEC of 2.25 thus it is theoretically able to take up (exchange) 1997.84 mg of decatungstate ($W_{10}O_{32}^{4-}$ from the solution) per gram of material. It can be concluded that the adsorption of decatungstate ions on polymer adsorption centra under experimental conditions studied is of ion-exchange nature solely and

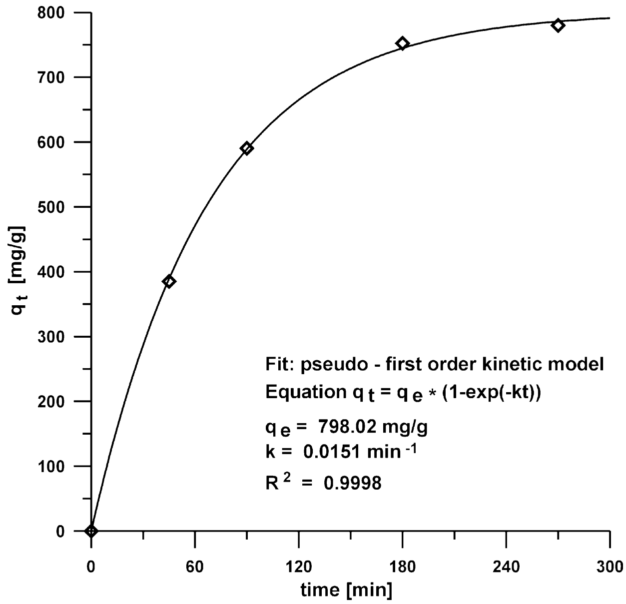

Fig. 2. Pseudo-first-order kinetic model fit of decatungstate sorption onto polymer support (material A) at room temperature; initial concentration of decatungstate 50 g dm^{-3}; the experimental data (diamonds).

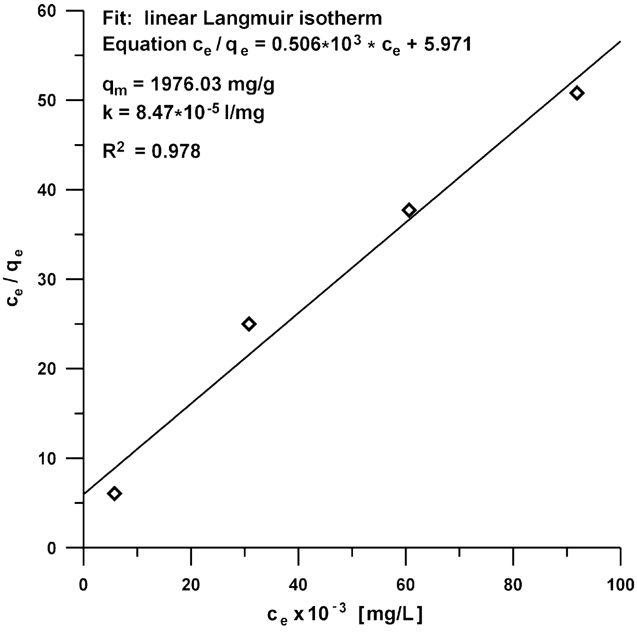

Fig. 3. Linearized Langmuir isotherm fit of decatungstate adsorption on polymeric support (material A) at room temperature; initial decatungstate concentrations range from 50 to 190 g dm^{-3}; the experimental data (diamonds).

the interactions between decatungstate and a organic resin studied have ionic character.The shape of the Langmuir isotherm can be investigated by dimensionless constant R_L defined as

$$R_L = \frac{1}{1 + kc_0},$$

where c_0 is the initial concentration of decatungstate (mg L^{-1}).

All R_L values for the studied system were found to be between 0 and 1, and ranged from 0.061 to 0.181 for the lowest and highest initial concentrations, respectively, indicating high-affinity adsorption. Low reversibility suggests that the adsorbed decatungstate is bound very tightly by surface charges and that the heterogenized decatungstate catalyst will be stable and it is not likely to leak to the solution.

3.3. Effect of the amount of catalyst on cyclohexane oxidation

In order to define the efficiency of decatungstate/A catalyst, the influence of the catalyst amount on the rate of oxidation and turnover was investigated. Plots of the concentration of the sum of oxygenated products (cyclohexanol and cyclohexanone) after 3 h irradiation of cyclohexane in acetonitrile and corresponding turnovers calculated as mmol of cyclohexanol and cyclohexanone per mmol of the catalyst versus catalyst concentration is shown in Fig. 4. At low catalyst concentrations the accumulation of oxygenated products (cyclohexanol and cyclohexanone) was directly proportional to the amount of catalyst and the highest values of turnovers were obtained. When the concentration of the decatungstate was reaching 10^{-5} mol dm^{-3}, which corresponds to 0.1 mg cm^{-3} of decatungstate/A catalyst in the mixture, the rate of oxygenation slowed down. The amount of oxygenated products (sum of cyclohexanol and cyclohexanone) increased slightly when decatungstate amounts was increased from 2×10^{-4} to 5.5×10^{-4} mol dm^{-3}, which meant the introduction of 2–5 g dm^{-3} of heterogeneous decatungstate/A. At low catalyst concentration the rate of photooxidation was directly proportional to the light intensity absorbed by decatungstate. When the catalyst was present in higher amounts the screening effect of polymer particles started to play the key role. Nevertheless the increase in catalyst concentration was followed by the increase in the reaction rate. Although not all the particles of organic polymer were illuminated, the probability of photon absorption by decatungstate ions dispersed on the resin appeared to rise with the number of decatungstate molecules. In heterogeneous systems when a photoactive compound is deposited on photocatalytically inert materials the light dependencies seem to be complex and need thorough studying, which is beyond the subject of the paper.

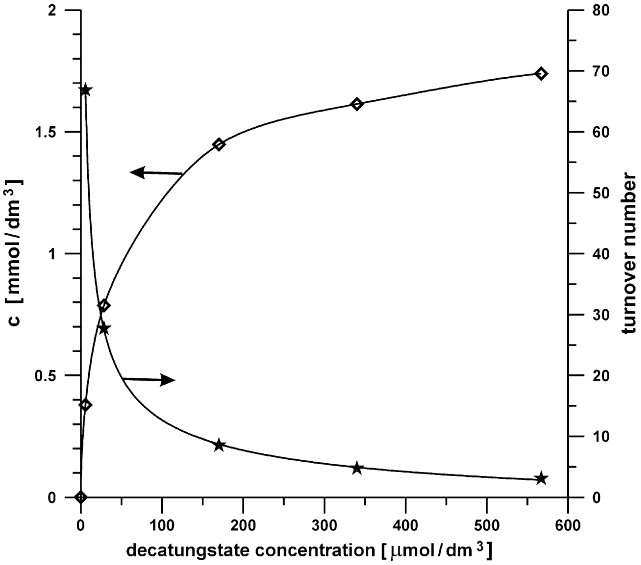

Fig. 4. The concentration of the sum of oxygenated products, cyclohexanol and cyclohexanone, after 3 h of irradiation of 5% (v/v) cyclohexane/acetonitrile solution with decatungstate/A vs. concentration of decatungstate (diamonds) accompanied by calculated turnover numbers, millimols of oxidized products per millimol of decatungstate $W_{10}O_{32}{}^{4-}$, (stars) fitted with inverse square root equation.

3.4. Effect of decatungstate loading on cyclohexane oxidation

To determine the effect of decatungstate loading, catalysts of various tungsten content were prepared and used during irradiation of cyclohexane/acetonitrile mixture. The turnover numbers observed after 3 h of irradiation were 4.41 at the catalyst concentration of 407 μmol dm^{-3}; 3.00 at 440 μmol dm^{-3}; 2.03 at 602 μmol dm^{-3}; 2.73 at 530 μmol dm^{-3} for the catalysts of 24.64, 32.03, 41.29 and 43.3% W, respectively. The turnovers matched the turnover curve of Fig. 4 for the catalyst of 20.86% tungsten content well. The change in decatungstate loading on support does not influence cyclohexane oxidation significantly. The process turnover appears to depend only on decatungstate concentration in the irradiated mixture. The decay in the turnover number with the increase in catalyst concentration is of power nature. The turnover number is inversely proportional to the square root of catalyst concentration: $\text{TN} = 170.32 C_{W_{10}O_{32}}^{-0.5} - 4.56$ ($R^2 = 0.999$), where TN is the turnover number and $C_{W_{10}O_{32}}$ is the concentration of decatungstate during irradiation (μmol dm^{-3}).

3.5. Kinetics of cyclohexane oxidation

In order to determine the progress and selectivity of cyclohexane oxidation with decatungstate/A catalyst the kinetics of the reaction was investigated. The samples of photolyte were collected in 15 min intervals for 3 h and analyzed for cyclohexanone and cyclohexanol content by GC before and after the treatment of the sample with triethylphosphine. The method of the two chromatograms comparison delivers not only the information about the levels of alcohol and ketone in the solution but also about the existence or non-existence of cyclohexyl hydroperoxide [30,31]. Cyclohexyl hydroperoxide present in non-treated sample subjected to GC analysis totally decomposes in the chromatograph onto cyclohexanol and cyclohexanone. When an excess of triethylphosphine is added to the sample before the GC the peroxide is quantitatively reduced to cyclohexanol. On the chromatogram an increase in cyclohexanol peak and a decrease in cyclohexanone peak are observed. The cyclohexanone peak after reduction represents real concentration of the compound in the solution. By comparing the data of chromatographic analysis of the reaction solution before and after reduction with the phosphine, the amounts of cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide formed during irradiation can be estimated quantitatively.

The evolution of the oxidation products during irradiation of cyclohexane/acetonitrile solution in the presence of decatungstate/A catalyst of various decatungstate loading is presented in Figs. 5 and 6 for the catalysts of 20.86 and 43.3% W content, respectively. The upper graphs present the concentration of cyclohexanol and cyclohexanone before and after the reduction with triethylphosphine. The estimated from upper graphs real concentrations of cyclohexyl hydroperoxide and cyclohexanol are presented in the middle graphs. The bottom graphs show the percentage of real cyclohexanone and the concentration ratio of cyclohexanone before and after reduction. The concentration plots before and after the reduction differs significantly. It is apparent that besides cyclohexanone and cyclohexanol cyclohexyl hydroperoxide is formed during cyclohexane photocatalyzed oxidation with decatungstate/A catalyst. The amount of produced cyclohexanone is higher for the catalyst of lower decatungstate loading. It oscillates around 30% while for the catalyst of higher decatungstate loading it does not excide 13% of the total concentration of cyclohexanone, cyclohexanol and cyclohexyl peroxide accumulated. The investigation of the ratio of cyclohexanone concentration before and after reduction with triethylphosphine allows to indicate which system generates more cyclohexyl peroxide. The cyclohexanone concentration after reduction is equal to its real concentration in the photolyte whereas that before reduction is a sum of real cyclohexanone concentration and cyclohexanone that is a product of cyclohexyl hydroperoxide decomposition in the chromatograph. The higher the ratio the more hydroperoxide is present in the sample. The real concentrations of cyclohexyl hydroperoxide and cyclohexanol were also estimated from before and after reduction with triethylphosphine cyclohexanol and cyclohexanone data. When two catalysts of different decatungstate loading were used the photocatalytic system employing the catalyst of higher content of decatungstate produced more cyclohexyl hydroperoxide. It is a dominant product in this case. The observations were confirmed when the catalyst of 24.39% tungsten content was used. The percentage of cyclohexanone and the ratio of cyclohexanone concentration before and after reduction with triethylphosphine were around 25 and 2.4, respectively.

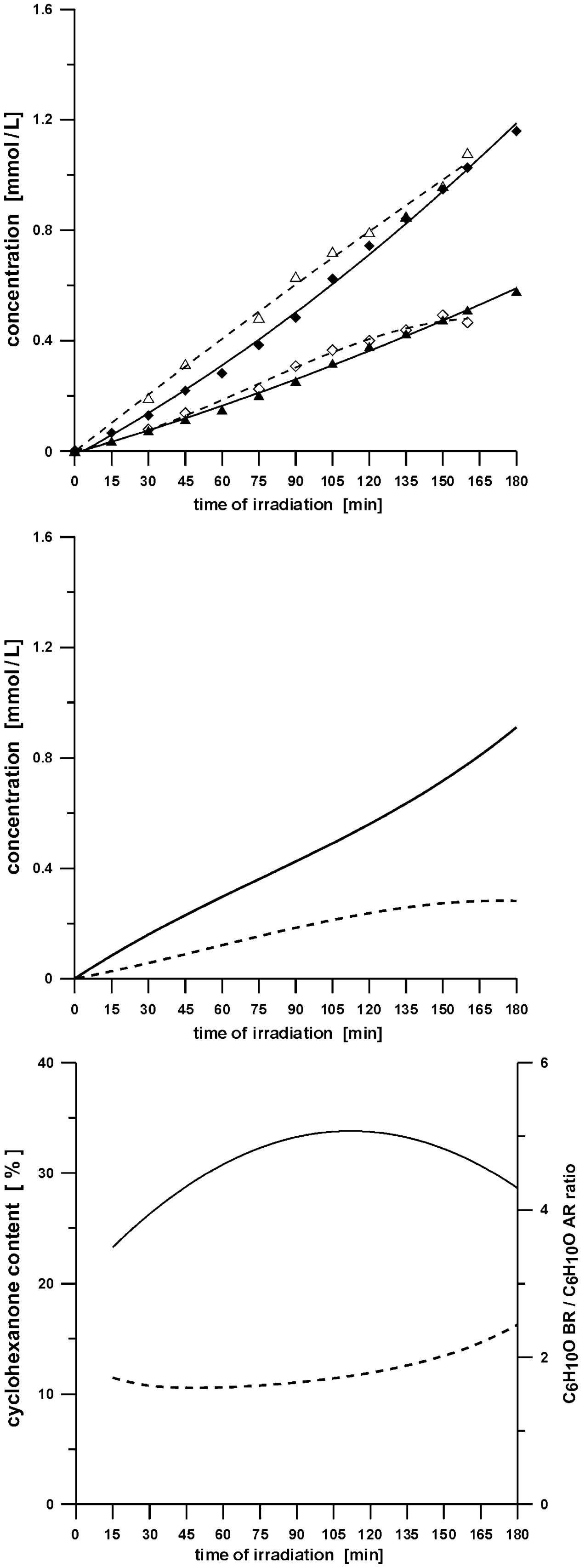

Fig. 5. Kinetics of the oxidation of cyclohexane in acetonitrile in the presence of decatungstate/A photocatalyst. (Top) The accumulation of cyclohexanol and cyclohexanone: before the reduction with triethylphosphine—black triangles and diamonds, respectively; after the reduction with triethylphosphine—white triangles and diamonds, respectively. (Middle) The calculated (real) concentration of cyclohexyl hydroperoxide and cyclohexanol—a solid and dashed line, respectively. (Bottom) Cyclohexanone percent content after reduction with triethylphosphine—a solid line, the ratio of cyclohexanone before reduction (BR) to after reduction (AR) concentrations—a dashed line. Catalyst tungsten content: 20.86%; decatungstate concentration in irradiated solution 5.7×10^{-4} mol dm^{-3}.

It is generally accepted that illumination of $W_{10}O_{32}{}^{4-}$ generates a charge-transfer excited state $W_{10}O_{32}{}^{4-*}$, which decays in about 30 ps to a longer-lived species, which does not react with O_2 but exclusively with organic substrates (RH) through hydrogen abstraction, to give radicals, which in presence of oxygen may lead to formation of peroxy compounds [19]. It appears that heterogenized decatungstate/A, decatungstate immobilized by ionic interactions on a ion-exchange organic resin A, revealed similar properties. In the investigated catalytic system the cyclohexyl hydroperoxide formed as the major product was stable under the reaction conditions, the other oxygenated products (cyclohexanol and cyclohexanone) derived from it through subsequent reactions involving radical species, oxygen and the decatungstate in its oxidized and photoreduced forms. Cyclohexanon is believed to be a product of the consecutive direct photocatalyzed oxidation of cyclohexyl hydroperoxide similarly as in homogeneous catalysis with decatungstate [32].

To determine the effect of catalyst concentration on the catalyst selectivity, the cyclohexanone and cyclohexanol concentration before and after reduction were measured in cyclohexanol/acetonitrile irradiated with decatungstate/A of 20.86% W. Three decatungstate concentrations were examined 570, 340 and 170 μmol dm^{-3}. Samples were collected in 15 min intervals for 3 h. It was found that for all concentrations both the cyclohexanone percent content and the cyclohexanone before- to after-reduction-concentration ratio were similar (i.e. approaching 30 and 2, respectively).

To summarize, the lower loading of decatungstate on material A promoted cyclohexanone production whereas the catalysts of high decatungstate loading generated more cyclohexyl hydroperoxide. Cyclohexyl hydroperoxide was produced in all examined samples. In contrast to decatungstate loading the change of decatungstate concentration in the irradiated solution did not cause the change in cyclohexane oxidation selectivity.

Simultaneous monitoring of the photocatalyzed oxidation of cyclohexane in acetonitrile in the presence of supported decatungstate/A by iodometric titration and by GC was carried out and demonstrated that the total quantity of hydroperoxides in the photolyte exceeded that of cyclohexyl hydroperoxides indicating that acetonitrile oxidation occurred. The irradiation of acetonitrile in the presence of heterogenized decatungstate/A also confirmed the accumulation of a hydroperoxide. The solvent acetonitrile was reported previously to act as substrate, which was related to an extraordinarily strong precomplexation of decatungstate anion with CH_3CN. The contribution of acetonitrile to overall hydroperoxide production was the lowest

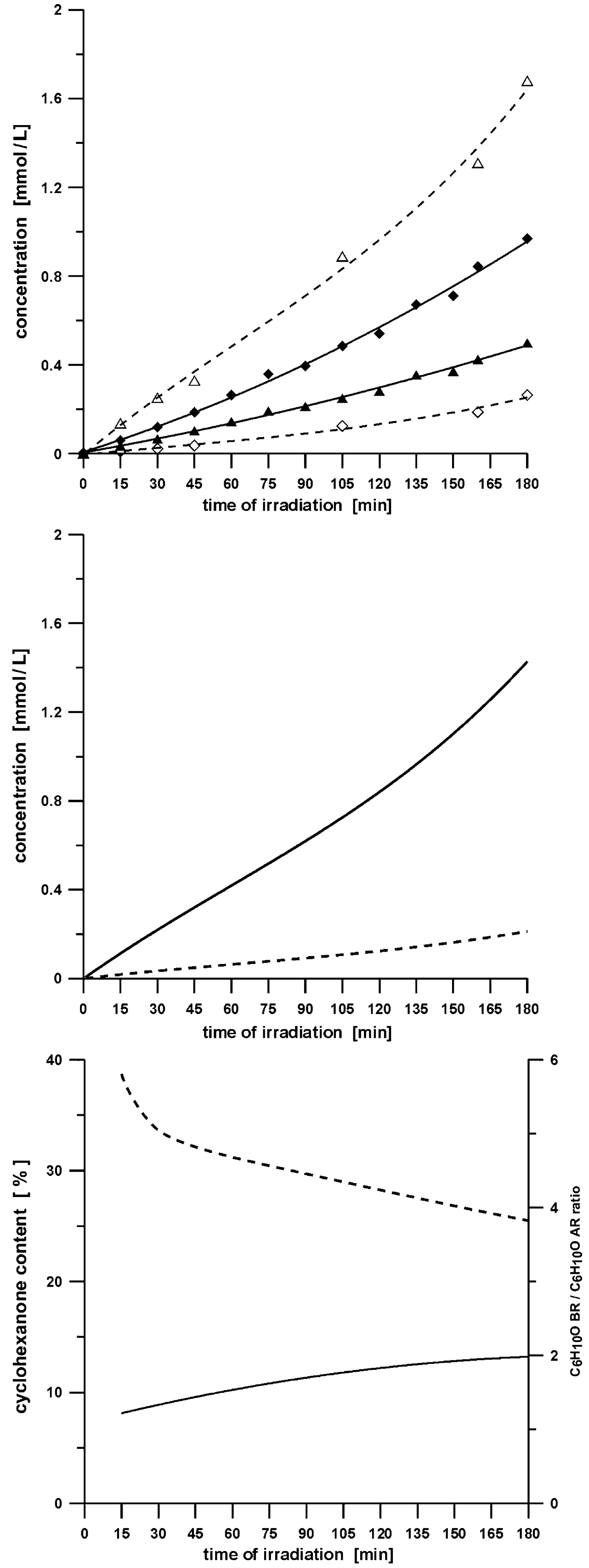

Fig. 6. Kinetics of the oxidation cyclohexane in acetonitrile in the presence of decatungstate/A photocatalyst. (Top) The accumulation of cyclohexanol and cyclohexanone: before the reduction with triethylphosphine—black triangles and diamonds, respectively; after the reduction with triethylphosphine—white triangles and diamonds, respectively. (Middle) The calculated (real) concentration of cyclohexyl hydroperoxide and cyclohexanol—a solid and dashed line, respectively. (Bottom) Cyclohexanone percent content after reduction with triethylphosphine—a solid line, the ratio of cyclohexanone before reduction (BR) to after reduction (AR) concentrations—a dashed line. Catalyst tungsten content: 43.3%; decatungstate concentration in irradiated solution 5.3×10^{-4} mol dm^{-3}.

for the catalyst of the highest decatungstate loading, after 3 h of irradiation the proportion of hydroperioxides of cyclohexane to the acetonitrile hydroperoxides was 75:25 for the catalyst of 43.3% tungsten content.

3.6. Catalyst recovery

To examine the possibility of decatungstate/A re-using, two subsequent 6-h irradiations of cyclohexane/acetonitrile solutions were carried out. After the first irradiation catalyst was recovered, washed with acetonitrile, dried and used for the second irradiation. The relevant turnovers were calculated as millimols of oxidized products per millimol of $W_{10}O_{32}{}^{4-}$. For the first irradiation turnovers after 3 and 6 h of irradiation were found to be 7.36 and 14.22, respectively, and for the second 6.21 and 11.06, respectively. The decrease in the catalyst efficiency was observed by approximately 20%, which is a significant drawback that may limit its applicability and usability.

4. Conclusions

The heterogeneous catalysts obtained by immobilization of decatungstate on organic resins and a carbon material proved to be active in photocatalytic oxidation of cyclohexane in acetonitrile. In the case of decatungstate supported on organic resins the immobilization was strong enough to prevent decatungstate from releasing into solution during 3 h of irradiation. However, when carbon material was used as a support the leak of decatungstate anions was observed. The highest turnover numbers were obtained for cyclohexane oxidation in the presence of decatungstate supported on poly(4-vinylpyridine), cross-linked, methyl chloride quaternary salt (material A). Decatungstate deposition on this support is governed by pseudo-first kinetic and Langmuir isotherm laws. Decatungstate loading on the support, contrary to catalyst concentration in the irradiated solution, has an influence on and determines the oxidation selectivity, i.e. the formation of cyclohexanone, cyclohexanol and cyclohexyl hydroperoxide. The higher loading of decatungstate favours production of cyclohexyl hydroperoxide. The catalyst could be recovered, dried and re-used for another photocatalytic reaction. However, turnover numbers for two 6-h subsequent reaction decreased by approximately 20%.

Acknowledgement

We would like to dedicate this work to the memory of Pierre Potier, the late Director of CNRS, to acknowledge his profound interest in our research.

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