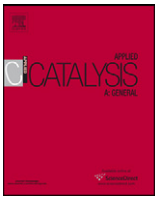
Applied Catalysis A: General 391 (2011) 118–124

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Evidence for the presence of alternative mechanisms in the oxidation of cyclohexanone to adipic acid with oxygen, catalysed by Keggin polyoxometalates

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ARTICLE INFO

Article history:
Received 27 February 2010
Received in revised form 30 March 2010
Accepted 15 April 2010
Available online 22 April 2010

Keywords:
Adipic acid
Cyclohexanone oxidation
Keggin polyoxometalates
Reaction mechanism
Redox mechanism
Autoxidation

ABSTRACT

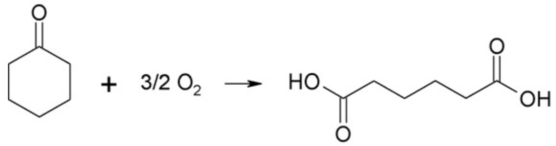
This report deals with the results of a study on the oxidation of cyclohexanone to adipic acid with air, catalysed by Keggin-type polyoxometalates of composition $H_{3+x}PMo_{12-x}V_xO_{40}$ ($x = 1$ and 2), which was carried out in a semi-continuous stirred-tank reactor. It was found that when conducted in the presence of a water-only solvent, the reaction proceeds with a redox mechanism, in which the step of reoxidation of the reduced POM by oxygen is rate limiting. When, however, the reaction was carried out with an acetic acid co-solvent, a radical-chain autoxidation mechanism prevailed, especially when very low amounts of catalyst were used. Autoxidation overlapped with the redox mechanism when the catalyst-to-cyclohexanone ratio was increased. Moreover, the composition of the polyoxometalate, that is, the number of V atoms per Keggin unit, affected the relative importance of the two mechanisms. The selectivity to adipic acid achieved was a function of the reaction mechanism, but also was affected by cyclohexanone conversion, due to the presence of a complex reaction network.

1. Introduction

Adipic acid (AA) is one of the most used chemicals in the world. The global AA capacity is around 3 million metric tons per year; currently, the growth of AA production is close to 3% per year; nylon 6,6 accounts for the greater part of the total AA consumption [1–4].

The principal industrial process is done in two steps. The first step is the oxidation of cyclohexane with air to form a mixture of cyclohexanol and cyclohexanone—the so-called KA oil; the yield of this step is between 85% and 90%. In a variant of this first step, cyclohexanol is obtained by the hydrogenation of phenol. The second step is the oxidation of KA oil with an excess of 50–60% HNO_3 and a Cu/V catalyst. The molar yield obtained at total KA oil conversion is as high as 95%; the by-products are glutaric acid (GA) and succinic (SA) acid. The co-products of oxidation with nitric acid are nitrogen oxides; NO and NO_2 can be reoxidized and recycled, whereas N_2O is a pollutant gas that has to be abated before the emission of tail-gases into the atmosphere.

This synthetic approach by two-step oxidation was developed during the 1940s but several technological improvements have been adopted with positive results on energy consumption, the final quality of the product, and the safety and environmental impact of the process. In any case, the study of an alternative synthetic pathway in which air is the oxidising agent is a challenge for modern chemistry, with potential industrial applications due to the savings resulting from the elimination of both the nitric acid production and the recovery plant.



Various catalysts were proposed in the literature for the aerobic oxidative cleavage of cyclic ketones, vicinal diols and α-ketols under mild conditions [5–12], including Keggin-type polyoxometalates [13], V oxo and dioxo salts and complexes [14], and heterogenized VO catalysts [15]. Table 1 shows some literature results for cyclohexanone oxidation to AA. Keggin-type polyoxometalates (POMs) offer a unique structural versatility that makes it possible to tune the composition in function of the requirements of the reaction [16,17]. For instance, POMs are amongst the very few systems that catalyse the oxidation of organic substrates with air at a moderate reaction temperature through a redox-type mechanism [18–24]. To this regard, experimental evidence was reported for O-transfer from the oxidized POM to anthracene (to produce anthraquinone) and xanthene (to produce xanthone), whereby the reduced lacunary POM is then reoxidized by O_2 [21,22], in the same

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doi:10.1016/j.apcata.2010.04.032

Table 1
A summary of catalysts used in the literature for the aerial oxidation of cyclohexanol (Ol) and cyclohexanone (One) to adipic acid (AA).

Catalyst	Reactant	Solvent, T (°C)	Conversion (%)	Sel. AA (mol%)	Ref.
Pt/charcoal	Ol	Water, 150 °C	100	50	[5]
Pt/Carbon/monolith	One	Water, 140 °C	100	21	[6]
$Mn(OAc)_2/Co(OAc)_2$	Ol/One	Acetic acid, 70 °C	100	77	[7]
$Mn(OAc)_2$	One	Acetic acid/CF_3COOH, 65 °C	99.8	75	[8]
$Mn(NO_3)_2/Co(NO_3)_2$	One	Acetic acid + catalytic HNO_3, 40 °C	97.5	93.4	[9]
$H_7PMo_8V_4O_{40}$	One	Acetic acid/water, 70 °C	99	51	[10]
$H_5PMo_{10}V_2O_{40}$	One	Acetonitrile/methanol, 60 °C	98	55	[11]
Co/Mn cluster	One	Acetic acid/water (MEK), 100 °C	97.6	86.6 (wt%)	[12]

way as it occurs in the Mars-van Krevelen mechanism with mixed oxides catalysts in gas-phase oxidations.

In a previous paper, we reported on the catalytic behaviour of Keggin-type P/Mo/V POMs in the aerobic oxidation of cyclohexanone to AA conducted in water solvent; it was found that reactivity performance was greatly affected by the POM composition, e.g. the number of V atoms incorporated in the Keggin anion and the nature of the cation [20]. However, the cyclohexanone conversion and AA yield achieved were relatively low. In this paper, we have analysed the reactivity of the same catalysts under conditions that are more favourable to achieving higher cyclohexanone conversion, and investigated the reaction mechanism in the presence of acetic acid solvent.

2. Experimental

Catalytic experiments were carried out in a semi-continuous stirred autoclave reactor (100 mL volume) made out of glass, at an operating pressure of between 1 and 10 atm (Buchi Miniclave). The reactor was equipped with a vapours condenser (cooling fluid temperature: −10 °C), to avoid major loss of cyclohexanone during reaction. Oxygen was fed continuously to the reactor, with a standard flow rate of 300 N mL/min. The liquid phase was loaded batchwise; typical reaction conditions, unless otherwise specified, were the following: 25 mL cyclohexanone (Sigma–Aldrich, purity >99.5%), and 25 mL of solvent (either water or water + acetic acid mixtures; acetic acid Sigma–Aldrich, purity >99.7%) were loaded, together with an amount of polyoxometalate (POM) ranging from a minimum of 0.02 g to a maximum of 1.6 g. There was not a single-phase liquid phase; because of the limited solubility of cyclohexanone in water (approx 9 g/100 mL), an emulsion developed. The POM completely dissolved in the solvent.

The analysis of the reaction products was carried out by means of the following procedure: the reaction mixture was heated (65 °C) under vacuum to evaporate both the unconverted cyclohexanone and the reaction solvent; the residual solid was mixed with an excess of methanol and with BF_3 (dissolved in methanol), at 80 °C for 1 h in a sealed vessel, in order to transform the diacids produced (AA, GA and SA) to the corresponding methyl diesters. The esters were then extracted with *n*-hexane (this also lead to the separation of the POM and of BF_3 from the mixture); the extraction procedure was repeated several times. Finally, the solution of diesters in *n*-hexane was analysed by GC (internal standard *n*-decane). This method allowed the identification of acids in the form of methyl esters, of some residual cyclohexanone (and, in general, carbonyl groups in aldehydes or ketones) in the form of the corresponding methyl acetals, and alcohols (and in general hydroxy groups) as the corresponding methyl esters. Since the caprolactone eventually formed would bring to the ring-opened compound during methanolysis in acid conditions, the formation of this product and of other by-products was checked by means of the extraction of soluble compounds with *n*-hexane from the reaction mixture (before esterification), and gas-chromatographic analysis. The same procedure was also adopted to estimate the C atomic balance, by comparing cyclohexanone conversion with the sum of yields to all products, the latter obtained with the esterification method described above. In general, atomic balances were good, although not excellent; typically the ratio: (C atoms contained in all products/C atoms in converted cyclohexanone) was between 0.90 and 0.95. However, this value, lower than 1.00, was mainly due to the small but not negligible loss of cyclohexanone in the vapours stream, as confirmed by a mass balance made by comparing the initial and final reactor weight loading (calculated also including the amount of O incorporated in products and the C lost in the form of CO_2).

The gas chromatography for the analysis of the reaction products used a capillary HP5 column and a FID (internal standard *n*-decane). The oven temperature was programmed at 50–280 °C (heating rate 10°/min). GC–MS was used for the identification of products. Incondensable gases (carbon oxides) were analysed by two methods: (i) by sampling, from time to time during the reaction, 1 mL of gases in the effluent stream, and injecting it into a GC equipped with a Carbosieve SII column (oven temperature programmed at 40–240 °C, heating rate 10°/min) and a TCD; (ii) by bubbling the effluent stream in a sodium hydroxide aqueous solution and determining the final amount of excess NaOH by titration—providing an integral amount of CO_2 produced over the entire experiment time.

The catalysts, Keggin-type polyoxometalates with the composition $H_4PMo_{11}VO_{40}$ (POMV1) and $H_5PMo_{10}V_2O_{40}$ (POMV2) were prepared by following a procedure similar to that developed by Matveev and co-workers [26]. An aqueous solution was prepared by dissolving MoO_3 and H_3PO_4 in an abundant amount of water, at a temperature close to 100 °C (but avoiding boiling of the solution); it took about 15–20 h for a complete dissolution. A second solution was prepared by dissolving V_2O_5 in water containing 5% H_2O_2, at 4 °C; in this case, complete dissolution was achieved in less than 1 h, even though it was then left at rest overnight. The former solution was heated again at 90 °C, and the second solution was added drop by drop; then the mixed solution was left at 90 °C for 8 h, in order to let most of the solvent evaporate, and was finally left at 80 °C overnight in order to complete the evaporation of the solvent. The wet solid obtained was finally dried at 110 °C for 4 h. The dried solid was characterised by means of FT-IR and Raman spectroscopy in order to confirm the formation of the desired Keggin compound.

3. Results and discussion

3.1. Experimental evidence of the presence of two different mechanisms

The use of water as the solvent for cyclohexanone oxidation has positive implications from the environmental point of view, due to both lower corrosion problems and avoiding of toxic solvents, although at the end of the process additional costs have to be borne in order to degradate organic contaminants in water before disposal. A solvent is necessary, however, because the reac-

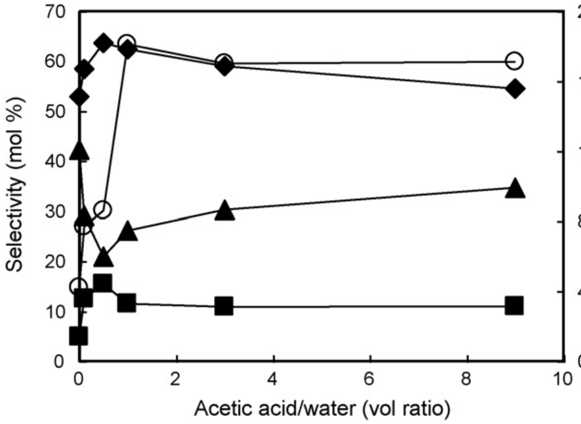


Fig. 1. Conversion of cyclohexanone and selectivity to products as functions of the acetic acid-to-water volumetric ratio. $T = 70\,^{\circ}C$, $P = 1$ atm, O_2 feed 300 N mL/min, reaction time 6 h. Liquid-phase composition: 25 mL cyclohexanone, 25 mL solvent (acetic acid/water), catalyst POMV1, amount 1.6 g (POM-to-cyclohexanone molar ratio 0.0037). Symbols: conversion of cyclohexanone (○), selectivity to AA (♦), to CO_2 (▲) and to GA + SA (■).

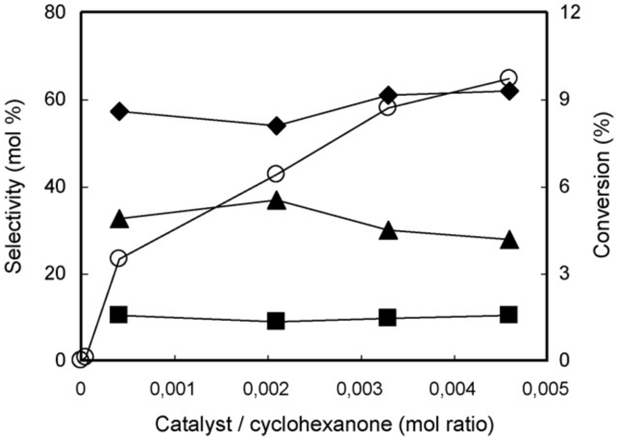


Fig. 2. Conversion of cyclohexanone and selectivity to products as functions of the POM-to-cyclohexanone molar ratio. $T = 70\,^{\circ}C$, $P = 4$ atm, O_2 feed 300 N mL/min, reaction time 6 h. Liquid-phase composition: 25 mL cyclohexanone, 25 mL solvent (water); catalyst POMV1, in variable amounts. Symbols: conversion of cyclohexanone (○), selectivity to AA (♦), to CO_2 (▲) and to GA + SA (■).

tion is strongly exothermal, and a ballast component contributes to the removal of the heat generated. However, the problem encountered with water as the only solvent is that of a limited conversion achieved when homogeneous Keggin-type polyoxometalates are used as catalysts for the reaction; usually, either long reaction times, high pressure of oxygen or high catalyst-to-substrate ratio are necessary to achieve high cyclohexanone conversion with water solvent [10,20,23,24].

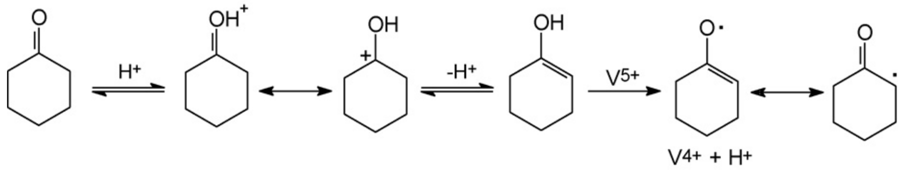
The use of acetic acid as the co-solvent greatly enhanced the reaction rate, as shown in Fig. 1 by plotting the conversion of cyclohexanone in function of the acetic acid/water volume ratio (whilst keeping constant the overall volume of solvent) with the POMV1 catalyst. The increase in the acetic acid concentration led to a pronounced increase in cyclohexanone conversion, up to a maximum value achieved for an equivolumetric ratio of the two solvents. After that, higher concentrations of acetic acid did not lead to a further increase in conversion. In regard to the distribution of products, Fig. 1 also reports the selectivity to AA, to GA + SA and to CO_2. No hydroperoxide was detected, which indicates that these possible reaction intermediates (that indeed have never been isolated in the literature on cyclohexanone aerial oxidation) are quickly transformed into more stable diacids. Moreover, neither 6-hydroxyhexanoic acid nor 6-oxohexanoic acid – possible reaction intermediates in AA formation – were produced.

The presence of acids is known to catalyse autoxidation of cyclohexane using Mn and Mn/Co catalysts [25–31]; in the Asahi process, the one-step oxidation of cyclohexane to AA uses Co acetate catalyst and acetic acid solvent (that instead is not used in the oxidation of cyclohexane to KA Oil with air). In general, the stronger the acid, the faster the oxidation rate. Rhodia recently reported on the use of a lipophilic acid, 4-*ter*-butylbenzoic acid, instead of acetic acid, in order to facilitate the separation and recycling, showing outstanding effects in the acceleration of the reaction rate [32]. A similar acceleration effect has also been reported in the aerial cyclohexanone oxidation to AA, catalysed by Co/Mn acetates, which was developed by Asahi [7]. A possible explanation for this effect is the acceleration of the tautomerism between cyclohexanone and the corresponding enolic form, which is more easily activated by radicalic H abstraction than cyclohexanone itself (Scheme 1). An alternative explanation is the *in situ* formation of peracetic acid, by acetic acid oxidation, that may eventually act as an oxidant on cyclohexanone; however, separate tests of acetic acid oxidation with oxygen and POMV1 catalyst led us exclude the formation of any peracid, as inferred by iodometric titration. On the other hand, the protonation of cyclohexanone may eventually facilitate the dissolution of the substrate in the aqueous phase, where the POM is dissolved.

Data in Fig. 1 show that in the solvent composition range considered, where a remarkable acceleration of the reaction rate occurred, there was also an important effect on product distribution. We expected a fall of selectivity to AA, because of the increased cyclohexanone conversion experimentally observed after acetic acid addition, which should favour the consecutive oxidative degradations of AA to CO_2; in contrast, the addition of acetic acid led to an increased selectivity to AA and lighter acids, as well as to a pronounced decline of selectivity to CO_2. Then, a further increase of acetic acid above the ratio of 1 caused a reduced selectivity to AA and lighter acids, with a corresponding increase of selectivity to CO_2, even though conversion was not affected. The highest cyclohexanone conversion and selectivity to AA were reached at the optimal volume ratio of 1. These effects suggest that acetic acid did not simply accelerate the reaction rate, but favoured a change in the reaction mechanism.

Fig. 2 shows the effect of the catalyst-to-cyclohexanone molar ratio on catalytic behaviour for tests carried out with a water-only solvent and POMV1 catalyst. There was an almost proportional effect of the catalyst amount on cyclohexanone conversion, whereas the selectivity to the products was not affected much by the conversion. It is worth noting that in the absence of catalysts there was no cyclohexanone conversion. Moreover, the addition of very small amounts of a catalyst (with a POM-to-cyclohexanone molar ratio as low as 4×10^{-5}) had practically no effect on conversion, which remained below the detection limit; the same was observed also at a higher temperature, i.e. 90 °C (conversion 0.50%, yield to AA 0.35%). This observation is important, in view of the behaviour shown by the same catalyst in the presence of acetic acid (see below). These results indicate a direct participation of the catalyst in the rate-determining step of the process, and suggest that the POM has a catalytic effect on the process rate.

The effect observed when an equivolumetric acetic acid/water mixture (Fig. 3) was used was quite different from that observed without acetic acid. Firstly, even with no catalyst at all, there was a non-negligible cyclohexanone conversion (1.6% in 6 h reaction time) that provides additional evidence for the role of acetic acid in promoting a radicalic-type, thermal oxidation of cyclohexanone. Moreover, even a truly negligible amount of catalyst (corresponding to a molar ratio POM-to-cyclohexanone as low as 4×10^{-5}) caused a rapid increase of conversion. This clearly indicates that the



Scheme 1. The activation of cyclohexanone via protonation and tautomerisation.

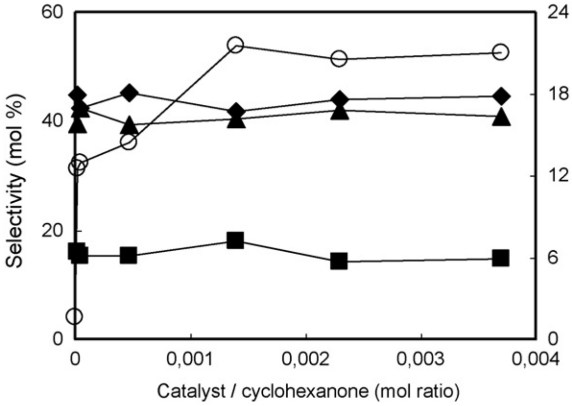


Fig. 3. Conversion of cyclohexanone and selectivity to products as functions of the POM-to-cyclohexanone molar ratio. $T = 90\,^{\circ}C$, $P = 4$ atm, O_2 feed 300 N mL/min, reaction time 6 h. Liquid-phase composition: 25 mL cyclohexanone, 25 mL solvent (acetic acid/water 1/1), catalyst POMV1, in variable amounts. Symbols: conversion of cyclohexanone (○), selectivity to AA (♦), to CO_2 (▲) and to GA + SA (■).

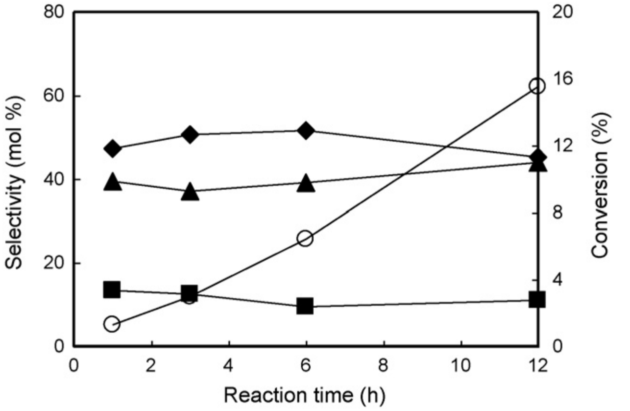


Fig. 4. Conversion of cyclohexanone and selectivity to products as functions of the reaction time. $T = 70\,^{\circ}C$, $P = 4$ atm, O_2 feed 300 N mL/min. Liquid-phase composition: 25 mL cyclohexanone, 25 mL solvent (water), catalyst POMV1 (POM-to-cyclohexanone molar ratio 0.002) Symbols: conversion of cyclohexanone (○), selectivity to AA (♦), to CO_2 (▲) and to GA + SA (■).

catalyst indeed acts as an initiator of the reaction, and is strongly in favour of a radicalic-type autoxidation process.

After the initial rapid increase, a further addition of catalyst led to a less pronounced effect on conversion; this saturation effect might be due to the well known chain-termination effect that may occur in the presence of relatively large amounts of catalyst-initiator [31]. Moreover, it cannot be excluded that under conditions of high POM-to-cyclohexanone molar ratio, a redox-type mechanism may either prevail over autoxidation, or nevertheless give an important contribution to cyclohexanone conversion. The distribution of products showed only marginal variations in function of the amount of catalyst.

The data obtained suggest the presence of two different reaction mechanisms for cyclohexanone conversion—a radicalic autoxidation mechanism and a redox-type mechanism. The former is preferred in the presence of acetic acid, whereas the latter may occur in the presence of a water-only solvent. The two mechanisms, however, may overlap in the presence of acetic acid co-solvent when relatively high POM-to-cyclohexanone ratios are used. As shown in Fig. 1, the two mechanisms also show different selectivity with regard to AA; in fact, when the reaction is carried out in the presence of acetic acid, the selectivity to AA achieved is higher than that achieved without acetic acid, despite the higher cyclohexanone conversion.

Other evidences supporting the overlapping of two different reaction mechanisms, where the prevailing one is a function of reaction conditions used, were obtained by examining the effect of both reaction time and of partial oxygen pressure on the catalytic behaviour.

Figs. 4 and 5 compare the effect of reaction time on both the cyclohexanone conversion and the distribution of products, for tests carried out with either a water-only solvent (Fig. 4) or the acetic acid/water mix (Fig. 5). In view of the different reaction performances in the two cases (see Fig. 1) we carried out experiments in different conditions, in order to obtain similar values of cyclohexanone conversion in the two sets of experiments. For example, tests with acetic acid co-solvents were carried out with a minimal catalyst amount, that is, under conditions in which the redox mechanism involving the direct oxidation of the substrate by the catalyst should be minimal; on the other hand, tests with the water-only solvent were carried out with a higher POM-to-substrate ratio, in order to favour the redox mechanism.

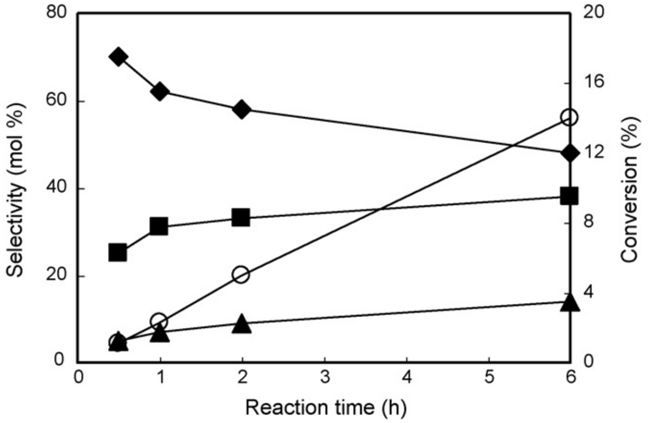


Fig. 5. Conversion of cyclohexanone and selectivity to products as functions of the reaction time. $T = 90\,^{\circ}C$, $P = 4$ atm, O_2 feed 300 N mL/min. Liquid-phase compositions: 25 mL cyclohexanone, 25 mL solvent (acetic acid/water 1/1), catalyst POMV1 (POM-to-cyclohexanone molar ratio 0.00046). Symbols: conversion of cyclohexanone (○), selectivity to AA (♦), to CO_2 (▲) and to GA + SA (■).

It is shown that the two cases showed quite different behaviour, especially in regard to both the selectivity to AA and the nature of the reactions yielding GA and SA by-products. Firstly, the selectivity to AA was greater in the presence of acetic acid (in average, about 50% without acetic acid, above 50% with acetic acid co-solvent, in both cases for a cyclohexanone conversion lower than 15%). Secondly, in the former case, AA was stable and did not undergo significant consecutive reactions of oxidative degrada-

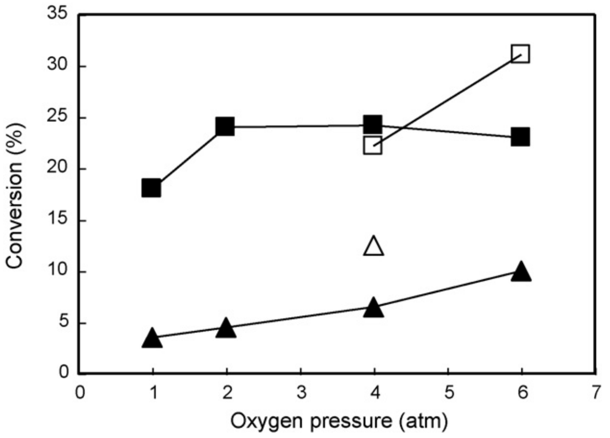


Fig. 6. Conversion of cyclohexanone in function of the oxygen pressure. $T = 70\,^{\circ}\mathrm{C}$, O_2 feed 300 N mL/min, reaction time 6 h. Liquid-phase composition: 25 mL cyclohexanone, 25 mL solvent (water ▲,△; acetic acid/water 1/1 vol ratio ■, □), other conditions as in Fig. 1. Catalysts: POMV1 (▲,■); POMV2 (△,□) (POM-to-cyclohexanone molar ratio 0.0014).

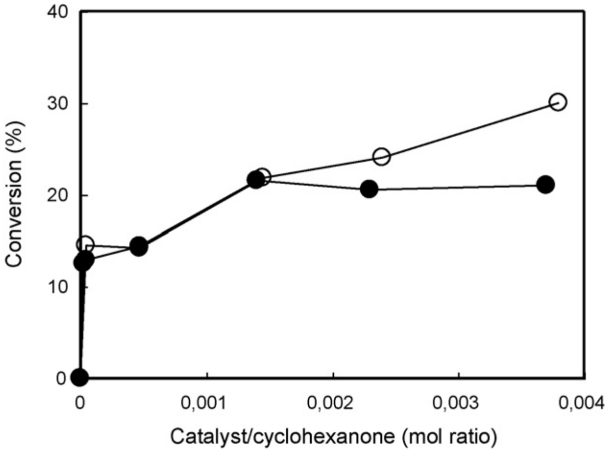


Fig. 7. Conversion of cyclohexanone in function of the POM-to-cyclohexanone molar ratio. Catalysts: POMV1 (●) and POMV2 (○). $T = 90\,^{\circ}\mathrm{C}$, $P = 4$ atm, O_2 feed 300 N mL/min, reaction time 6 h. Liquid-phase composition: 25 mL cyclohexanone, 25 mL solvent (acetic acid/water 1/1).

tion; the low selectivity to AA was due to the presence of parallel reactions for the formation of GA, SA and CO_2. In the presence of acetic acid co-solvent, instead, the initial selectivity to AA was very high (apparently almost total if extrapolated to nil conversion), but AA readily underwent consecutive oxidative degradations to form lighter diacids and CO_2. Remarkably, the two lighter acids (and also possibly CO_2) did not form by direct, parallel reaction, but exclusively via secondary reactions. We found the same behaviour – with a substantial absence of parallel oxidative degradation reactions – when experiments were carried out with acetic acid co-solvent, but at milder reaction conditions ($T = 70\,^{\circ}\mathrm{C}$, $P = 1$ atm). This difference once again confirms the existence of different reaction mechanisms, which implies different reaction networks occurring with either water-only or the acetic acid/water mix.

Another important difference concerned the effect of oxygen pressure. This is shown in Fig. 6, when comparing the effect of oxygen pressure on cyclohexanone conversion, with and without acetic acid co-solvent, but with other reaction conditions remaining similar in the two cases. In the case of tests carried out without acetic acid, the cyclohexanone conversion appeared to be proportional to the oxygen partial pressure; this means that oxygen is involved in the rate-determining step of the reaction. This agrees with findings from Matveev and co-workers [33]. The authors showed that in the aerobic oxidation of methylnaphthol to menadione – catalysed by Keggin POMs, in which the mechanism is redox-type with electron transfer from the substrate to the POM, excess electrons being then released to molecular oxygen – the rate limiting step of the process is the reoxidation of the reduced POM by O_2. Moreover, again in agreement with Matveev's findings, the reactivity of the POMV2 was higher that that of POMV1. Conversely, when the same experiments were performed with acetic acid co-solvent, the cyclohexanone conversion was not greatly affected by oxygen partial pressure—a clear indication that the steps involving molecular oxygen are not rate limiting. It might be objected that in such conditions, mass transfer of oxygen may become limiting; however, when we used POMV2 (a compound showing a good propensity for electron-transfer interactions with hydrocarbons and functionalised hydrocarbons [18]) as the catalyst, the increase in O_2 pressure (from 4 to 6 atm) had an important effect on cyclohexanone conversion. This last experiment provides further information: the type of prevailing mechanism may be a function of the POM composition, and it may be expected that in the co-presence of both redox and autoxidation mechanisms, the former may become more important when POMV2 is used.

This hypothesis was confirmed by the experiments shown in Fig. 7, when comparing the conversion of the two POMs as a function of the POM-to-cyclohexanone ratio. The two catalysts showed quite similar behaviour for low POM-to-cyclohexanone ratios, that is, under conditions that favoured the autoxidation mechanism, but their behaviour diverged when higher ratios were used. That confirms that it is possible to accelerate the reaction rate by using a catalyst with enhanced redox properties, even under conditions in which the POMV1 did not provide any further improvement of the cyclohexanone conversion. With POMV2, the higher redox potential leads to a more pronounced effect of the catalyst amount on substrate conversion.

3.2. Reactivity tests carried out in the presence of a radical scavenger

In order to find out whether radicalic intermediates play a role in the reaction under the different reaction conditions used, we added increasing amounts of 2,6-di-*ter*-butyl-1-hydroxy-4-methylbenzene (BHT), which is known to be amongst the most efficient radical scavengers. Experiments were carried out using acetic acid co-solvent, at both low and high POM-to-cyclohexanone feed ratios, because the results obtained suggested that the two different mechanisms – i.e. a redox mechanism with direct involvement of the POM and an autoxidation mechanism – gave a different contribution in function of the POM-to-cyclohexanone ratio used.

The results of these experiments are summarised in Fig. 8, which shows the conversion of cyclohexanone as a function of both the BHT-to-cyclohexanone ratio (top figure) and the BHT-to-POM ratio (bottom figure), for two different POMV1 catalyst amounts, that implied different POM-to-cyclohexanone feed ratios. It is shown that the effect of the added BHT was quite different in function of the POM-to-cyclohexanone feed ratio used. In fact, for tests carried out in conditions of low feed ratio, the BHT caused a rapid fall of cyclohexanone conversion in correspondence of very low BHT-to-cyclohexanone ratio; on the contrary, for tests carried out with high POM-to-cyclohexanone feed ratio, there was almost no effect on cyclohexanone conversion up to a BHT-to-cyclohexanone ratio of ca 0.1. It is worth noting that cyclohexanone conversion was almost nil in the case of tests carried out at low POM-to-cyclohexanone ratio, when a BHT-to-cyclohexanone ratio of 0.1 was used. It is evident that the added BHT – even a small amount – has a remarkable effect on the reaction rate, under conditions in

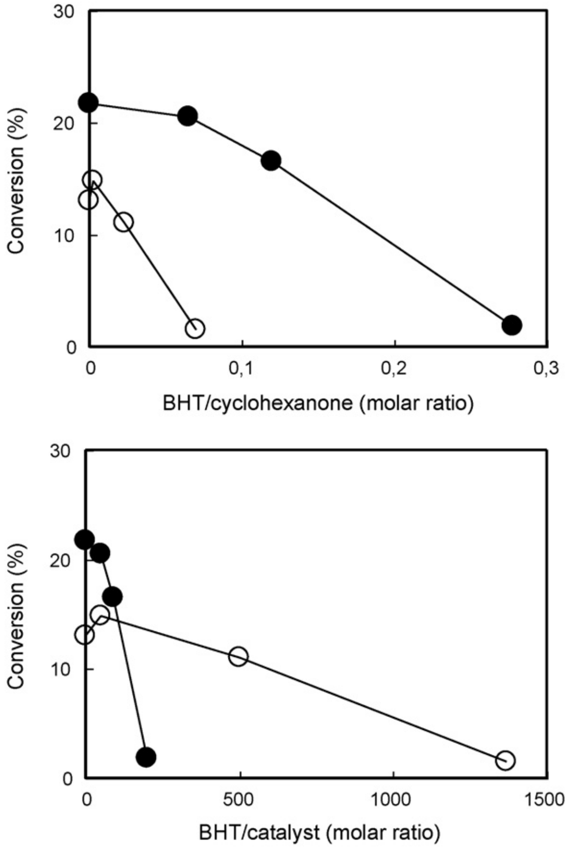


Fig. 8. Cyclohexanone conversion as a function of the BHT-to-cyclohexanone molar ratio (top) and of the BHT-to-POM molar ratio (bottom). Catalyst POMV1. POM-to-cyclohexanone molar ratio 4.5×10^{-5} (○), 1.4×10^{-3} (●). $T = 90\,^\circ$C, reaction time 6 h. Solvent 25 mL (acetic acid/water 1/1).

which reactivity tests suggested the presence of a radicalic-chain autoxidation mechanism.

On the other hand, BHT caused a decline of cyclohexanone conversion, although only for high BHT-to-cyclohexanone ratios, even under conditions in which the redox mechanism contributed to cyclohexanone conversion (i.e., at high POM-to-cyclohexanone feed ratio). This suggests that in the case of the redox mechanism, the activation and oxidation of cyclohexanone also occurs with the involvement of radicalic intermediates. In this case, however, the mechanism does not occur via a chain-reaction with free radicals reacting with O_2; rather, it would likely involve the electron transfer from the substrate to the POM and the development of a complex by coordinating the substrate and intermediates [14]. This hypothesis is also confirmed by the plot in Fig. 8 (bottom). It is shown that when the BHT-to-POM ratio was taken into consideration, the effect of BHT on cyclohexanone conversion was more pronounced for experiments carried out using high POM-to-cyclohexanone feed ratio. In fact, with low feed ratio (i.e. with a low POM amount in the reaction medium), the BHT added had a non-negligible effect on the reaction rate only for extremely high BHT-to-POM ratio.

With a water-only solvent, an experiment was carried out at both high POM-to-cyclohexanone (0.012) and high BHT-to-cyclohexanone (0.25) molar ratio, at 90 °C and a pressure of 4 atm. Again in this case, cyclohexanone conversion dropped from 7% (measured in the absence of BHT) to 2% (in the presence of BHT); moreover, in the latter case the selectivity to AA was almost nil, with CO_2 being the only product formed. This confirms the role of radicalic intermediate species even under conditions at which the redox mechanism prevails.

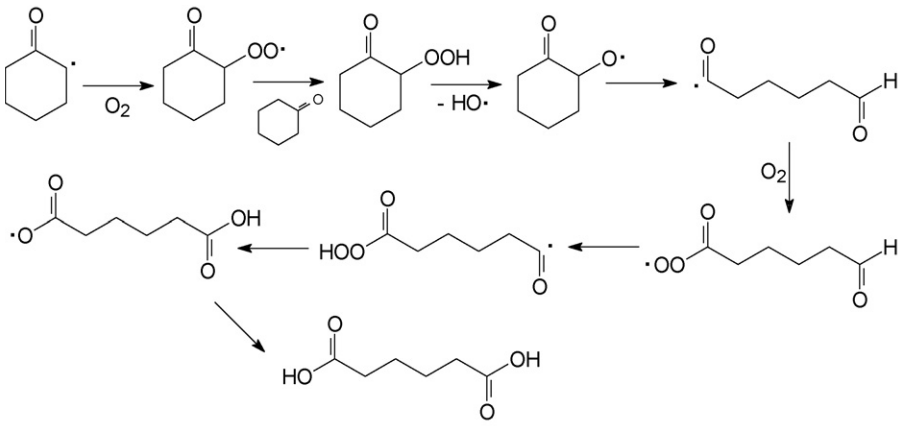
3.3. Some considerations on the reaction mechanism

The mechanism of the aerobic oxidative cleavage of cyclic ketones, vicinal diols, and α-ketols, catalysed by V(V) complexes, precursors of pervanadyl $(VO_2)^+$ species, and by POMs has been investigated by Brégeault and co-workers [14,23,24]. The interaction between the ketone (or the hydroxyketone) and the V(V) complex is driven by the Lewis-type acid properties of the latter. As a key step in the process, the authors suggested that the $ROO^\bullet$ peroxyl radical – formed after the addition of O_2 to the radicalic species formed by $H^\bullet$ abstraction from the substrate – might oxidize V(IV) to V(V) forming a V(V) peroxo derivative. The simultaneous C–C and O–O cleavage in this complex, then leads to ring opening and oxoacid formation, still coordinated to the V(V) atom, which is the precursor for the formation of AA and, eventually, also of partially oxidized by-products. The authors, however did not exclude the possibility that the reoxidation of the reduced $[V(IV){=}O]^{2+}$ complex might occur via the 4-electron redox process and O_2 reduction. In an alternative mechanism, the interaction of the radical intermediate with O_2 may produce an endoperoxide species that, by the simultaneous fission of C–C and O–O bonds, finally yields AA.

In our case, under conditions leading to the redox mechanism as the prevailing one, and after the proposal of Brégeault of coordination of the substrate to the monovanadyl species $(V{=}O)^{3+}$ in the POM and formation of a ring-opened intermediate, the development of a $-C(O)O^\bullet$ group at the terminal C atom might lead either to the production of AA or to the release of CO_2 and the consequent production of lighter diacids. Therefore, a common intermediate for the diacids would explain the parallel formation of these compounds (Fig. 4). On the other hand, it is likely that the reversible complex between AA and the POM may help in saving AA from consecutive oxidative degradation (to either light diacids or CO_2), which occurs in the liquid phase via the autoxidation process.

The mechanism of thermal and catalytic cyclohexane autoxidation has also been studied in depth [1,3 and refs therein]; however, it has been revisited recently by Hermans and co-workers [34–37]. These authors reported that a $^\bullet OH$-radical breaking away from cyclohexylhydroperoxide – the latter formed by reaction between cyclohexyl radical and O_2 to generate the peroxyl radical – abstracts a weakly bonded αH-atom from cyclohexanone (one reaction product), forming water and the ketonyl radical, stabilized by resonance. The ketonyl radical then reacts to finally yield AA. According to these authors, however, in the absence of acetic acid the main route to AA is not that involving cyclohexanone, but rather the transformation of the intermediate cyclohexylhydroperoxide radical (a key component in the reaction network) into the $CyO^\bullet$ radical, that converts into 6-hydroxyhexanoic acid, the latter being finally oxidized to AA. The hydroxyacid is also the precursor for the formation of lighter diacids: that would imply a kinetic parallel scheme if the intermediate hydroxyacid is readily converted into the final compounds. In the mechanism proposed by Shimizu et al. [7] for the Co/Mn acetate catalysed autoxidation of cyclohexanone, carried out in acetic acid solvent, AA, GA and SA also form by parallel routes.

In our case, we observed that the formation of lighter diacids mainly occur via consecutive reaction upon AA, with negligible contribution of parallel reactions. The instability of AA under conditions that favour autoxidation indicates that this compound may still undergo activation by radicalic species and decarboxylation. Moreover, we did not detect the formation of any partially oxidized compound, e.g. either 6-hydroxy- or 6-oxohexanoic acid. The mechanism proposed in Scheme 2 might explain the absence of these compounds during cyclohexanone oxidation, because the ring opening via C–C scission occurs before the formation of the hydroxylactone [7] and leads to the radical species $OHC{-}(CH_2)_4{-}C({=}O)^\bullet$; successive steps bring about the production of AA without forming any partially oxidized compounds.



Scheme 2. A possible mechanism for the formation of adipic acid from activated cyclohexanone without intermediate formation of partially oxidized products.

4. Conclusions

The reactivity of homogeneous Keggin-type P/Mo/V polyoxometalates as catalysts for the liquid-phase oxidation of cyclohexanone with oxygen was investigated under various conditions. The use of acetic acid as a co-solvent led to a strongly enhanced cyclohexanone conversion with respect to the reaction carried out with water-only solvent. The conditions used for catalytic experiments also affected the reaction mechanism: either with a water-only solvent, or in the presence of acetic acid/water solvent but with high catalyst-to-cyclohexanone molar ratio, the prevailing mechanism was redox-type, with direct involvement of the POM in the reaction. Conversely, when the catalyst-to-cyclohexanone ratio used was low, in the presence of acetic acid co-solvent, the prevailing mechanism was a radicalic chain-reaction autoxidation. The latter was more selective to AA than the redox mechanism, due to the lower contribution of parallel reactions of cyclohexanone oxidative degradation leading to lighter acids and CO_2. On the other hand, consecutive oxidation reactions led to the formation of significant amounts of the mentioned by-products, which instead gave a minor contribution under conditions of prevailing redox mechanism. Tests carried out in the presence of a radical scavenger confirmed the hypothesis formulated on the presence of two different reaction mechanisms.

Acknowledgements

The ISA (Institute of Advances Studies), The University of Bologna, is acknowledged for their financial support to K.R.

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