Oxidation of 1,2-Cyclohexanediol to Adipic Acid with Oxygen: A Study Into Selectivity-Affecting Parameters

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The oxidation of 1,2-cyclohexanediol to adipic acid with oxygen: a study on selectivity affecting parameters

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Dedication ((optional))

This paper deals with a study of the aerobic oxidation of trans-1,2-cyclohexanediol, aimed at the synthesis of adipic acid. Two classes of catalysts are compared, (i) alumina-supported $Ru(OH)_3$, and (ii) Keggin type P/Mo/V heteropolycompounds. These two classes are emblematic examples, since they are active in alcohol oxidation under quite different reaction conditions. In the former case, basic conditions are needed in order to activate the substrate, whereas with polyoxometalates, acid conditions are used. Their catalytic behaviour showed remarkable differences in two cases; in basic conditions, the reaction network was very complex, and several side reactions led to a number of by-products, with a low selectivity to adipic acid in the end. In fact, the supported $Ru(OH)_3$ catalyst was very efficient in 1,2-cyclohexanediol oxidative dehydrogenation to 1,2-cyclohexanedione, but several undesired reactions occurred starting from this key intermediate under basic conditions: rearrangement into 6-hydroxycaprolactone and 1-hydroxycyclopentanecarboxylic acid, and formation of the product of aldol condensation. The former compound was also an intermediate for adipic acid formation, but this reaction gave only a minor contribution to the reactant conversion. Polyoxometalates were extremely selective in 1,2-cyclohexanediol conversion into adipic acid, but under acid conditions the product reacted with the unconverted reactant to yield the corresponding ester.

Introduction

The oxidative cleavage of aliphatic cyclic vicinal diols is used for the synthesis of dicarboxylic acids, a reaction of practical interest for the chemical industry. The reaction is usually carried out by using stoichiometric oxidants such as periodates, lead tetraacetate and others, which cause the formation of inorganic waste compounds; therefore, the use of both oxygen as the stoichiometric oxidant and a heterogeneous catalyst would considerably increase the sustainability of these reactions. [1-4]

In this context, the oxidative cleavage of *trans*-1,2-cyclohexanediol (CHD) has been taken into consideration as a possibly more sustainable route for the production of adipic acid (AA).[4-6] In general, the reaction can be carried out with either hydrogen peroxide (HP) or oxygen as the oxidant. For example, CHD was selectively oxidized into AA (77% selectivity at 44% CHD conversion) using hydrogen peroxide (HP) and a Ti-Y catalyst; cyclohexene oxide was cleaved with similar selectivity.[7] Indeed, the hydroperoxidation of CHD is one of the steps in the multi-step (but one-pot) oxidation of cyclohexene into AA.[8,9] Heterogeneous catalysts were also investigated for the direct oxidative cleavage of cyclohexene; Ti-MMM-2, Ce-SBA-15, TAPO-5, and Ti-AlSBA-15 proved to be active with either HP[10,11] or *t*-butylhydroperoxide.[12]

Other papers deal with the use of either surfactant-type polyoxometalates or amphiphilic quaternary ammonium salts of tungstophosphates (precursors for the corresponding peroxometalates after contacting with HP) for the oxidative cleavage of vicinal diols to carboxylic acids; AA yields higher than 90% in CHD hydroperoxidation have been reported.[13-16] Ti-containing sandwich-type As/W polyoxometalates, too, are catalysts for the oxidation and oxidative cleavage of cyclohexene into the epoxide, CHD, 2-hydroxycyclohexanone, 6-hydroxycaprolactone, adipic aldehyde, and adipic acid.[17]

Regarding the use of O_2 – a cheaper oxidant than HP – in their fundamental work, Brégeault and co-workers demonstrated that the aerobic catalytic oxidative cleavage of ketones, α-ketols, and α-diols can be catalyzed by various transition metal ions: V, Cu, Fe, and Mn.[18-22] P/Mo/V polyoxometalates are among the

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most efficient catalysts, in which the Keggin compound may act as a truly redox system[23-27] (however, a free-radical autoxidation pathway may also contribute to the substrate conversion, at least in cyclohexanone oxidation, depending on the reaction conditions used).[28] For example, the oxidative cleavage of CHD is carried out at 75°C in ethanol, and AA diethylester is obtained with 90% selectivity at 62% conversion, using a P/Mo/V heteropolyacid catalyst.[1,29] It was hypothesized that vicinal diols are cleaved via a ternary complex among polyoxometalate, O_2, and the diol, which leads to simultaneous C-C and O-O bond cleavage. Conversely, Neumann et al. proposed an electron-oxygen transfer (ET-OT) mechanism (similar to the redox MVK mechanism which typically occurs in the gas phase), in which primary alcohols and vicinal diols are cleaved by the acidic $H_5PV_2Mo_{10}O_{40}$; at first their reaction yields aldehydes, but carbonyl products react further with the alcohol substrate to yield esters via further oxidative transformations.[30,31]

Another class of catalysts which received a great deal of attention for the aerobic oxidative cleavage of diols and ketones is based on Ru as the active species. Indeed, Ru-based catalysts are typically used for the oxidation of alcohols into the corresponding aldehydes or ketones.[3,32] Examples include supported Ru,[33-37] supported and bulk $Ru(OH)_x$,[38-44] and ruthenate and perruthenate-based systems.[45-48] The combination of Ru with other elements, such as Cu,[49] Mn,[50] Co/Ce,[51,52] Co,[53] and Mn/Ce[54] in supported or grafted/tethered catalysts[55,56] was also investigated. In experiments reported in literature the reaction is usually carried out by using organic solvents, such as toluene, trifluorotoluene, acetonitrile, ethylacetate and others. Ru^{2+} and Ru^{3+} complexes (for example, incorporated into polyoxometalates) can also efficiently catalyze the aerobic epoxidation of olefins.[57-61] However, it has also been reported that Ru-based systems can be used in an aqueous medium; recently, Vennat and Brégeault[62] reported that homogeneous systems with Ru^{2+}/Ru^{3+} acetate complexes or $[Ru(H_2O)_6]$ $(tosylate)_2$ catalyze the aerobic oxidative cleavage of α-substituted cycloalkanones into oxo-acids; the acid environment accelerates the reaction rate, because the enol form of the original ketone is involved in the mechanism.[1,21,28] $RuCl_3$ can even catalyze the oxidative cleavage of 1-methylcyclohexene into 6-oxoheptanoic acid in acetonitrile/water medium, under conditions at which RuO_4 is generated in-situ.[63,64] Under alkaline conditions, oxidative cleavage of vicinal diols into the dicarboxylic acid is catalyzed by Ru-based pyrochlore oxides, $A_{2+x}Ru_{2-x}O_{7-y}$ (with A = Pb, Bi; $0 < x<1$; $0<y < 0.5$), at room temperature.[65,66] In fact, the direct oxidation of alcohols into acids brought about with Group VIII elements is usually carried out under basic conditions.[67-75]

In the present work, we report the use of alumina supported $Ru(OH)_3$ catalysts under conditions aimed at bringing about the oxidative cleavage of CHD and obtaining AA; we also compare the catalytic behavior with that obtained when using Keggin-type polyoxometalates. Since the two classes of catalysts operate under quite different conditions, the aim of this paper is also to compare the effect of conditions on the reaction network and, lastly, on the selectivity to AA.

Results and Discussion

Supported $Ru(OH)_3$ catalysts: the effect of Ru content

Preliminary experiments were carried out with the aim of checking the stability of the supported $Ru(OH)_3$ catalysts under basic conditions. Catalysts used contained 0.6, 1.3, 2.5 and 4.9 g Ru per 100 g alumina support (codes Ru0.6, Ru1.3, Ru2.5 and Ru4.9, respectively). In fact, even though the catalyst is prepared in a basic medium, the amphoteric behavior of alumina may lead to its dissolution during reaction; therefore, we measured the amount of catalyst which had dissolved after 5h reaction time at pH 13.4 and 90°C (typical conditions used for reactivity experiments). We found that the degree of catalyst dissolution was an inverse function of the Ru loading: the Ru0.6 catalyst dissolved by 31%, the Ru1.3 by 16%, whereas for the Ru2.5 and Ru4.9 the amount of catalyst dissolved was negligible (less than 1%). This indicates that the $Ru(OH)_x$ anchored to the alumina support protects the latter from dissolution under strongly basic conditions, when its amount is sufficient to react with all the surface Al-OH groups. Experiments aimed at determining the existence of leaching phenomena for the Ru species during the use of Ru2.5 and Ru4.9 catalysts (those which were stable during reaction) are described later on in this paper.

Figure 1a compares the CHD conversion depending on the reaction time, for the catalysts which have different Ru content; in spite of the fact that Ru0.6 and Ru1.3 were not stable, this comparison may provide useful information on the reactivity of homogeneous and heterogeneous Ru species. Figures 1b-1e compare the yield to adipic acid (AA), glutaric acid (GA), succinic acid (SA), and 1-hydroxycyclopentanecarboxylic acid (HCPA). The following remarks are worthy of mention:

(a) With regard to CHD conversion, it is shown that the conversion was not much affected by the Ru content in catalysts. For all samples the conversion increased with time, but already at 0h reaction time (which corresponds to the time when oxygen started to be fed, once the desired reaction temperature had been reached) the conversion was close to 20%. Worthy of note, even with the Ru-free alumina the initial conversion was about 12%, due to the formation of dimeric compounds obtained by means of CHD condensation; these were the only products formed under these conditions. During the first 30 min, CHD conversion showed a minor increase with time only; after 30 min, a more rapid raise of conversion was observed. After 1h reaction time, the highest conversion was reached with the Ru0.6; the rank of conversion was: Ru0.6 ≥ Ru4.9 > Ru2.5 > Ru1.3. In terms of TOF (ie, referred to the Ru loading), the rank was instead: Ru0.6 >> Ru1.3 > Ru2.5 > Ru4.9. Even though this scale is obviously affected by the extent of the catalyst which dissolved with Ru0.6 and Ru1.3 (as reported above), it nevertheless offers an indication that in catalysts with the highest amount of Ru (Ru2.3 and Ru4.9), a low number of Ru atoms was available for the reaction. The characterization of samples will confirm this hypothesis (see below).

(b) With regard to the formation of AA (Figure 1b), samples showed differences depending on the Ru content. In the case of Ru0.6, the formation of AA did not occur during the initial 30 min reaction time, but then increased with the same trend already observed for CHD conversion, up to a maximum of 10% after 3h. After 5h reaction time, however, the yield decreased to about 5%. It is also shown that the maximum yield to AA (obtained in all samples after 3h reaction time), decreased in proportion to the increase of Ru content. However, the behavior displayed by Ru1.3, Ru2.5, and Ru4.9 was different from that observed with Ru0.6; in fact, with the former catalysts there was apparently no induction period. It is probable that the relatively higher AA yield observed with Ru0.6 is a consequence of both the dissolution of the catalyst and the release of Ru^{3+} in the reaction medium – a phenomenon which probably took about 1h to begin, and which may explain the need for the induction time observed.

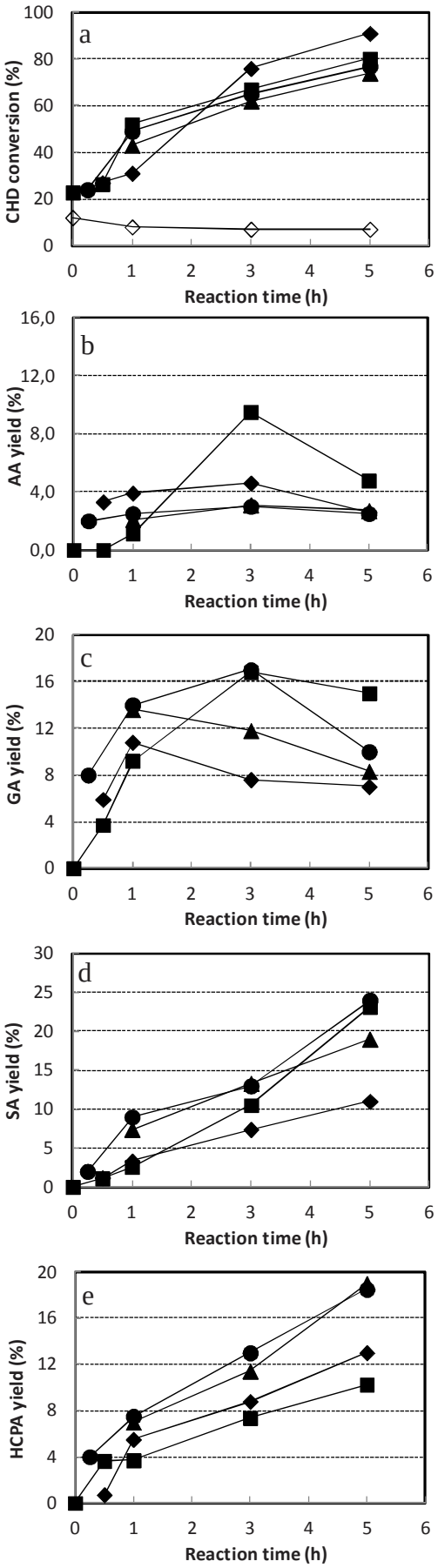


Figure 1. *trans*-1,2-Cyclohexandiol (CHD) conversion, yield to adipic acid (AA), glutaric acid (GA), succinic acid (SA), and 1-hydroxycyclopentanecarboxylic (HCPA) based on reaction time, for catalysts Al_2O_3 (◇), Ru0.6 (■), Ru1.3 (◆), Ru2.5 (▲) and Ru4.9 (●). Temperature 90°C.

With Ru1.3, there is no induction because the Ru amount was high enough to catalyze the formation of AA from the very beginning. This catalyst was slightly more active in AA formation than Ru2.5 and Ru4.9 because of both the better Ru dispersion and the catalyst dissolution (which, however, occurred to a much lesser degree than with Ru0.6), but it was not as active in AA formation as the Ru0.6.

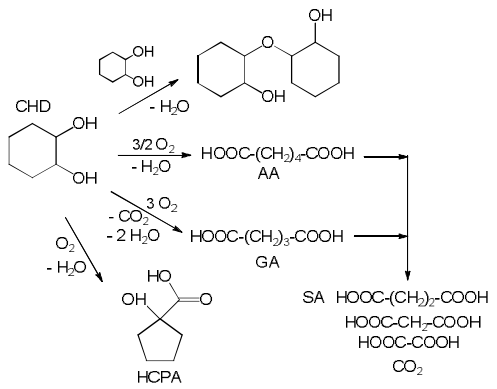
(c) GA, SA and HCPA were the prevailing products (Figures 1c-1e). The behavior displayed by the yield to both GA and HCPA is that typically observed with primary products, whereas SA was apparently a secondary product; this product was largely prevalent with longer reaction times, and the significant increase in yield observed after 3h reaction time occurred in concomitance with the decrease in the yield to both GA and AA (the latter decreased much more with Ru0.6, as shown in Figure 1b). HCPA, instead, did not undergo any consecutive transformation. The higher yield to GA was shown by Ru0.6 and Ru4.9 (Ru0.6 ≈ Ru4.9 > Ru2.5 > Ru1.3), which suggests that the larger the amount of Ru loading was, the greater the contribution of the parallel reaction of GA formation was. Also in the case of SA, the rank of the experimentally observed increasing yield was the same as that of the Ru content in catalysts, once again with the exception of Ru0.6. Lastly, the formation of HCPA was also affected by the Ru content, the greater yield being shown by samples with the greatest Ru content. Once again, the anomalous behavior of the Ru0.6 can be attributed to the high degree of dissolution shown by this catalyst.

(d) The yields to AA, GA, SA, and HPCA correspond to about 70-75% of the converted CHD; the remaining by-products (which, however, were not quantified) were propanedioic acid, oxalic acid, and carbonic acid. For all these by-products, the overall relative amount was very low for shorter reaction times, and increased when reaction time was increased; therefore, they formed by consecutive oxidative degradation reactions. We also detected very small amounts of 1,2-cyclohexanedione (CHDO); in all cases, however, the yield was lower than 0.2%. With regard to the formation of 2-hydroxycyclohexanone (HCO), we could detect it only at very short reaction times; its yield was 0.6% with the Ru1.3 catalyst. Lastly, in addition to the dimeric products of CHD self-condensation, we could also detect the formation of esterification products obtained by the condensation between CHD and dicarboxylic acids. The relative amount of CHD dimers decreased when the reaction time was increased, whereas the relative amount of esters was not affected so much by reaction time. We also carried out some experiments by reacting either CHD alone, or CHD and AA; these experiments confirmed the formation of the above-mentioned condensation by-products. For example, by reacting CHD and AA (initial molar ratio 2/1) for 3h, under the same reaction conditions as for the catalytic experiments (except for oxygen, which was not fed), we obtained around 15-20% conversion for both compounds, with the formation of the CHD diester of AA.

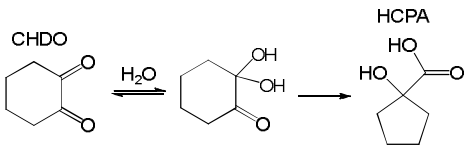
As a preliminary conclusion of these reactivity experiments, we can say that the distribution of products was affected by the catalyst composition; for example, the Ru0.6 catalyst was poorly selective to AA for short reaction times (0-1h), because of the formation of both GA and HCPA. This was due to the fact that – in the first hour – the catalyst had not yet dissolved, while the Ru content was too low to catalyze the formation of AA; under these conditions, GA and HPCA were the prevailing compounds, because both products formed without any involvement of the Ru species (see below the section dealing with the reaction mechanism). However, for intermediate reaction times, the yield to AA increased rapidly, because of catalyst dissolution, while

yields to by-products were lower than those observed with Ru-richer catalysts; therefore, under these conditions, the Ru0.6 catalyst was the most selective to AA, but this better performance is attributable to the Ru species which had leached because of catalyst dissolution. Conversely, more stable catalysts, i.e. those which did not undergo dissolution phenomena in the reaction medium, were less selective to AA than Ru0.6 and Ru1.3, because of both the greater contribution of the parallel reaction of GA and HCPA formation, and the consecutive oxidative degradation into SA. Overall, all of these systems showed a very low selectivity to AA; additional experiments were carried out with the aim of finding the reasons for this poor, but unexpected, catalytic behavior, through a more detailed investigation of the reaction scheme (see below).

Results indicate that the reaction network (Scheme 1) consists of the direct transformation of CHD into AA, GA, HCPA and CHD dimers (primary products); consecutive reactions contribute to the formation of SA, lighter diacids and esters formed by the reaction between unconverted CHD and carboxylic acids. In literature, HCPA is reported to form under basic medium by CHDO hydrolysis and rearrangement (Scheme 2).[78,79] This compound might be the precursor for GA formation via decarboxylation (that would explain why such a large amount of the latter acid is formed in the reaction); however, data shown in Figures 1c and 1e demonstrate that there is no kinetic relationship between HCPA and GA.



Scheme 1. The reaction network in CHD oxidation, showing a summary of kinetically primary and secondary compounds.



Scheme 2. The transformation of CHDO into HCPA in basic conditions.

The experiments shown in Figure 1 were carried out at pH 13.4; such strongly basic conditions were necessary for the purpose of activating the reactant CHD; in fact, when the reaction was carried out at less basic pH (more precisely, at pH 10.3 and 12.6), the conversion of CHD was negligible. At pH 10.3, the conversion was about 6-7% in the entire reaction time range; at pH 12.6 conversion was less than 20%, with the formation of condensation compounds and traces of HCO.

The literature indicates that basic conditions are needed for the activation of hydroxy groups during the aerobic oxidation of alcohols; for example the oxidation of glycerol into glyceric acid, of glucose to gluconic acid, and of 5-hydroxymethyfurfural into 2,5-furandicarboxylic acid – all catalyzed by supported noble metals – is carried out under basic conditions.[67-75] Since the oxidation of CHD into CHDO is the first in the multi-step reaction, preliminary to the oxidative scission into dicarboxylic acids, it is not surprising that basic conditions are needed in our case also. On the other hand, since the pKa of each single hydroxo group in CHD is lower than that of the hydroxo group in the partially oxidehydrogenated compound HCO, and since the latter compound is a possible precursor for the oxidative scission into dicarboxylic acids (see experiments on HCO reactivity, reported below), these data indicate that either the strongly basic pH is needed to produce first HCO and then CHDO (the former then being quickly oxidized into dicarboxylic acids, and the latter transformed mainly into HCPA), or it is a peculiarity of the catalyst to coordinate and oxidehydrogenate both hydroxo groups into CHD, thus directly yielding CHDO without the intermediate formation of HCO. In this latter case, CHDO is the precursor for the formation of both HCPA and dicarboxylic acids. In our case, albeit in a very limited number of experiments, we could identify HCO as the very first reaction intermediate; this, however, does not rule out either of the two above-mentioned theories. Specifically designed experiments will contribute to the understanding of this issue (see below).

Catalysts Ru2.5 and Ru4.9, which showed no dissolution in the reaction medium, were also used for some experiments aimed at finding the possible leaching of the Ru species from the support. These experiments were carried out using two different approaches: (i) first filtering off the catalyst after 3h reaction time and then carrying out the reaction again in the absence of catalyst (*leaching experiments*), and (ii) first filtering off the used catalyst and then reusing it with fresh reactants in order to check whether either the catalyst had maintained its original activity or any deactivation phenomena had occurred (one possible reason for deactivation being the leaching of Ru) (*recyclability experiments*).

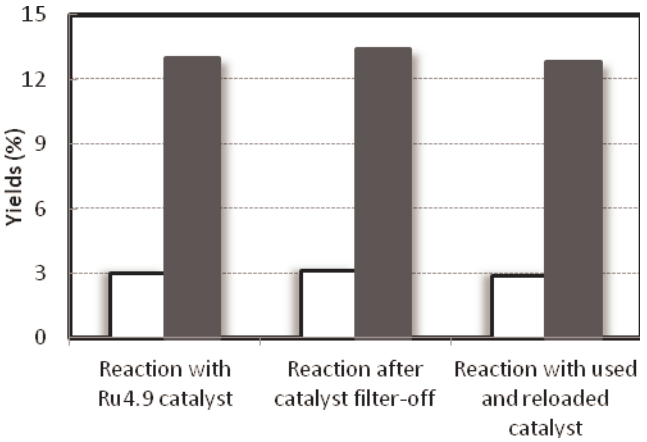


Figure 2. Yields to AA (white bar) and SA (grey bar) for the Ru4.9 catalyst (i) after 3h reaction time, (ii) after removal of the catalyst by filtration and 3h more reaction time, and (iii) with the Ru4.9 recovered from the first experiment and reused as such, for 3h reaction time.

Figure 2 compares the results of leaching and catalyst recyclability experiments, showing the yield to AA for fresh Ru4.9, used Ru4.9, and of the solution after catalyst filter-off. The yields to AA and SA were used as benchmarks, because the formation of these products required the presence of the catalyst (see below for experiments aimed at the determination of the reaction

scheme and of steps requiring the catalyst), whereas for most of the primary oxidation products this was not the case. Moreover, even though the yield to AA was not much affected by reaction time, the yield to SA (a consecutive product) was greatly affected by this parameter (see Figure 1d). The results obtained are strongly in favor of the absence of Ru-leaching phenomena during reaction. By means of ICP, we also analyzed the Ru content of both fresh and used Ru4.9 catalyst, and found that it was the same (within the experimental error) for both samples.

Supported $Ru(OH)_3$ catalysts: reactivity of 1,2-cyclohexanedione (CHDO) and 2-hydroxycyclohexanone (HCO)

Reactivity experiments indicate that a key role in the reaction scheme is played by CHDO. It is necessary to mention that this product was detected in non-negligible amounts with Ru-rich catalysts only for very short reaction times. This might indicate that either it is a very reactive intermediate, and thus quickly transformed into consecutive products, or it was only a minor by-product of the reaction, and was not involved in the pathway leading to carboxylic acid formation. On the other hand, it is also evident that the formation of HCPA, one of the most important by-products, may occur only via CHDO as the intermediate. With the aim of better understanding the role of CHDO, we carried out selected experiments starting from this compound; the results are shown in Table 1.

First, we tested the reactivity of CHDO on the basis of pH (entries 1-3), in the presence of both O_2 and the catalyst (we conducted experiments with both Ru0.6 and Ru4.9). After 3h, CHDO conversion was complete at pH 12 and 13.4, whereas it was 60-70%% at pH 6. At the more basic pH, the distribution of products was quite similar to that obtained from CHD; this definitely confirms that the key intermediate of the reaction from CHD is CHDO, and that HCO, although formed, is rapidly converted into CHDO, while the direct oxidation path of HCO into dicarboxylic acids makes a negligible contribution; in fact, if the opposite were true, we should obtain a much more selective formation of AA (see below experiments from HCO). Worthy of note, at these conditions there were also some by-products, those also observed from CHD. At less basic pH, the HCPA was no longer formed, and the yields to all dicarboxylic acids were higher than those obtained at pH 13.4; however, we noticed the formation of both 6-hydroxycaprolactone and the dimer obtained by aldol condensation of CHDO. The former compound may form by means of an intramolecular Cannizzaro-type reaction which transforms the cyclic diketone into a cyclic hydroxyl ester. It is worth noting that this compound can be a precursor for AA formation, via oxidative dehydrogenation into adipic anhydride (which can be successively hydrolyzed into AA), or via hydrolysis followed by oxidehydrogenation into AA. Indeed, adipic anhydride was found after CHDO reaction at pH 6. Since there was no formation of AA, this indicates that in a neutral pH, the anhydride did not react further, whereas with a more basic pH, it was hydrolysed into AA salts.

When the reaction from CHDO was carried out at the same conditions as for the experiment in entry 3, but without a catalyst (entry 4), the products were HCPA and GA; lastly, when oxygen was also withdrawn (entry 5), HCPA was the prevailing product. In this latter case, GA was not observed; therefore, this product was formed by the reaction with O_2 of a very reactive intermediate, but did not need a catalyst to be formed. By analogy with the highly reactive HCO (see below) – which also reacted with O_2 without needing a catalyst – we can speculate that the 6-hydroxycaprolactone (one main product of CHDO transformation in basic medium) is oxidized by the reaction with O_2 to yield a 6-hydroperoxide-6-hydroxycaprolactone, which is then hydrolyzed (with ring opening), decarboxylated, and oxidized to yield GA.

Table 1. Reactivity experiments from CHDO and HCO

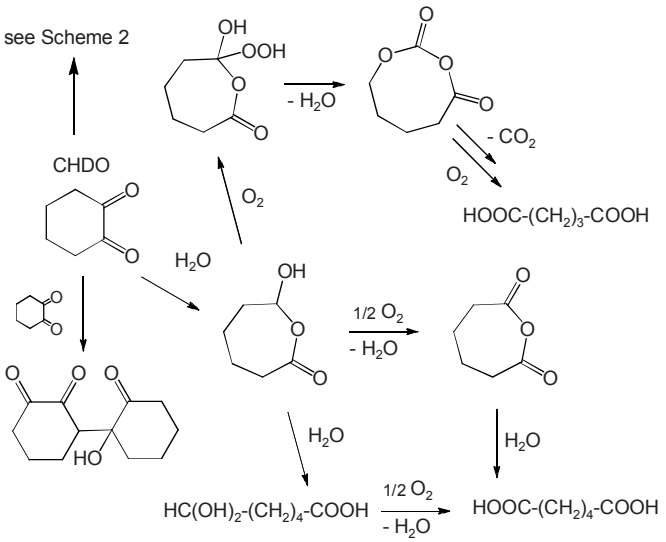
Test n, reactant[]	T (°C), t (h), pH	O_2	Cat.	Conv. (%)	AA Y, %[b]
1, CHDO	90, 3, 6	Yes	Ru0.6 Ru4.9	76 68	Traces Traces
2, CHDO	90, 3, 12.9	Yes	Ru0.6 Ru4.9	100 100	10 16
3, CHDO	90, 3, 13.4	Yes	Ru1.3 Ru4.9	100 100	3 2
4, CHDO	90, 3, 13.4	Yes	No	100	0
5, CHDO	90, 3, 13.4	No	No	100	0
6, CHDO	45, 3, 13.4	No	No	78	0
7, HCO	90, 3, 12.9 90, 3, 12.8	Yes Yes	Ru0.6 Ru4.9 Ru4.9	99 99 95	55 62 29
8, HCO	90, 3, 13.4	Yes	Ru0.6 Ru4.9	100 100	9 8
9, HCO	90, 3, 10.1	Yes	No	100	4
10, HCO	90, 3, 12.5	Yes	No	100	71
11, HCO	90, 3, 13.4	Yes	No	100	20

Test n, reactant	HCPA Y, %	GA Y, %[b]	SA Y, %[b]	Identified by-products[a]
1, CHDO	0 0	0 0	0 0	HCL, AAN, DHCH, AC HCL, AAN, DHCH, AC
2, CHDO	0 0	22 4	7 19	HCL, AC HCL, AC
3, CHDO	21 61	7 3	0 0	HCL, AC HCL, AC
4, CHDO	38	28	0	Not identified
5, CHDO	61	0	0	Not identified
6, CHDO	53	0	0	AC
7, HCO	0 0 0	3 2 10	0 4 tr	HCL, AC HCL, AC HCL, AC
8, HCO	73 54	6 5	5 tr	Traces Traces
9, HCO	0	3	0	CHDO (2% yield)
10, HCO	0	6	3	HCL, AC, CHDO (0.4% yield)
11, HCO	52	15	11	Traces

[a] CHDO: 1,2-cyclohexandione; HCO: 2-hydroxycyclohexanone; HCL=6-hydroxycaprolactone; AAN=adipic anhydride; DHCH=2,2-dihydro-cyclohexanone; AC=aldol condensate.[b] Y=yield.

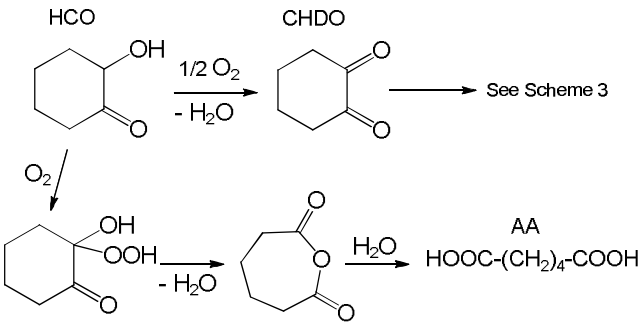
When experiment 5 was repeated at 45°C (entry 6), the CHDO conversion was lower than 100%; the products were HCPA and aldol condensate. Therefore, at both 90 and 45°C, and in the absence of the catalyst, the formation of AA, SA, and lighter acids was negligible.

Scheme 3 summarizes the reactions involved in CHDO transformation, as inferred from experiments from both CHD and reaction intermediates.



Scheme 3. A summary of reactions involved in CHDO transformation.

Table 1 also shows the results of some experiments carried out with HCO as the reactant. The results demonstrate that HCO is very rapidly oxidized into AA even in the absence of a catalyst, especially at pH 12.5; the reaction likely occurs because the H atom on the α C atom is very easily abstracted to generate a radical species, which is soon transformed into a quaternary C hydroperoxide-hydroxide species.[80-82] The latter may dehydrate and rearrange to yield adipic anhydride, which is finally hydrolysed into AA. This route is evidently much more selective than the one passing through CHDO as the key intermediate. Conversely, at a more basic pH (that is, under the same conditions to be used when CHD is the reactant), there was still a significant formation of AA and of other dicarboxylic acids, but the prevailing product was HCPA; this occurred especially in the presence of the catalyst which accelerated the oxidative dehydrogenation of HCO into CHDO. The latter was found as a reaction product at pH 10.3, a condition in which no AA formed. Reactions involved in HCO transformation are summarized in Scheme 4.



Scheme 4. A summary of reactions involved in HCO transformation.

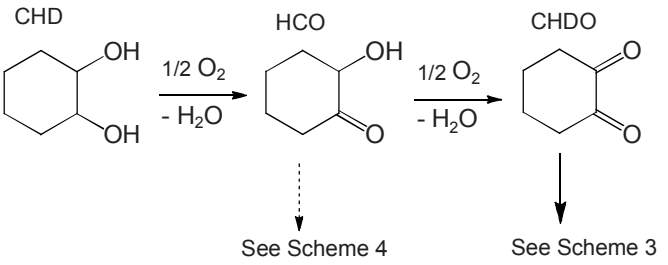
In conclusion, concerning the reaction mechanism, the experiments carried out demonstrate the following:

(a) The oxidation of CHD catalyzed by supported $Ru(OH)_3$ only occurs under strongly basic conditions, at which the reactant is rapidly oxidehydrogenated into HCO and then CHDO. One might expect that the former intermediate generates a radical species at the C_2 atom which may then form a hydroperoxo radical by the reaction with O_2. However, this reaction does not occur, either because the oxidehydrogenation is very fast at the strongly basic pH used, or because the Ru^{n+} active species coordinates the two vicinal hydroxyl groups in CHD, with an almost concomitant transformation of the two groups into carbonyls.

(b) The CHDO is the key intermediate species, and gives rise to a series of reactions, all of them favoured under basic conditions, leading to HCPA, to the aldol condensation product, and to 6-hydroxycaprolactone. The two former compounds are stable, whereas the lactone undergoes further transformations into AA and GA; the former reaction needs the catalyst to occur (which means an oxidehydrogenation as the key step), whereas the latter occurs without a catalyst. Therefore, in the latter case, the reaction includes the formation of an intermediate which readily generates a reactive radical and, by reaction with O_2, a hydroperoxide species. The further rearrangement, decarboxylation and oxidation leads in the end to GA.

(c) SA and lighter acids form by consecutive reactions mainly on AA and GA; these reactions occur preferably in the presence of the catalyst.

A summary of the proposed reaction mechanism for CHD oxidation in basic conditions is shown in Scheme 5. It is worth noting that kinetic experiments showed that with Ru1.3, Ru2.5, and Ru4.9 catalysts the main products, i.e. AA, GA and HCPA, formed by kinetically parallel reactions. This means that all the intermediate compounds shown in the scheme were extremely reactive; in fact, neither 6-hydroxycaprolactone, nor adipic anhydride, glutaric anhydride, or any hydroperoxo species was isolated during the reaction from CHD. These compounds could only be isolated starting from the key intermediates, HCO and CHDO (Table 1), which means in the presence of a great concentration of these compounds in the reaction medium. The case of the Ru0.6 catalyst was slightly different; in this case, the Ru content was probably too low to catalyze oxidehydrogenation reactions. Both the conversion of CHD into HCO and CHDO and the formation of AA were delayed, and started only after the catalyst had dissolved because of the basic medium.



Scheme 5. The overall reaction mechanism in CHD oxidation.

Supported $Ru(OH)_3$ catalysts: the characterization of samples

Figure 3 shows the XRD pattern of Ru4.9, which is the sample containing the greatest amount of Ru; patterns of all other

samples were coincident with this. Despite the relatively large amount of Ru loaded, no reflection attributable to any crystalline Ru hydroxide or oxide phase could be identified. This indicates that either the $Ru(OH)_x$ is dispersed in the form of a "bidimensional" monolayer, with formation of Ru-O-Al species linking monomeric units to the support, or it is present in the form of nanoparticles.

Figure 4, reporting some selected TEM images relative to the Ru2.5 sample, shows the presence of Ru hydroxide nanoparticles with average diameters of 1.2 nm (see the distribution in the bottom section); this evidence, however, does not rule out the presence of a bidimensional structure containing $Ru(OH)_x$ monomeric or oligomeric species and covering the alumina surface. The thermal treatment of the sample at 400°C in air led to the development of crystalline RuO_2, as shown in Figure 3.

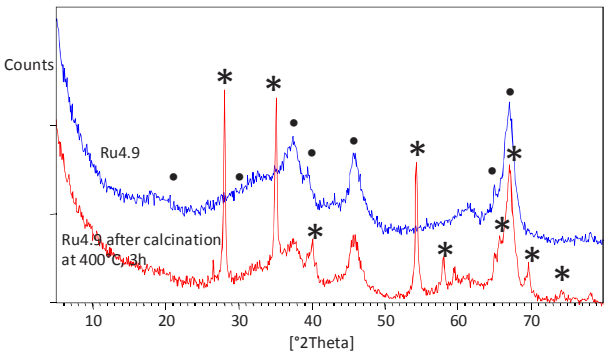
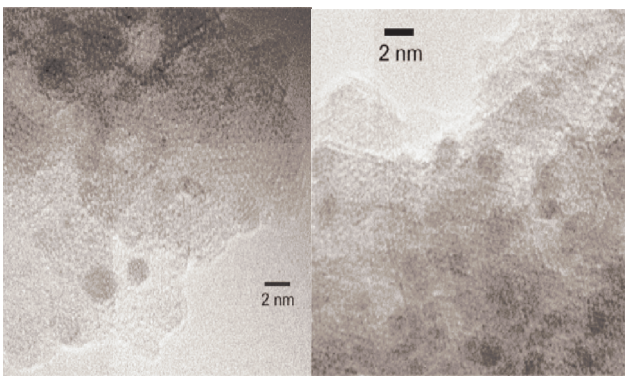


Figure 3. XRD patterns of Ru4.9 catalyst, and of Ru4.9 catalyst after calcinations at 400°C, in air, for 3 h. Symbols: ● alumina; ⁎ RuO_2

Thermal Programmed Reduction experiments provide further information on the nature of the Ru species; TPR profiles for samples Ru2.5 and Ru4.9 are shown in Figure 5. The reduction profiles were similar for all the samples, with a first main peak at low temperature associated to the reduction of an easily reducible species, and a second main peak at above 500°C; moreover, other reduction peaks of lesser intensity were seen at intermediate temperatures. The relative intensity of the peaks changed on varying the Ru content in samples, which may reflect the different type of Ru^{n+} species that formed in function of Ru content: either monomeric and oligomeric $Ru(OH)_x$ species anchored to the alumina surface, or bulk nano-sized agglomerates. Accordingly, Mizuno et al.[76] reported that monomeric and polymeric Ru^{3+} hydroxide species develop over the alumina surface, in function of Ru loading.



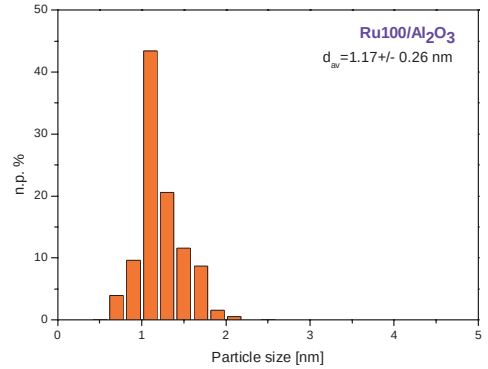


Figure 4. TEM picture of fresh Ru2.5 catalyst, and particle size distribution of $Ru(OH)_x$ nanoparticles as inferred from TEM pictures.

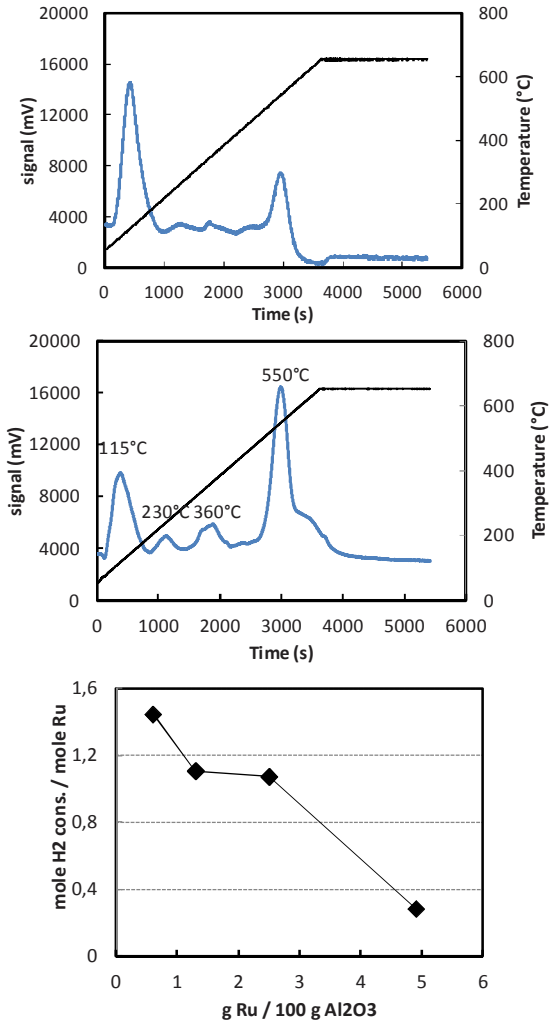


Figure 5. TPR experiments with Ru2.5 (top), and Ru4.9 (center) catalysts, and specific H_2 consumption based on Ru loading (bottom)

Moreover, the type of Ru species greatly affected their reducibility, probably because of the presence of different Ru oxidation states. This was confirmed by the evaluation of the overall amount of H_2 consumed per Ru atom in samples, also shown in Figure 5. In fact, in the case of Ru0.6, the ratio corresponds well to the theoretical one for the total reduction of Ru^{3+} into metallic Ru (stoichiometric ratio 1.5). However, the experimental value becomes smaller in proportion to the Ru content, indicating that higher Ru loadings favoured the formation

of Ru^{n+} species with n < 3. This may also explain why the TOF experimentally observed for AA production decreased on increasing the Ru content in catalysts.

Keggin polyoxometalate catalysts

With both POMV1 and POMV2 catalysts, the reaction at acid pH, temperature 90°C and 5h reaction time gave a similar value of CHD conversion: 36% and 37%, respectively (Table 2); the pH of the aqueous solution was 2.0. Unexpectedly, however, we did not detect any dicarboxylic acid – AA, GA, or SA – among the reaction products. Moreover, not even one of the by-products which had formed under basic conditions was observed after reaction with POM catalysts. An analysis of the reaction mixture by means of ESI highlighted that the reaction products formed were the cyclic ester obtained by esterification of the two carboxylic groups in AA with the two C-OH groups in CHD; and small amounts of the linear ester formed by esterification of 1 AA molecule with 2 CHD molecules. This means that AA actually formed, but soon reacted with the unconverted CHD to form the corresponding esters; these compounds were not eluted by either HPLC or GC analysis. Therefore, in order to quantify the amount of the products formed, we carried out a transesterification of the reaction mixture with a large excess of methanol (see Experimental for a detailed description of the procedure used), and then analyzed the methyl esters of dicarboxylic acids by means of GC. The results are summarized in Table 2 (showing the yields to dimethylcarboxylate after transesterification and the CHD conversion, for some selected experiments). It is shown that the conversion of CHD was greater than the overall yield to dimethylcarboxylates, because for each mole of dicarboxylic acid produced, either two or three moles of CHD had reacted (one for the synthesis of the acid, and one or two for the synthesis of the corresponding esters). This hypothesis was confirmed by reacting AA and CHD, in the absence of O_2, with and without POMV1 catalyst; we found that the esterification reaction between the two compounds was highly fostered under the acid conditions used for oxidation experiments. However, in addition to the esters of AA, GA, and SA, we also detected the ether formed by the condensation of two CHD molecules; this compound formed especially during the initial part of the reaction, and then decreased, becoming negligible after 5-6h reaction time.

Figure 6 reports the yield to dimethyladipate (after transesterification of the CHD esters of the dicarboxylic acids), for experiments carried out at increasing reaction time, with two different temperatures. Both the dimethylglutarate and dimtheylsuccinate yields were negligible; hence the selectivity to the adipate was very high (higher than 97%), but was lower for reaction times shorter than 3h, because of the formation of the CHD ether. The POMV2 catalyst was less selective (Table 2).

In conclusion, POMs catalysts proved to be very selective in CHD oxidation to AA, since all the side reactions occurring under basic conditions did not contribute here. Moreover, the formation of lighter dicarboxylic acids was minimal, especially with the POMV1 catalyst. However, the AA reacted with the unconverted CHD, to yield the corresponding esters; therefore, an additional step of ester hydrolysis would be necessary to obtain the pure AA. Another drawback of POMs catalysts is that they are completely soluble in the reaction medium, and the only method to separate from the reaction mixture is to precipitate them in the form of insoluble salts, which can then be recovered by filtration. We carried out this procedure by adding CsCl in large excess, and attempted to reuse the recovered salt as such for a further experiment; however, the activity of the POMV1 Cs-salt was much lower than that of the starting acid POM, even in the presence of HCl (which was necessary to lower the pH of the solution to the desired value).

Table 2. Selected experiments with POMV1 and POMV2 catalysts.

Cat.	T (°C), t (h), P_{O2} (bar)	Yield to AA, GA & SA dimethyl esters (%)	CHD conv. (%)
POMV1	90, 6, 4	12, traces, traces	36
POMV2	90, 6, 4	9.5, 0.4, 0.1	37

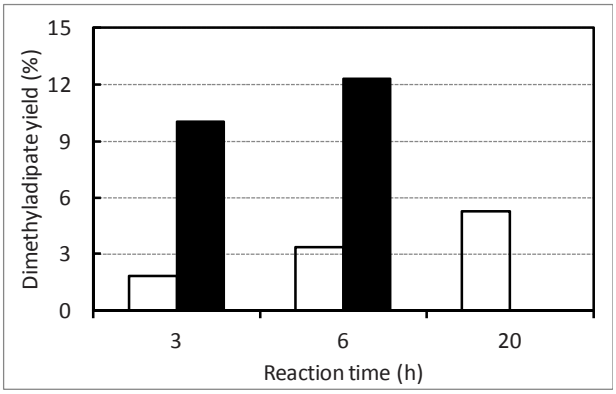


Figure 6. Dimethyladipate yield after transesterification with methanol of the reaction mixture obtained after reaction at 70°C (white bars) and 90°C (grey bars) based on reaction time.

Lastly, we conducted experiments aimed at the determination of the reaction mechanism. When we used CHDO as the reactant, in the presence of both O_2 and POMV2 catalysts, conversion was total after 1h, even though we did not observe the formation of AA; the only products were light acids, formed by oxidative degradation, including GA and SA (which instead did not form using CHD as the reactant). We then carried out the reaction with CHD, with the POMV2 catalyst but in the absence of oxygen, in order to isolate possible reaction intermediates formed in the acid reaction environment. We did not detect the formation of either 1-hydroxycyclohexene, 3-hydroxycyclohexene (both products being possibly formed by the acid-catalyzed dehydration of CHD), or cyclohexanone (the keto form of 1-hydroxycyclohexene); however we observed the formation of HCO. Worthy of note, in the absence of oxygen the catalyst turned from the initial orange color to black, thus suggesting the occurrence of an extensive reduction of POM. These data suggest that the reaction mechanism occurs via the catalyzed oxidehydrogenation of CHD into HCO, which however is not oxidized into CHDO, but instead is further oxidized into AA. It is important to note that, in this case, the formation of HCO occurs under acid conditions.

In order to confirm the possible role of HCO as an intermediate, we carried out experiments reacting this molecule; results are summarized in Table 3. It can be seen that HCO was much more reactive than CHD, its conversion being higher than 90% already after 1h reaction time. However, the formation of AA showed an induction period of 20 min; the highest yield to AA was 35%. On the other hand, GA formed from the early reaction time, a clear indication that the mechanism by which GA formed was different from that leading to AA. On the other hand, the formation of SA was clearly consecutive to both GA and AA. Other products identified were 6-hydroxycaprolactone, adipic anhydride, and heavier condensation compounds. However, adipic anhydride disappeared after 20 min reaction time, because of the

consecutive hydrolysis into AA. When the reaction was carried out at the same conditions, but without the POMV2 catalyst, and at the same pH of 2 (by means of sulphuric acid addition), we again noticed the formation of 6-hydroxycaprolactone and adipic anhydride, but the reaction was much slower than it was in the presence of the catalyst; in fact, HCO conversion after 3h was just 15%. It is worth noting that when the reaction was carried out starting from CHD, the conversion achieved was much lower than that obtained by reacting HCO under the same conditions; moreover, at low conversion, the reaction from CHD yielded only AA as the oxidation product.

Table 3. Reactivity experiments from HCO with POMV2 catalyst

Time (min)	HCO Conv. (%)	AA, GA, SA Yield (%)	Other products
0	32	0, 0, 0	HCL, condensation compounds
5	46	0, 5, 0	AAN, HCL, cond. compounds, light dicarboxylic acids
10	47	0, 10, tr	AAN, HCL, cond. compounds, light dicarboxylic acids
20	63	24, 12, tr	light dicarboxylic acids (HCL)
30	79	32, 9, tr	light dicarboxylic acids (HCL)
60	96	32, 4, 8	light dicarboxylic acids
120	99.8	34, 4, 9	light dicarboxylic acids
180	100	32, 2, 11	light dicarboxylic acids

Conditions: T 90°C, pH 2, catalyst POMV2

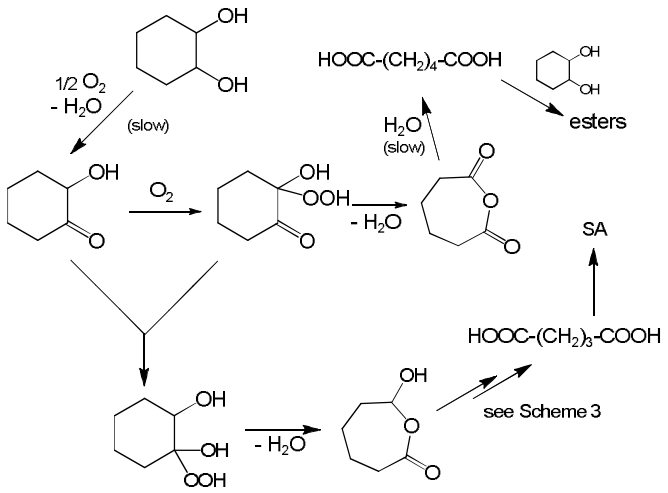
These results indicate the following:

a. In CHD oxidation, the oxidehydrogenation of CHD into HCO is slower than the consecutive oxidation of the latter compound.
b. HCO is oxidized by means of two parallel pathways, one leading to the formation of adipic anhydride, the other leading to GA.
c. Adipic anhydride is slowly hydrolized into AA; both AA and GA undergo consecutive oxidative degradation into SA.

Since no GA formed starting from CHD, it may be possible that the presence of the parallel pathway leading to GA is due to the reaction conditions used for HCO oxidation, as shown in Scheme 6. The hydroperoxide formed by the oxidation of the α-C atom in HCO either rearranged into adipic anhydride, or – due to the high concentration of HCO in experiments conducted starting from this compound – acted as an oxidant toward HCO itself, with formation of 6-hydroxylactone via a Criegee-type intermediate. As shown in Scheme 3, lactone is a possible precursor for GA formation, thus explaining the presence of this compound during HCO oxidation, but not during CHD formation. In the latter case, in fact, once formed from CHD, HCO soon reacted with oxygen to produce adipic anhydride and then AA.

Conclusion

The aerobic oxidation of *trans*-1,2-cyclohexanediol, aimed at the synthesis of adipic acid, has been investigated using either supported $Ru(OH)_3$ catalysts, under basic conditions, or Keggin-type P/Mo/V polyoxometalates, under acid conditions. In the former case, the catalyst was very efficient in the double oxidehydrogenation of the two C-OH groups to yield the corresponding diketone (1,2-cyclohexanedione); the latter compound, however, underwent several undesired side reactions which were responsible in the end for the low yield to adipic acid. The formation of adipic acid occurred via the intermediate formation of 6-hydroxycaprolactone, the latter being formed by intramolecular Cannizzaro-type disproportionation of 1,2-cyclohexanedione. Polyoxometalates were extremely selective to adipic acid (especially the compound with composition $H_4PMo_{11}VO_{40}$), but under acid conditions, adipic acid reacted with 1,2-cyclohexanediol to yield the corresponding ester. Overall, the possibility to selectively transform 1,2-cyclohexanediol into adipic acid is limited either by the characteristics of the key reaction intermediate which forms under basic conditions, 1,2-cyclohexanedione, or by the nature of the reactant itself.



Scheme 6. The overall reaction mechanism in CHD oxidation catalyzed by the POMV in acid conditions.

Experimental Section

Preparation of catalysts

Supported $Ru(OH)_3$ catalysts were prepared according to the procedure reported by Yamaguchi and Mizuno.[40,76] Specifically, we first dissolved $RuCl_3.xH_2O$ (38-42 wt% Ru, Aldrich) in 60 mL of distilled water (pH of the solution 2), in the amount necessary to obtain the desired Ru content in catalysts (e.g. 0.126 g to obtain the 2.5 wt% Ru on alumina); then, 2.0 g of γ-Al_2O_3 were added (precalcined at 500°C for 3h in static air; surface area 106 m^2/g). The system was left at room temperature, under stirring for 30 min; at these conditions, there was no precipitation of $Ru(OH)_3$. Afterwards, the pH of the slurry was increased by means of anhydrous NaOH addition, until pH 13.2 was reached; the slurry was left under stirring for 24 h. At these conditions, the Ru species in solution, $[RuCl_x(OH)_y(H_2O)_{6-x-y}]^{(3-x-y)+}$, react with the Al-$O^-$ surface groups on alumina, to generate anchored Ru species :

$$Al\text{-}O^- Na^+ + [RuCl(OH)_2] \rightarrow Al\text{-}O\text{-}Ru(OH)_2 + NaCl$$

The analysis of the Ru content in both catalysts and the surnatant solution showed that this method allows the quantitative deposition of the Ru species. Lastly, the solid was filtered, washed with abundant water, and let dry in the open air for 24 h. Then it was used as such for reactivity experiments.

The 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.[77] An aqueous solution was prepared by dissolving MoO_3 and H_3PO_4 in abundant water, at a temperature close to 100°C (but avoiding bringing the solution to a boil); complete dissolution took about 15-20h. 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 1h, even though it was then left to rest overnight. The former solution was heated again at 90°C, and the second solution was added drop by drop; next the solution was left at 90°C for 8h, in order to let most of the solvent evaporate, and was then 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 hours. The dried solid was characterized by means of FT-IR spectroscopy in order to confirm the formation of the desired Keggin compound.

Catalytic experiments

Catalytic experiments were carried out in a semi-continuous stirred autoclave reactor (100 mL volume) made out of glass, at an operating pressure of 4 atm (BuchiMiniclave). The reactor was equipped with a vapor condenser (cooling fluid temperature: -10°C), to avoid major loss of CHD during reaction. Oxygen was fed continuously to the reactor, with a standard flow rate of 300 NmL per minute. The liquid phase was loaded batchwise. For reactions in basic medium, unless otherwise specified, typical reaction conditions were: 0.3 g CHD (Sigma-Aldrich, purity 98%), 25 mL of water, 0.1 g of supported $Ru(OH)_3$ catalyst. The pH was adjusted to 13.4 by adding anhydrous NaOH (or in some experiments a lower pH was used). Conditions for reaction in acid medium were: CHD 5.5 g, catalyst 1.6 g, water 50 mL, oxygen feed 300 NmL/min; the catalyst completely dissolved in the reaction medium; the pH of the aqueous solution was 2. For both reaction conditions, at first the reaction mixture was heated up to the desired temperature under stirring, and then oxygen started to be fed; this was the zero time of reaction.

The analysis of reaction products was carried out by means of the following procedure: in the case of experiments carried out with the supported $Ru(OH)_3$ catalyst, the reaction slurry was first cooled down to room temperature, then filtered off to separate the catalyst, and finally the pH was decreased by means of 98% H_3PO_4 addition, down to the value of 2.5. The accuracy of the final pH value was essential, since all the calibrations curves for HPLC analysis were carried out at this pH value. The separation and determination of the concentration both for the unconverted reactant and for the reaction products were carried out by means of HPLC (Thermo SP) using an isocratic method with an eluent phase made of 0.01 M phosphoric acid and acetonitrile (95/5 vol ratio, 0.8 mL/min), and a Hypersil BDS inverse phase C_{18} on silica (5µm of active phase, 250 x 4,6 mm column), operating at room temperature; the UV detector was set at 210 nm wavelength. In the case of experiments carried out with the POM catalyst, the catalyst was first precipitated by adding an excess of CsCl, and filtered off. Then, the reaction mixture was analyzed as described above.

The concentration of AA was also confirmed by means of another procedure; after filtration of the solid (or precipitated) catalyst, the reaction mixture was heated (65°C) under vacuum to evaporate both the unconverted CHD 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 1h in a sealed vessel, in order to either transform the AA produced to the corresponding methyl diesters, or carry out a transesterification of the esters obtained by reaction between AA and CHD. The esters were then extracted with *n*-hexane (this also led to the separation both of the POM catalyst and of $BF_3$from the mixture); the extraction procedure was repeated several times. Lastly, the solution of AA diester in *n*-hexane was analyzed by GC (internal standard *n*-decane). 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°C-280°C (heating rate 10°/min). Worthy of note, the two analytical methods gave exactly the same concentration of AA.

GC-MS (Agilent 6890N) and ESI/MS (Waters micromass ZQ 4000) were used for the identification of products. For some of the identified products it was possible to prepare aqueous solutions with known concentration, which made it possible to prepare a calibration curve and to determine the precise UV response factor (RF) for HPLC analysis. The RF of 1-hydroxycyclopentanecarboxylic acid (HCPA) was calculated by reacting 1,2-cyclohexandione (CHD) at pH 13.4, in the absence of both oxygen and catalyst; under these conditions, the only product of CHD transformation was HCPA. A calculation of the number of CHD moles converted made it possible for us to determine the RF of HCPA. HCPA was identified by combining ESI analysis and the NMR spectrum (Varian Mercury 400).

In the case of experiments carried out in acid medium, the gas phase was also analyzed, since CO_2 did not remain in the liquid phase (instead, in the case of experiments carried out under basic conditions, no CO_2 was found in the gas phase). CO_2 was analyzed 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°C-240°C, heating rate 10°/min) and a TCD. Then the average value of CO_2 produced during the reaction time, obtained from 3-4 samplings, was taken as the measure of the CO_2 yield.

Characterization of catalysts

Supported $Ru(OH)_3$ catalysts were characterized by means of X-ray diffraction (XRD), Transmission Electron Microscopy (TEM) and H_2-Thermal-Programmed-Reduction (TPR). XRD patterns were recorded using a Ni-filtered Cu Kα radiation (λ = 1.54178 Å) on a Philips X'Pert vertical diffractometer equipped with a pulse height analyzer and a secondary curved graphite-crystal monochromator. TPR experiments were carried out using a Thermoquest TPDRO1100 instrument. Samples were loaded into a quartz reactor and pretreated in flowing He at 150°C for 30 min to eliminate weakly adsorbed species. After cooling at room temperature, He was replaced by the analyzing gas (5% H_2 in Argon) while the temperature was linearly increased up to 700°C (thermal ramp: 10°C/min). Hydrogen consumption was calculated by integration of the corresponding TCD signal. High-Resolution transmission electron microscopy (HR-TEM) images were obtained with a Jeol 3010-UHR instrument (acceleration potential 300 kV, LaB_6 filament). Samples were dry dispersed on lacey carbon Cu grids.

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Keywords: Adipic acid · 1,2-Cyclohexandiol · Ruthenium hydroxide · Polyoxometalates · Reaction mechanism · Selective oxidation

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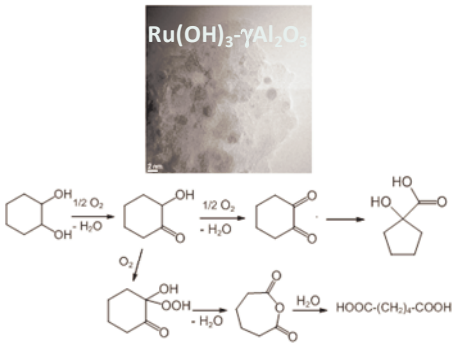
The synthesis of adipic acid by means of the aerobic oxidative cleavage of *trans*-1,2-cyclohexanediol was investigated under basic and acid conditions. In the former case, supported $Ru(OH)_3$ catalysts were active but poorly selective, because of the several side reactions starting from the key reaction intermediate, 1,2-cyclohexanedione. Under acid conditions, Keggin polyoxometalates were selective to adipic acid, but the latter then reacted with the unconverted reactant to yield esters.



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The oxidation of 1,2-cyclohexanediol to adipic acid with oxygen: a study on selectivity affecting parameters