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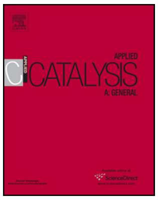

Two alternative routes for 1,2-cyclohexanediol synthesis by means of green processes: Cyclohexene dihydroxylation and catechol hydrogenation

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ABSTRACT

In this paper we compare two different reactions, aimed at the synthesis of 1,2-cyclohexanediol. Specifically: (a) the direct epoxidation and hydrolysis (dihydroxylation) of cyclohexene to *trans*-1,2-cyclohexanediol, with an aqueous solution of hydrogen peroxide, and (b) the hydrogenation of catechol to a mixture of *cis* and *trans*-1,2-cyclohexanediol, in an attempt to establish green protocols for the synthesis of diols. Both reactions, the dihydroxylation of cyclohexene and the hydrogenation of catechol, were carried out without organic solvents. In the former case, an unprecedented 97.4% yield to the glycol was obtained, by selecting proper reaction conditions and using a tungstic acid/phosphoric acid catalyst, in a biphasic system with a phase-transfer agent. In the second approach, a heterogeneous alumina-supported $Ru(OH)_x$ catalyst was used, and a 90% yield to the glycol was obtained. A comparison of the two processes allowed to show the lower environmental impact of the catechol hydrogenation route.

1. Introduction

1,2-Diols are molecules widely employed as intermediates in the perfume and fragrance industry, as well as in drug and lubricant synthesis. Dihydroxylation of olefins may occur either via one-pot epoxidation and water hydrolysis of the oxirane ring into the *trans*-diol, or via formation of cyclic inorganic ester, for example, by reaction with $KMnO_4$ or OsO_4, then hydrolyzed into the *cis*-diol. While various conventional oxidants are typically used for *syn*- and *anti*-dihydroxylation, including for instance $KMnO_4$, OsO_4, alkylhydroperoxides, and peracids [1–4], a greener oxidant such as hydrogen peroxide is desired, due to both better atom efficiency and the coproduction of water [5–7]. For these reasons, intensive research has been conducted with the aim of developing reaction systems which may efficiently transform the olefin into 1,2-diols with H_2O_2, possibly under organic solvent-free conditions. In this context, several authors have reported the dihydroxylation of olefins with H_2O_2 catalyzed by transition metal complexes, i.e. H_2WO_4, polyoxometalates or CH_3ReO_3, and by various solid catalysts as well [8–33]. The use of zeolites or other heterogeneous catalysts allows dihydroxylation in the absence of organic solvents, but selectivity is no higher than 60% because of the formation of epoxides, alcohols, ketones, and/or ethers: $(NH_4)_{10}W_{12}O_{41}$/hydrotalcite [14], Ti-β [15,16], Ti-MCM [17,18], Nb-MCM-41 [19], Ti-MMM and Ce-SBA [33] are examples of the catalytic systems investigated. In cyclohexene epoxidation with H_2O_2 and Ti–silicates catalysts, the obtained products are typical of both two-electron oxidation mechanisms, i.e., cyclohexene epoxide and *trans*-cyclohexane-1,2-diol, and one-electron oxidation mechanisms (2-cyclohexene-1-ol and 2-cyclohexene-1-one) [9,20–31,33], even though the selectivity to allylic oxidation products can be lowered by means of specific approaches, e.g., the dropwise addition of hydrogen peroxide [24]. The use of a resin-supported sulfonic acid makes it possible to conduct the dihydroxylation of cyclohexene with 30% H_2O_2 without any solvent, at 70 °C, with 98% yield to the diol [32].

In literature one of the most investigated catalytic systems for epoxide synthesis is based on tungstate anions, because the latter's unique chemistry is more conducive to oxygen transfer over

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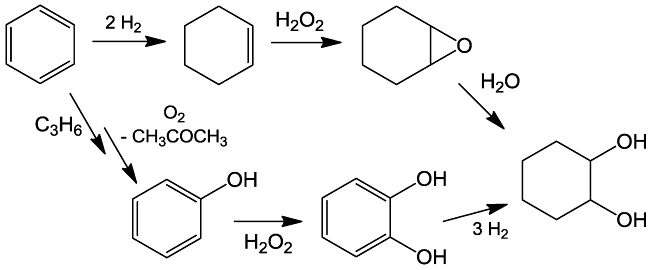
peroxide disproportionation [34–53]. Systems based either on the Venturello or the Ishii conditions, by using phase-transfer catalysis in organic solvents, involve similar oxoperoxo anions [36–41,54], which are well known as very efficient epoxidizing agents. Under typical conditions, the Venturello system gives 96% conversion with 91% selectivity (81 epoxide + 10 glycol). In the case of Keggin P/W polyoxometalates (POM), the latter are precursors of the true catalytic complexes, $[PO_4\{WO(O_2)_2\}_4]^{3-}$ and $[HPO_4\{WO(O_2)_2\}_4]^{2-}$, and/or other low nuclearity species [45,48,55,56]. Various authors have investigated the use of amphiphilic quaternary ammonium tungstophosphate in emulsion or microemulsion systems [57–61]. The same systems have also been suggested for the dihydroxylation of alkenes [28,54,58,62–65]. With regard to the mechanism of H_2O_2 activation, it is believed that the key step of activation is the heterolytic cleavage of the O—O bond, because homolytic cleavage generates free radicals in solution (Fenton-type chemistry), thus leading to undesired reactions. The formation of cyclohexene epoxide may occur via two different pathways, a direct epoxidation by H_2O_2 and an indirect epoxidation by cyclohexenyl hydroperoxide, the formation of the latter compound occurring by involvement of radicalic steps [22]. For all the systems described in literature for cyclohexene epoxidation, the catalyst features and reaction conditions affect the final selectivity into either the epoxide, diol, or allylic oxidation products, or even the products of oxidative C—C cleavage (mono or di-carboxylic acids); as a consequence, the selectivity to a specific compound is often not very high.

An alternative pathway for the synthesis of 1,2-cyclohexanediol is the selective hydrogenation of catechol: when compared to the oxidative route from cyclohexene, this process might offer the advantage of a better availability of the starting material, as compared to cyclohexene which, conversely, is currently supplied by very few companies. As an example, Asahi Chemical, which developed the process for the selective hydrogenation of benzene into cyclohexene [66], uses the olefin produced for its own transformation processes, i.e., for hydration into cyclohexanol and nitric oxidation of the alcohol into adipic acid. Existing methods for aromatic ring reduction typically require excess amounts of reagents and harsh reaction conditions because of the stabilization of the aromatic ring. Catalytic hydrogenation with transition-metal catalysts is a simple and sustainable method [67–70], especially when easily separable and recyclable catalysts – based on, i.e., Ni, Rh, Ru, Pt, and Pd – are used. However, conventional methods using heterogeneous catalysts generally require high pressures (>1 MPa) and temperatures and/or strongly acidic or basic conditions. Only a few examples of mild hydrogenation methods applicable for aromatic nuclei have been reported [71,72]; therefore, a simple multipurpose catalytic approach is highly desirable. Some of us reported the use of Ru-based catalysts for the hydrogenation of phenol into cyclohexanone [73], driven by the increasing price difference between Pd (typically used for phenol hydrogenation [74–76]) and Ru. In the case of catechol hydrogenation, systems used in the literature include Pt and Rh [77] or Ru/C catalysts [78].

For our hydrogenation experiments, we decided to use catalysts based on $Ru(OH)_x$ grafted over alumina, which in recent years was reported to be an easily recoverable heterogeneous system. It is active and selective for a variety of reactions, including catalytic hydrogen transfer for allylic alcohol reduction [79], racemization of alcohols and amines [80], oxidation of both alcohols and diols [81] and of amines [82,83] with oxygen, ammoxidation of primary alcohols to nitriles [84], synthesis of tertiary and secondary amines directly from alcohols, and urea and N-alkylation of amines with alcohols [85].

Here we report on the comparison between the two different catalytic routes for the synthesis of 1,2-cyclohexanediol: (a) the selective dihydroxylation (epoxidation + hydrolysis) of cyclohexene by means of the homogeneous tungstate/phosphoric acid catalytic system, the reaction being carried out in a biphasic system by using an aqueous solution of H_2O_2, in the presence of a phase-transfer-agent (PTA) and without any organic solvent; and (b) the direct hydrogenation of catechol, by means of the heterogeneous alumina-supported $Ru(OH)_x$ catalyst, once again by using water as the solvent. Both catechol and cyclohexene are obtained from benzene (Scheme 1), and the full sequence involves in both cases one hydrogenation and at least one oxidation. 1,2-Cyclohexanediol can be used as a starting material for the synthesis of adipic acid by means of oxidative scission [86,87].



Scheme 1. Two different reaction strategies for the synthesis of 1,2-cyclohexanediol.

2. Experimental

2.1. Catalysts preparation

The catalyst for cyclohexene dihydroxylation was prepared as follows: tungstic acid and phosphoric acid were dissolved in H_2O_2/H_2O; the hydrogen peroxide solution was prepared by adding water to a 30 wt.% H_2O_2 aqueous solution, until the desired H_2O_2 concentration (typically, 7.5 wt.%) was reached. The relative amount of each component was varied for each reactivity experiment, as described in detail in Tables 2–6; in a typical experiment, the following quantities were used (e.g., in experiment 4 in Table 2): 190 g of H_2O_2 (7.5 wt.% aqueous solution), 0.96 g H_2WO_4 99%, and 0.22 g H_3PO_4 85%.

It is worth noting that the Venturello system $[PO_4\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}_2]^{3-}$, can be prepared either ex situ by means of crystallization, as described in refs [11,57], and then added to the reaction mixture, or can form in situ, by adding the various components of the catalyst in aqueous solution directly to the reaction system, as reported in refs [35,37,38]. It should also be noted that the ratio between the reaction components, i.e., the substrate, the tungstate anion, the phosphate anion and the PTA can change in function of the reaction type. This is shown in Table 1, comparing the molar ratios between substrate and catalysts components from some literature sources. For our experiments, we decided to use conditions closer to those used for cyclohexene epoxidation, but with a lower amount of phosphate anion, with a W/P ratio close to that of the Venturello system.

Supported $Ru(OH)_x$ catalysts were prepared according to the procedure reported by Yamaguchi and Mizuno [80]. Specifically, we first dissolved $RuCl_3{\cdot}xH_2O$ (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 the catalysts (i.e. 0.126 g to obtain the 2.5 wt.% Ru on alumina); then, 2.0 g of $\gamma\text{-}Al_2O_3$ were added (precalcined at 500 °C for 3 h in static air; surface area 106 m^2/g). The system was left at room temperature, under stirring for 30 min; in 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. In these conditions, the Ru species in the solution, $[RuCl_x(OH)_y(H_2O)_{6-x-y}]^{(3-x-y)+}$, react

Table 1
Molar ratios between substrate and catalyst components used with the Venturello-type system.

Ref.	Reaction	Substrate	PTA	Na_2WO_4 or H_2WO_4	H_3PO_4
[11]	Dihydroxilation of cyclohexene to 1,2-cyclohexanediol	100	–	0.27 $[(nC_8H_{17})_3NCH_3]_3[PO_4[WO(O_2)_2]_4]$	
[35]	Epoxidation of cyclohexene	100	0.5	1.25	2.5
[37]	Oxidative scission of 1,2-cyclohexanediol to adipic acid	100	–	4	2
[57]	Oxidative scission of cyclohexene to adipic acid	100	–	1.2 $[(nC_8H_{17})_3NCH_3]_3[PO_4[WO(O_2)_2]_4]$	
[42]	Oxidative scission of cyclohexene to adipic acid	100	1	1	–
This work (best conditions)	Dihydroxilation of cyclohexene to 1,2-cyclohexanediol	100	0.25–0.75	1	0.25–0.5

with the Al—O$^-$ surface groups on alumina, to generate grafted Ru species: Al—O$^-$ Na$^+$ + $[RuCl(OH)_2] \rightarrow$ Al—O—Ru$(OH)_2$ + NaCl. Finally, the solution was filtered off, and the solid was dried at room temperature for 2 days; the catalysts were used as such for reactivity experiments, without any preliminary thermal or reactive treatment.

The analysis of the Ru content in both catalysts and in the solution showed that this method permits the quantitative deposition of the Ru species. Three $Ru(OH)_x/Al_2O_3$ samples were prepared with this procedure: Ru1.3 (1.3 wt.% Ru), Ru2.5 (2.5 wt.% Ru), and Ru3.7 (3.7 wt.% Ru). A commercial catalyst containing metallic Ru was also used for reference: the 5 wt.% Ru/Al_2O_3 catalyst was purchased from Aldrich and used as received.

2.2. Catalytic experiments: cyclohexene dihydroxylation

Reactions were carried out using a 3-neck 250 ml glass reactor, with magnetic stirring. The aqueous solution containing the catalyst and hydrogen peroxide was heated to 50 °C for 15–30 min, with stirring at 700 rpm. Then, a PTA/cyclohexene solution was prepared; the following quantities were used (e.g., in experiment 4 in Table 2): 31.7 g cyclohexene 99%, and 0.75 g PTA 98% (in most experiments, Aliquat 336); this solution was then added dropwise to the solution containing the catalyst and hydrogen peroxide (addition rate ca 5 g/min), while the stirring was raised up to 1000 rpm. The reaction temperature spontaneously started to rise in a few minutes; the heating bath was regulated to maintain the temperature at the desired level (typically, 70 °C), and the reaction was carried out for the desired reaction time (for example, 1 h). Lastly, the reaction was completed in one more hour; during this final period the released heat was negligible, and the bath temperature was the same as that of the reaction mixture, i.e. 68–70 °C. We also conducted an experiment under optimal conditions, but changing the way in which the reactants were mixed: the aqueous solution containing H_2O_2, tungstic acid and phosphoric acid was added dropwise to the cyclohexene/PTA solution, under stirring. The obtained results were similar to those achieved with the standard procedure.

When the reaction time was completed (overall reaction time 2–2.5 h), the reaction mixture was weighed, and then filtered twice (first with paper filter and then with a 0.45 μ syringe filter), to separate suspended particles or particles in emulsion of the PTA. The filtered solution was then divided into two parts: (a) one part of the aqueous phase was analyzed to determine the dissolved carboxylic acids (ionic chromatograph Dionex 2000isp, column IonPac ICE AS1e and suppressor AMMS ICE, eluent octanesolphonic acd 1 mM 2.5% in isopropanol), the remaining part was titrated with $KMnO_4$ to determine the residual H_2O_2; (b) a second part was heated under vacuum to completely eliminate water; the organic residue was weighed, dissolved in methanol, and then analyzed by means of GC (Agilent 6850 GC, equipe with PTV injector, FID detector, capillary column HP-INNOWax Polyethlene Glycol, T ramp from 50 °C to 230 °C), to determine the non-acid reaction products: 1,2-cyclohexanediol, 2-cyclohexe-1-ol, and 2-cyclohexe-1-one. In some cases, the produced 1,2-cyclohexanediol was purified to determine the effective weight yield; in this case, purification was carried out by means of recrystallization in acetone. Specifically, acetone was added to the reaction mixture after water evaporation and concentration (acetone/organic residue 2.5/1 vol ratio), heated until complete dissolution, and then cooled under mild stirring to foster recrystallization. The solid was then separated, washed twice with cold acetone, dried, and then weighed.

2.3. Catalytic experiments: catechol hydrogenation

The hydrogenation reactions were carried out in a 300 ml mechanically stirred Parr 4560 autoclave equipped with a P.I.D. 4843 controller. In a typical procedure, the proper amount of the chosen Ru-based catalyst was introduced into the autoclave under inert atmosphere. Then the autoclave was closed, evacuated up to 0.5 mm Hg, and a solution containing the substrate (0.6 g of catechol) in 50 ml of water was introduced by suction, followed by pressurization with hydrogen to 0.2 MPa. Afterwards, the reactor was heated up to the chosen temperature and, once it was reached, the autoclave was pressurized with hydrogen to the desired pressure, under stirring. The pressure value was held constant at the chosen value manually by repeated hydrogen feeds. The course of the reaction was monitored both by periodically sampling the liquid from a sampling valve and by analyzing it through gas chromatography and GC–MS. When the reaction was completed, the autoclave was rapidly cooled, the gas was discharged, and the liquid mixture was immediately analyzed after dilution with acetone. Recycling experiments of the solid catalyst were carried out in a similar manner, but after removing the liquid reaction mixture through the sample valve, the autoclave containing the solid catalysts was evacuated and again charged with the fresh catechol

Table 2
Reaction conditions and results of experiments of cyclohexene dihydroxylation into *trans*-1,2-cyclohexanediol: effect of the PTA and phosphoric acid concentration.

Exper.	Molar ratio of reactants with respect to H_2WO_4					Reaction	Y CHD	Y DA	Y others	Conv.	Residual
N	H_2WO_4	H_3PO_4	PTA	CH	HP	Time, h	mol%	mol%	mol%	CH, %	HP, %
1	1	0.5	0	100.4	111.5	3.4	n.d.	0.7	n.d.	7.6	97.8
2	1	0.5	0.25	100.3	110.2	2.6	90.3	0.6	9.1	100	3.5
3	1	0.5	0.32	99.5	110.6	2.7	96	0.6	3.4	100	0.9
4	1	0.5	0.5	100.5	110.1	2.7	97.2	0.4	2.4	100	0.4
5	1	0	0.48	100.4	112.6	3.3	78.1	1.9	2.9	82.9	4.9
24	1	0.27	0.74	100.0	113.1	3.0	97.4	0.2	2.4	100	0.2

PTA, phase-transfer-agent; Y, yield; CH, cyclohexene; HP, H_2O_2; CHD, *trans*-1,2-cyclohexanediol; DA: dicarboxylic acids. Temperature 70 °C; HP concentration 7.5 wt%.

solution for a subsequent catalytic cycle. Catechol, *trans* and *cis*-1,2-cyclohexanediol were purchased from Sigma Aldrich and used as received. 2-Hydroxycyclohexanone was not commercially available and was synthesized by oxidation of 1,2-cyclohexanediol with $NaBrO_3/NaHSO_3$ as previously reported [88].

GC analyses of reactant and products were carried out with a HP 5890 gas chromatograph equipped with a HP 3396 integrator, a flame ionization detector, and a PONA capillary column (50 m × 0.25 mm × 0.25 μm) with a 100% dimethylpolysiloxane stationary phase (carrier gas nitrogen, flow 1 mL/min). The reproducibility of repeated catalytic runs was within 5%. GC–MS analyses were carried out using the instrument Hewlett-Packard HP 6890 with one MSD HP 5973 detector with a Phenomenex Zebron G.C. column characterized by a stationary phase of 100% dimethylpolysiloxane (length of the column: 30 m, inner diameter: 0.25 mm, and thickness of the stationary phase: 0.25 μm). The transport gas was helium 5.5 and the flow rate was 1 ml/min.

2.4. Catalysts characterization

$Ru(OH)_x/Al_2O_3$ catalysts were characterized by means of XPS, surface area measurements (BET) and Raman spectroscopy. X-ray photoelectron spectroscopy (XPS) measurements were performed on a SPECS spectrometer with a 150 MCD-9 detector and using a non monochromatic AlKα (1486.6 eV) X-ray source. Spectra were recorded using analyzer pass energy of 30 V, an X-ray power of 200 W, and under an operating pressure of 10^{-10} MPa. Only the Ru3p peak was used for the evaluation of the Ru oxidation states since the more intense Ru3d peak is completely masked by the C1s peak of contaminating carbon. Spectra treatment was performed using the CASA software. Binding energies (BE) were referenced to Al2p at 74.5 eV. Laser Raman spectra were recorded using a Renishaw 1000 spectrometer, with laser source Argon ion (514 nm), equipped with a Leica DMLM microscope.

3. Results and discussion

3.1. The direct hydroxylation of cyclohexene into 1,2-cyclohexanediol

The performance of most homogeneous epoxidation systems is greatly enhanced by adding molecules that coordinate to some component in the reaction mixture; these additives may consist of tertiary heterocyclic amines (i.e. pyridines, pyrazoles, and imidazoles) or carboxylates (i.e. acetates, benzoates, or glyoxylates); for tungsten-based epoxidations, an optimal additive for tungstic acid is phosphate anion [11,34,35,37,57]. We investigated the reactivity behavior of cylohexene by using H_2WO_4 as the active component, in the presence of phosphoric acid as co-catalyst and Aliquat 336 as the PTA.

We first investigated the role of both the PTA and phosphoric acid. Results are summarized in Table 2, reporting the effect of the molar ratio between the PTA and cyclohexene, while keeping the concentration of all other reactants constant; experiment 5 was carried out with the optimal amount of PTA, but in the absence of phosphoric acid. It is shown that in the absence of either PTA (experiment 1) or phosphoric acid (experiment 5), the cyclohexene conversion was lower than in the presence of both components, even though the effect of PTA was much greater than that shown by phosphoric acid. With an equimolar amount of PTA and phosphoric acid, it was possible to obtain a 97.2% yield to *trans*-1,2-cyclohexanediol, with a very low amount of unconverted H_2O_2, which was used in 10% molar excess only with respect to the stoichiometric requirement for cyclohexene dihydroxylation. By-products mainly consisted of acidic compounds of 1,2-cyclohexanediol overoxidation, such as 6-hydroxyhexanoic and 6-oxohexanoic acids (overall yield 2.4%) and dicarboxylic acids (overall yield 0.4%). We also carried out an experiment by using a phosphate/tungstate ratio close to ¼, which corresponds to the stoichiometry of the Venturello system (experiment 24 in Table 2); with an amount of PTA even greater than that used in experiment 4, we could achieve 97.4% yield to 1,2-cyclohexanediol, thanks to the slightly decreased formation of dicarboxylic acids. Worth of note, under the conditions shown in Table 1, Venturello and Gambaro [11] obtained the best yield of 87% in cyclohexene dihydroxylation to *trans*-1,2-cyclohexanediol, at 70 °C, in a two-phase mixture of acidified (pH 1.5) aqueous hydrogen peroxide and a benzene solution of the alkene, containing the catalyst.

Decreasing the PTA concentration led to a progressively lower yield to 1,2-cyclohexanediol, and a greater yield to monocarboxylic acid by-products; in the absence of PTA, the reaction did not progress (experiment no. 1). Therefore, the role of the PTA was not only that of bringing the activated form of the tungstate catalyst from the aqueous H_2O_2 layer to the organic cyclohexene layer, where cyclohexene epoxide was formed – which is the well-known role of a PTA in this phase-transfer catalysis – but also that of limiting the consecutive oxidation of 1,2-cyclohexanediol, by keeping it in the organic layer, as long as some unconverted cyclohexene remained. Finally, at total cyclohexene conversion, a single phase was obtained, but H_2O_2 was also completely converted; in these conditions, the 1,2-cyclohexanediol produced was stable because H_2O_2 was no longer available. The protecting effect of the PTA on 1,2-cyclohexanediol was probably effective only as long as a biphasic system was present; in fact, experiments carried out starting from 1,2-cyclohexanediol (see below) have shown that in a monophasic aqueous system the reactivity of the diol with regard to consecutive oxidation reactions was similar both in the presence and in the absence of the PTA component (Table 5, see below). This behavior was also observed at 90 °C, in the presence of an excess H_2O_2. On the other hand, the hydrolysis/ring opening of cyclohexene epoxide may occur at the interface between the organic layer and the water layer.

We expected the phosphoric acid to have also the role of accelerating the hydrolysis of cyclohexene epoxide, but this was not observed. Indeed, the acid apparently had the role of accelerating the cyclohexene and H_2O_2 conversion, but it did not show an important effect on selectivity. Therefore, the acidity of the aqueous phase (containing the tungstic acid) was sufficient to foster the oxirane ring opening.

The peculiarity of the reaction described is that a very high selectivity to 1,2-cyclohexanediol was obtained using only 1.1 mole H_2O_2 per mole of cyclohexene, with minimal or nil formation of both cyclohexene epoxide and acid by-products. This is an excellent result, especially if we consider that low H_2O_2/alkene ratios are typically used in cyclohexene epoxidation; in this way, high selectivity to cyclohexene epoxide + 1,2-cyclohexanediol with respect to both cyclohexene and H_2O_2 is obtained, but the conversion of cyclohexene is low [89,90]. On the other hand, in the oxidation of cyclohexene with stoichiometric H_2O_2, such a high selectivity to 1,2-cyclohexanediol in the reaction catalyzed by tungstate-based catalysts has never been reported up to now [33]. In general, with tungstate-based systems the catalyst acidity may lead to oxirane ring opening [27]. However, considerably different results are reported in the literature, depending on the reaction conditions used; for example, with Ti-containing W-based polyoxometalates, cyclohexene yielded cyclohexene epoxide with up to 98% selectivity and 84% conversion (or even 100% selectivity at 50% conversion) when 1 eq of H_2O_2 was used, but was oxidized up to adipic acid by using 4 equivalents of H_2O_2, working at 50–70 °C. In this case, the mechanism included the hydrolysis of cyclohexene epoxide to glycol, the oxidation of the latter into the 2-hydroxyketone, the

Table 3
Reaction conditions and results of experiments of cyclohexene dihydroxylation into *trans*-1,2-cyclohexanediol: effect of the H_2O_2 concentration.

Exper.	Molar ratio of reactants with respect to H_2WO_4					Reaction	HP	Y CHD	Y DA	Y others	Conv.	Residual
N	H_2WO_4	H_3PO_4	PTA	CH	HP	Time, h	wt.%	mol%	mol%	mol%	CH, %	HP, %
4	1	0.5	0.5	100.5	110.1	2.7	7.5	97.2	0.4	2.4	100	0.4
6	1	0.5	0.5	100.1	110.3	2.5	15.2	96.3	0.4	2.9	100	1.2
7	1	0.5	0.5	100.3	110.6	2.6	19.9	94.5	0.5	5.0	100	2.7
8	1	0.5	0.5	100.9	218.8	2.8	7.7	94.9	1	4.1	100	38.8
9	1	0.5	0.5	99.8	327.2	2.7	7.8	92.7	1.5	5.8	100	61.7
10	1	0.5	0.5	100.7	220.9	2.8	15.1	86.6	2.8	19.6	100	32.5
11	1	0.5	0.5	100.5	329.2	2.7	20	83.1	7	9.9	100	54.5

PTA, phase-transfer-agent; Y, Yield; CH, cyclohexene; HP, H_2O_2; CHD, *trans*-1,2-cyclohexanediol; DA, dicarboxylic acids. Temperature 70 °C.

Table 4
Experiments carried out by reacting cyclohexene epoxide.

Exper.	Molar ratio of reactants with respect to H_2WO_4					HP	Y CHD	Y DA	Y others	Conv.	Residual
N	H_2WO_4	H_3PO_4	PTA	CEP	HP	wt.%	mol%	mol%	mol%	CEP,%	HP, %
12	1	0.6	0.5	107	109.6	7.7	82.4	10.9	6.5	99.8	79.7
13	1	0	0.5	100.1	111.9	7.6	84.6	9.0	6.4	100	68.3
14	1	0.5	0	99.9	111.2	7.5	80.2	12.3	7.5	100	65.6

PTA, phase-transfer-agent; Y, yield; CEP, cyclohexene epoxide; HP, H_2O_2; CHD, *trans*-1,2-cyclohexanediol; DA, dicarboxylic acids. Temperature 70 °C; reaction time 3 h.

formation of adipic anhydride, and final hydrolysis into adipic acid [28,91].

The low selectivity to dicarboxylic acids experimentally observed in our case is attributable to both the low reaction temperature (70 °C) and the stoichiometric amount of H_2O_2 used; under our conditions, the consecutive reactions leading to the oxidation of 1,2-cyclohexanediol into adipic acid are kinetically unfavored. With regard to this point, we carried out experiments using different H_2O_2 concentrations and molar ratios between H_2O_2 and cyclohexene. Table 3 summarizes the results obtained. It is shown that an increase in H_2O_2 concentration had a moderate effect on 1,2-cyclohexanediol yield (with only a minor increase in the selectivity to by-products). The same minor effect was shown when a large excess of H_2O_2 with respect to the stoichiometric requirement was used; indeed, most of the H_2O_2 remained unconverted, an indication that, at the used reaction conditions, any consecutive oxidation upon 1,2-cyclohexanediol was kinetically unfavored. A more significant effect was observed when both a large H_2O_2 excess and a higher H_2O_2 concentration were used (experiments 10 and 11).

It was not possible to study the effect of temperature, because at 75 °C the mixture started refluxing; only once the organic phase containing cyclohexene had disappeared, could the temperature be raised up to 90 °C. As expected, the final result was similar to that obtained in the experiment carried out at 70 °C: 1,2-cyclohexanediol yield 96.9%, unconverted H_2O_2 0.48%, dicarboxylic acids yield 0.36%.

Some experiments were carried out by reacting cyclohexene oxide aimed at observing the effect of PTA and phosphoric acid on epoxide hydrolysis into 1,2-cyclohexanediol (Table 4). The achieved results demonstrate that the hydrolysis of cyclohexene epoxide is very fast at the conditions used (the epoxide turned out to be much more reactive than cyclohexene), and that the 1,2-cyclohexanediol produced is stable; in fact, the majority of the added H_2O_2 was found to be unconverted at the end of the experiment. With regard to the role of the PTA and phosphoric acid, the two compounds showed only a minor effect, with minimal variations in conversion and selectivity in the experiments carried out either without phosphoric acid (entry 13) or without the PTA (entry 14), as compared to the experiment carried out with both components (entry 12). With regard to the nature of the dicarboxylic acids formed, adipic acid was again the prevailing one, but with a significant amount of glutaric acid (for instance, in experiment 12: 7.0% adipic acid, 3.9% glutaric acid, traces of succinic acid).

These results indicate that 1,2-cyclohexanediol is stable under the conditions used, and does not undergo consecutive oxidative cleavage; the relatively low reaction temperature is likely to be the major factor contributing to high selectivity. In order to further confirm this hypothesis, we carried out experiments by reacting *trans*-1,2-cyclohexanediol; the results are summarized in Table 5. It is shown that:

(a) The reactivity of 1,2-cyclohexanediol was much lower than that of the olefin; products obtained were both 2-hydroxycyclohexanone and monocarboxylic acids (lumped into “Others” in the table) and dicarboxylic acids. These “Others” were in lower amount after reaction at 90 °C, being intermediates in the transformation of the diol into adipic acid.
(b) The PTA had negligible effects on 1,2-cyclohexanediol conversion (experiments 15 and 16 for tests at 70 °C; experiments 20 and 21 at 90 °C).

Table 5
Experiments carried out by reacting *trans*-1,2-cyclohexanediol.

Exper.	Molar ratios of reactants with respect to H_2WO_4					*T*, °C	Reaction	HP	Y DA	Y others	Conv.	Residual
N	H_2WO_4	H_3PO_4	PTA	CHD	HP		Time, h	wt.%	mol%	mol%	CHD, %	HP, %
15	1	0.5	0.5	101.1	111.1	70	3.2	7.6	6.4	16.7	23.1	17.5
16	1	0.5	0	100.8	111.5	70	3.1	7.6	3.5	16	19.5	14.1
17	1	0.5	0.5	101.4	333.6	70	2.9	7.6	2.8	14.4	17.2	79.5
18	1	0.5	0.5	99.7	337	70	3	31.1	14	12.4	26.4	37.7
19	1	0.5	0.5	99.9	332.1	90	3.1	31.1	91.8	5.6	97.4	1.5
20	1	0.5	0.5	100.5	333.7	90	6	31.1	93.3	4.1	97.4	0.05
21	1	0.5	0	100.5	333.8	90	6.2	31.1	93.9	4.2	98.1	0.03

PTA, phase-transfer-agent; Y, yield; HP, H_2O_2; CHD, *trans*-1,2-cyclohexanediol; DA, dicarboxylic acids.

Table 6
Experiments of cyclohexene oxidation carried out under selected conditions, in order to replicate tests reported in literature.

Exper.	Molar ratio of reactants with respect to WO_4^{2-}						T, °C	Reaction	HP	Y CEP	Y CHD	Y DA	Y others	Conv.	Resid.
N	Catalyst	H_3PO_4	PTA	CH	HP	Solvent		Time, h	wt.%	mol%	mol%	mol%	mol%	CH, %	HP, %
24	1 (H_2WO_4)	0.27	0.74[a]	100.0	113.1	–	70	3.0	7.6	0	97.4	0.2	2.4	100	0.2
22	1 (Na_2WO_4)	2.01	0.38[a]	184.5	60.5[d]	CH_3Cl[c]	70	1	7.9	23.1	6.5	0.4	5.2	35.1	2.8
23	1 (Na_2WO_4)	0.51	0.49[b]	50.8	75.2	–	74–79	4	30	0.2	46.2	15.7	7.5	69.6	2.7

PTA, phase-transfer-agent; Y, Yield; CH, cyclohexene; HP, H_2O_2; CHD, *trans*-1,2-cyclohexanediol; DA, dicarboxylic acids; CEP, cyclohexene epoxide.

[a] Aliquat 336.

[b] Methyltrioctylammonium hydrogensulfate.

[c] Solvent/cyclohexene weight ratio 0.6/1.

[d] The pH of the H_2O_2/H_2O solution has been adjusted to 3.2 with NaOH.

(c) At 70 °C, the adoption of a H_2O_2/1,2-cyclohexanediol molar ratio close to 3 had no important effect on conversion (compare experiment 15 with 17); however, when the greater H_2O_2 amount was used in more concentrated conditions (experiment 18), the highest 1,2-cyclohexanediol conversion (26.4%) with 14% yield to dicarboxylic acids was obtained.

(d) At 90 °C and H_2O_2/1,2-cyclohexanediol molar ratio 3, with H_2O_2 concentration 31% (that is, under conditions closer to those reported in literature for the one-step oxidative cleavage of cyclohexene into adipic acid), almost complete diol conversion was achieved with very high yield to dicarboxylic acids in 3 h reaction time (experiment 19); in these conditions, the PTA had no role (experiments 20 and 21).

(e) The prevalent dicarboxylic acid was, in all cases, adipic acid; for example, in experiment 21 the following distribution was observed: yield to adipic acid 92.1%, glutaric acid 1.6%, succinic acid 0.2%.

In conclusion, it is evident that temperature is the main factor responsible for the absence of further transformation of 1,2-cyclohexanediol into dicarboxylic acids when cyclohexene reacts with H_2O_2, even with a large excess of the latter. Furthermore, the PTA had no role in the two consecutive steps of cyclohexene epoxide hydrolysis into 1,2-cyclohexanediol and of 1,2-cyclohexanediol oxidation into dicarboxylic acids (in this step also, phosphoric acid played no role). Due to the fact that the two compounds both show a non-negligible effect on the rate and selectivity of cyclohexene transformation into 1,2-cyclohexanediol, we may conclude that the promotional effect of these components (especially of the PTA) is mainly on the first step of cyclohexene oxidation into cyclohexene epoxide.

Final experiments were carried out under reaction conditions similar to those reported by Venturello (experiment 22) [35], and those described in Noyori's papers (experiment 23) [92], both designed to obtain high yield to cyclohexene epoxide. Results are summarized in Table 6 and compared with the best ones obtained in our reaction conditions (experiment 24). It is shown that by using conditions similar to those reported by Venturello, the extent of cyclohexene epoxide hydrolysis was much lower than under our conditions; differences between the two procedures concerned the presence of a solvent, the type of catalyst and of PTA used, and the relative amount of the components. With regard to the Noyori's conditions, we could not exactly replicate those reported in the literature. We used phosphoric acid instead of aminomethylphosphonic acid, and were unable to raise the temperature above 79 °C (the reflux T of the mixture). In this case, under our conditions, the absence of the solvent led to the hydrolysis of the epoxide (cyclohexene epoxide formed with a very low yield); however, because of the excess H_2O_2 and the high temperature used, the yield to dicarboxylic acids (mainly adipic acid) was higher than that obtained using our standard conditions.

Table 7
Hydrogenation of catechol to 1,2-cyclohexanediol in the presence of sample Ru2.5.

T, °C	P H_2, MPa	Time, h	Catechol conv., %	Sel. to CHD, mol%[a]
90	5	8	99.6	90.2
190	5	0.5	100	87
90	3	5	35.9	78

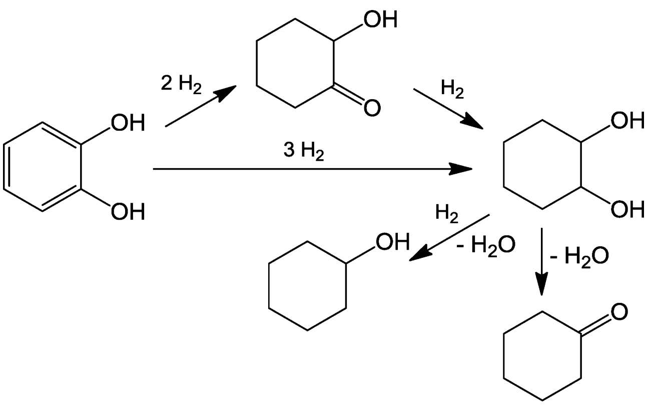
Reactions conditions: H_2O 50 ml, catechol 0.6 g, Ru: 5.1 mg.
CHD, 1,2-cyclohexanediol.

[a] The by-products were cyclohexanol, cyclohexanone, and traces of phenol.

4. The hydrogenation of catechol into 1,2-cyclohexanediol in aqueous medium

Catechol hydrogenation was first studied using a Ru2.5 catalyst; under the conditions used, the alumina-supported $Ru(OH)_x$ produced almost total catechol conversion after 8 h reaction time (Table 7). The main reaction was the selective hydrogenation of catechol to 1,2-cyclohexanediol (a mixture of *cis* and *trans* isomers), with 90% selectivity; the other by-products were the consecutive hydrogenolysis or dehydration compounds, cyclohexanol and cyclohexanone, respectively, with only traces of phenol (Scheme 2). No formation of the partially hydrogenated product, 2-hydroxycyclohexanone, occurred. When the reaction was carried out at 190 °C, total catechol conversion was achieved already after 0.5 h, but 1,2-cyclohexanediol selectivity was 87%, with 13% selectivity to hydrogenolysis compounds. Conversely, when the reaction was carried out at 3 MPa H_2 pressure and 90 °C, as expected, catechol conversion was 36% only after a 5 h reaction. On the basis of these results, further investigation was carried out at 90 °C, but using the higher pressure of 5 MPa of hydrogen.

With the aim of better understanding the suitability of $Ru(OH)_x/Al_2O_3$ catalysts in catechol hydrogenation, samples at different Ru loadings were prepared and tested (see Section 2). Hydrogenation tests were carried out at 90 °C under 5 MPa of H_2, keeping the catechol/Ru initial molar ratio constant at



Scheme 2. Products obtained in catechol hydrogenation.

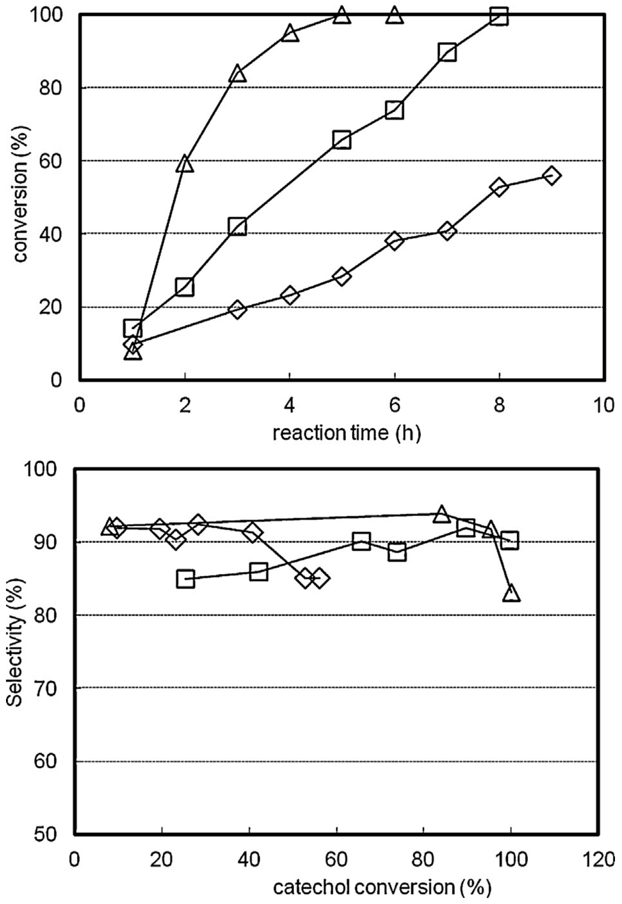


Fig. 1. Catechol conversion (%) based on reaction time (top) and selectivity to 1,2-cyclohexanediol (%) based on catechol conversion (bottom) with $Ru(OH)_x/Al_2O_3$ catalysts: sample Ru2.5 (□), sample Ru1.3 (◊) and sample Ru3.7 (△). Reactions conditions: 90 °C, 5 MPa of H_2, H_2O: 50 ml, catechol 0.6 g, Ru: 5.1 mg.

1.1×10^{-2} mol/mol; Fig. 1 shows the results. It can be seen that, despite the similar overall Ru content used for the experiments, sample Ru1.3 (containing the lower Ru content) was the least active catalyst, whereas the sample showing the highest activity was that containing the higher amount of Ru (sample Ru3.7), with an intermediate behavior shown by sample Ru2.5. With regard to 1,2-cyclohexanediol selectivity, samples Ru1.3 and Ru3.7 both showed a drop in selectivity to 1,2-cyclohexanediol depending on the catechol conversion; with sample Ru1.3, the decline in selectivity started already for catechol conversion higher than 40%, whereas with sample Ru3.7 the selectivity declined above 80% catechol conversion. The progressive decrease in selectivity with hydrogenation advancement was due to the undesired hydrogenolysis reaction, which increased with the longer reaction times. However, in the case of sample Ru2.5, which contained an intermediate amount of Ru loading, a slight increase in 1,2-cyclohexanediol selectivity was observed in the 20–60% catechol conversion interval, after which the selectivity was almost stable at 90% until total catechol conversion.

The differences in catalytic behavior experimentally observed were quite unexpected, especially with regard to the catalyst activity; in fact, we expected that in the sample containing the lowest Ru content (sample Ru1.3) a better dispersion of the active species over alumina would have led to a better intrinsic activity (referred to the amount of Ru). For the same reason, in the sample containing the highest Ru content (sample Ru3.7), we expected that the formation of either $Ru(OH)_x$ aggregates or oligomeric species over the support would lead to a lower availability for the Ru species in this catalyst. The obtained results were just the opposite of what we expected; the characterization of used samples will help clarify this point (see below).

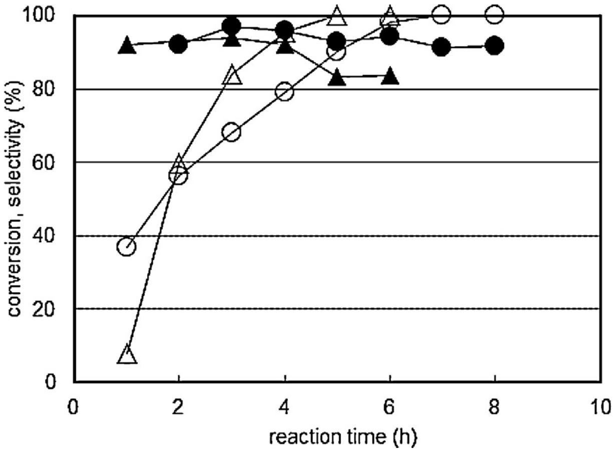


Fig. 2. Catechol conversion (%) (open symbols) and selectivity to 1,2-cyclohexanediol (full symbols) based on the reaction time. Catalyst: fresh sample Ru3.7 (△▲), and sample Ru3.7 recovered and reused without any regeneration treatment (○●). Reaction conditions: T 90 °C, 5 MPa H_2, H_2O: 50 ml, catechol 1.2 g, Ru: 10.0 mg.

On the basis of these encouraging results, sample Ru3.7 was recovered by filtration after use and reused without any regeneration procedure, by adding a fresh substrate: the results achieved are compared with those obtained with the fresh catalyst in Fig. 2. It can be seen that the recovered catalyst not only maintained a good efficiency, but also showed a higher activity than the fresh one at the beginning of the recycle test. However, the increase of conversion over time was slower than that observed with the fresh sample. Some differences were also observed with regard to the selectivity to 1,2-cyclohexanediol; in fact, the reused catalyst showed a better 1,2-cyclohexanediol selectivity, and also did not show any decline for longer reaction times, as was the case for the fresh sample. Overall, these results highlight some changes in the active phase features which had likely occurred during the first experiment (on the fresh catalyst), changes which were responsible in the end for the modified catalytic behavior shown by the reused catalyst.

We also carried out the reaction using the reaction mixture, after filtering off the catalyst; this experiment was carried out by stopping the reaction after 2 h (catechol conversion being close to 60% at that time), by carrying out the “hot filtration” of the reaction mixture, by adding fresh reactant and starting again the reaction at the same conditions previously used with the fresh catalyst. No reaction took place in the absence of catalyst, thus allowing us to rule out the presence of any active species leached from the catalyst to the liquid phase.

Lastly, an experiment was carried out using sample Ru2.5, with a very high initial catechol/Ru molar ratio (catechol/Ru: 3.65×10^3 mol/mol), with the aim of achieving moderate catechol conversion and thus identifying possible reaction intermediates; results are shown in Fig. 3. Actually, in this experiment, it was possible to identify by GC/MS the intermediate 2-hydroxycyclohexanone by comparison with the pure substance; in fact, due to the very high catechol/Ru molar ratio, the reaction progressed more slowly, and consequently the intermediate 2-hydroxycyclohexanone desorbed from the catalyst surface and dissolved into the liquid phase, thus being identified in the reaction mixture. In literature it is reported that this two-step reaction pathway is unfavorable for Ru, while the amount of intermediate 2-hydroxycyclohexanone is scarce, even at the beginning of the catalytic run [93]. Huang et al. reported that the reaction pathway,

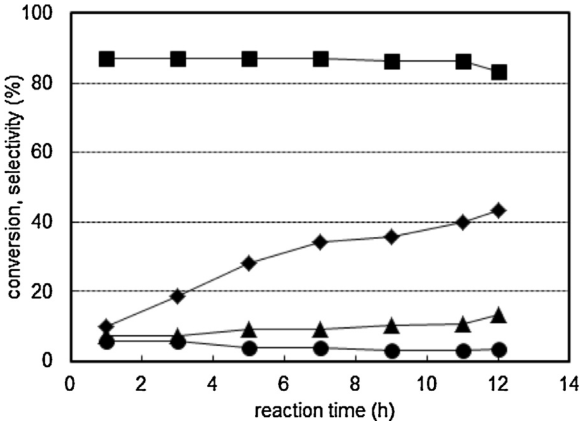


Fig. 3. Hydrogenation of catechol to 1,2-cyclohexanediol in the presence of sample Ru2.5. Reactions conditions: 90 °C, 5 MPa of H_2 H_2O: 50 ml, catechol 15.0 g, Ru: 3.8 mg. Conversion of catechol (♦), selectivity to 1,2-cyclohexanediol (■), to 2-hydroxycyclohexanone (●) and to cyclohexanol + cyclohexanone (▲).

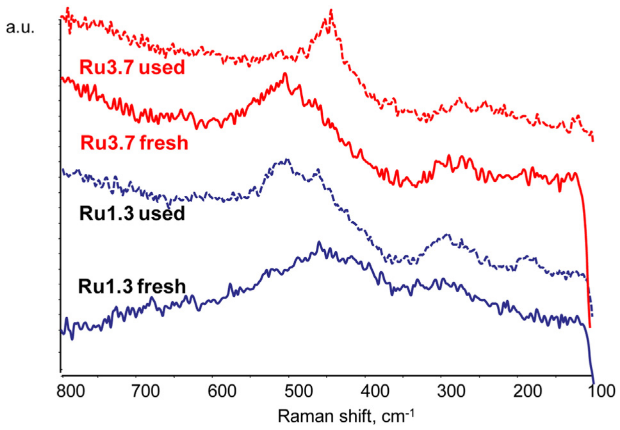


Fig. 4. Raman spectra of Ru1.3 and Ru3.7, both fresh and after use in hydrogenation of catechol to 1,2-cyclohexanediol.

either consecutive or direct hydrogenation, is influenced by the strength of oxygen affinity with the catalyst [93]. In the case of weak oxygen affinity catalysts, such as Pt and Pd, the intermediate 2-hydroxycyclohexanone can more easily desorb and dissolve in the liquid phase, and thus the consecutive hydrogenation mechanism takes place. Conversely, in the case of strong oxygen affinity catalysts, such as with Ru and Rh, the desorption of the intermediate is more difficult, and the contribution of the direct hydrogenation mechanism prevails over the two-step one.

5. Characterization of $Ru(OH)_x/Al_2O_3$ catalysts after use

For samples recovered after reaction, the XPS results referred to the $Ru3p_{3/2}$ peak are summarized in Table 8. Attribution of the Ru BE to different oxidation states is quite controversial in literature [80,94–96]. In general, it is recognized that on increasing the Ru oxidation state, the BE value shifts from around 458 eV (for metallic Ru), to around 466 eV for Ru^{6+}. In our case, for all the samples a single broad band was centered at around 462.5 eV, which seems to suggest the presence of Ru^{3+} as the main species. However, a shoulder centered at ca 458.5 eV, attributable to Ru^0, was present in the sample at higher Ru loading (Ru3.7), and this could suggest that for this sample Ru^{3+} is partially reduced during the reaction; by means of peak deconvolution, the relative amount of the metallic Ru was estimated to be around 10 ± 3% of the Ru content. The contribution of this lower BE peak was instead negligible for Ru1.3 and Ru2.5. This might explain the highest activity experimentally observed for sample Ru3.7, and also the change of catalytic behavior shown by the recycled catalyst. The formation of metallic Ru in sample Ru3.7 may be due to the presence of Ru species which develop a weaker interaction with the support, and are more easily reducible from Ru^{3+} to Ru^0. Conversely, in samples Ru2.5, and especially in sample Ru1.3, the higher dispersion of Ru^{3+} species led to a stronger interaction with the alumina support, which makes them less reducible and, in the end, less intrinsically active in catechol hydrogenation.

Catalysts were also characterized by means of Raman spectroscopy; spectra of both fresh and used Ru1.3 and Ru3.7 samples are shown in Fig. 4. The Ru^{3+} species which strongly interacts with La_2O_3 is reported to show a broad band centered at around 670 cm^{-1} [97]; in our samples, such a band was not observed (nor was it seen in fresh samples either). On the other hand, bands observed in both Ru1.3 and Ru3.7, not corresponding to any typical vibration observed in Ru oxides (i.e., RuO_2, RuO_3 or RuO_4) [98], can be attributed to Ru^{3+} species chemically interacting with the support. Indeed, in literature, a band at 470 cm^{-1} (also visible in spectra shown in Fig. 4) is attributed to hydrated RuO_2 (together with the band at 670 cm^{-1} which, however, is not observed in our case) [99], whereas the band at 510 cm^{-1} is close to that reported for crystalline RuO_2 dispersed over zirconia support [100]; typically of RuO_2, however, other bands should also be seen at 640 and 705 cm^{-1}, which instead are not present.

Table 8
XPS results of samples Ru1.3, Ru2.5 and Ru3.7 after use in hydrogenation of catechol to 1,2-cyclohexanediol at 90 °C, 5 MPa of H_2.

Sample	$Ru3p_{3/2}$ (BE 462.5 eV), %	$Ru3p_{3/2}$ (BE 458.5 eV), %
Ru1.3	100	0
Ru2.5	100	0
Ru3.7	90 ± 3	10 ± 3

The relative intensity of the two main bands observed in fresh samples, at around 460 and 510 cm^{-1}, was a function of the Ru loading. In sample Ru3.7, the latter was more intense than the former band, whereas the opposite was true in sample Ru1.3; therefore, based on these observations and by analogy with similar bands reported in literature, we can tentatively attribute the lower wavenumber band to an isolated Ru^{3+} species which is chemically grafted to the support, while attributing the band at around 510 cm^{-1} to a less dispersed, oligomeric Ru^{3+} species. It is interesting to note that the Raman spectrum of sample Ru3.7 showed the most significant changes after reaction, compared with the spectrum before reaction; more specifically, the band at 510 cm^{-1} almost disappeared in the spectrum of the used sample. The same relevant change was not observed in sample Ru1.3. These results can be attributed to the fact that mainly the oligomeric Ru^{3+} species, especially present in the Ru3.7 sample, underwent reduction down to the metallic state during contact with hydrogen in catechol hydrogenation. This evidence agrees with the development of a more active metallic Ru species during reaction in the presence of Ru3.7 catalyst.

Because of the suggested important role of the in situ-generated metallic Ru, we compared the reactivity of the Ru2.5 catalyst with that of a commercial catalyst having 5 wt.% Ru/Al_2O_3, with Ru in the metallic form. This catalyst was characterized in a previous work [73]; it shows an average Ru particle size of 4.9 ± 2.3 nm, greater than that shown by $Ru(OH)_x$ nanoparticles in fresh catalysts prepared in the lab [101]. Results are reported in Fig. 5, which shows catechol conversion and selectivity to 1,2-cyclohexanediol depending on reaction time. In the two experiments, the same catechol/Ru ratio was used (1.08×10^2 mol/mol, with 5.1 mg Ru), working at 90 °C under 5 MPa of hydrogen. In both cases, by-products were cyclohexanol and cyclohexanone, with only traces of phenol. It is

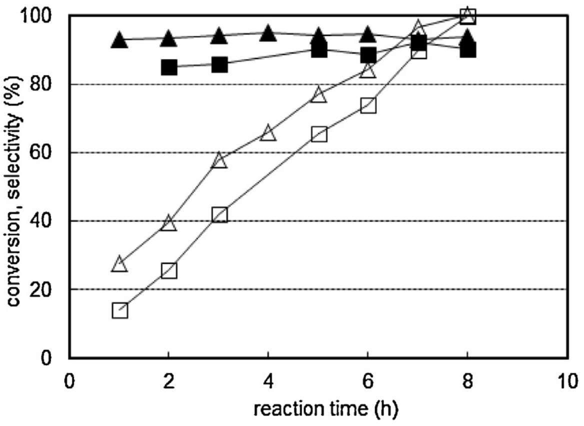


Fig. 5. Conversion of catechol (open symbols) and selectivity to 1,2-cyclohexanediol (full symbols) in the presence of sample Ru2.5 (□■), and a commercial 5 wt.% Ru/Al_2O_3 catalyst (△▲). Reactions conditions: 90 °C, 5 MPa of H_2, H_2O: 50 ml, catechol 0.6 g, Ru: 5.1 mg.

shown that despite the low fraction of metallic Ru present in the spent Ru2.5 catalyst, differences in activity between the two samples were small. The TON, calculated with respect to the overall Ru loading (catechol conversion after 2 h reaction time was taken), is shown to be lower for sample Ru2.5 than for the commercial sample [0.0080 $mol_{catechol}/(g_{Ru}\ h)$ for sample Ru2.5, vs 0.0144 for the commercial sample]. However, if we consider that the amount of metallic Ru in the spent Ru2.5 sample was no more than 10 ± 3% of the overall Ru loading, the TON calculated with respect to the metallic Ru species was by far greater with Ru2.5 than with the commercial sample. It can be speculated that the significant activity of the alumina-supported $Ru(OH)_x$ catalysts was due either to some synergic interaction between the different Ru^{n+} species, which led to an enhanced activity of metallic Ru, or to a direct participation of the oxidized Ru^{3+} species. The latter hypothesis is more likely, due to the activity shown by Ru1.3 and Ru2.5 catalysts, which showed no metallic Ru species in used samples.

Finally, we compared Ru2.5 and the commercial Ru/Al_2O_3 catalysts, using a greater concentration of the substrate (2.5 g instead of 0.6 g), and a greater amount of catalyst (20.5 mg Ru instead of 5.1 mg). The results are shown in Fig. 6; for both catalysts, we observed a lower conversion rate compared to the more diluted conditions (Fig. 5), whereas the selectivity to 1,2-cyclohexanediol remained unchanged.

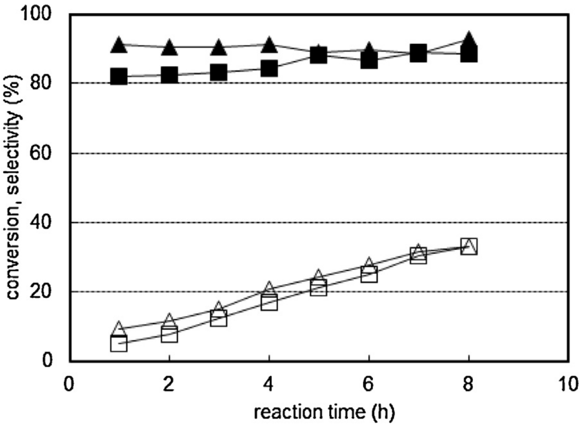


Fig. 6. Conversion of catechol (open symbols) and selectivity to 1,2-cyclohexanediol (full symbols) in the presence of sample Ru2.5 (□■), and a commercial 5 wt.% Ru/Al_2O_3 catalyst (△▲). Reactions conditions: 90 °C, 5 MPa of H_2, H_2O: 50 ml, catechol 2.5 g, Ru: 20.5 mg.

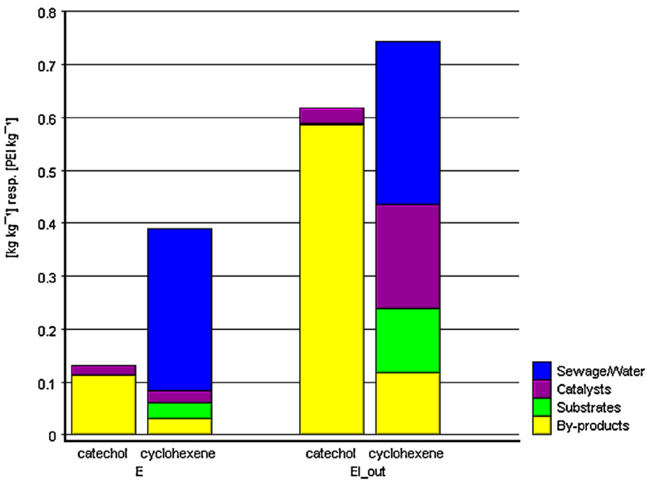


Fig. 7. Comparsion of E and EI factors for the processes of 1,2-cyclohexanediol synthesis by means of catechol hydrogenation and of cyclohexene dihydroxylation.

6. Comparing the sustainability of the two processes

Common aspects of the two processes investigated were the excellent yield to the desired product (especially in the case of cyclohexene dihydroxylation), and the absence of organic solvents; in both cases, the reactions were carried out in water solvent. On the other hand, the main disadvantage of the tungstate-based system is the recovery of the catalyst and of the PTA. Recently some papers reported about procedures for the recovery of the soluble W catalyst [102], or for the use of heterogeneous, hence more easily recovered, WO_3 catalyst [103]. Instead, the Ru-based catalyst is easily recoverable and reusable.

Concerning the starting reactant, catechol and cyclohexene, both are obtained from benzene. The current world production for cyclohexene is around 40,000 tons/y, mainly used by Asahi for hydration into cyclohexanol, precursor for the synthesis of adipic acid. Catechol is produced by phenol hydroxylation.

Fig. 7 presents a comparative assessment of the two alternative routes to 1,2-cyclohexanediol. The assessment is normalized to 1 kg of product and was made with the aid of the EATOS [104] tool. It takes into consideration both the masses (E-factor) as well as environmental impact of the substances released by the processes (Sheldon's Q) [105]. This assessment compares the two routes via oxidation of cyclohexene (Table 2, experiment 4) and via hydrogenation of catechol (Table 7, entry 1). The following assumption was made: the catechol route is a heterogeneous reaction and therefore both the solvent (water) and the catalyst have been considered easily recyclable at the 95% amount with only 5% of losses.

Comparison of E-factors shows that the route from cyclohexene produces 0.39 kg of wastes while route from catechol produces 0.13 kg. Inspection of EATOS graphical output allows also to see where these wastes come from. Much of the wastes produced in cyclohexene route (0.31 kg out of 0.39 kg; blue block) are aqueous waste and come from the aqueous reagents. Further inspection of this segment with EATOS tool shows that the remaining waste is unreacted reagents (green block) and catalyst (magenta block). Inspection of the wastes produced in the catechol route shows that most of them come from the by-products (0.11 kg out of 0.13 kg; yellow block).

For the assessment of the environmental impact of chemical processes, EATOS can take into consideration up to ten different substances ecotoxicological and human toxicological parameters, and each parameter can be given a different weight. Such parameters are then normalized (each parameter is made to vary from 1 to 10), and then combined to afford an environmental quotient

EI (much the same of Sheldon's *Q*). So each different component of the waste can be assigned a quantitative potential environmental impact PEI_{out} (much the same of Sheldon's environmental quotient *EQ*), defined as the product of its mass (relative to the product unit mass) with its *EI*. In this work the parameters taken into account for the assessment of EI_{out} of the waste were: MAK, TLV, Hazard Symbol, or LX_{50} for human acute toxicity; any suspect carcinogen, mutagen or teratogen for chronic human toxicity; and WGK or LC_{50} to fish for ecotoxicology. These data were obtained from substances Material Safety Data Sheets. The quantitative comparison of potential environmental impact of waste (PEI_{out}) is also reported in Fig. 7. The figure allows to see immediately that the route from cyclohexene is at 0.74 PEI unit/kg product while the route from catechol is at 0.62 PEI unit/kg product, that is the catechol route achieves a net 20% reduction in waste potential environmental impact. It is worth of note that a significant contribution to the environmental impact of the cyclohexene route comes from the unrecovered homogeneous catalyst (magenta block).

7. Conclusions

Two different strategies for 1,2-cyclohexanediol synthesis were adopted, with the aim of developing a high-yield and sustainable method for the production of glycol, which can act as a starting material for a new oxygen-based oxidation process for adipic acid. The one-pot epoxidation and hydrolysis (dihydroxylation) of cyclohexene to *trans*-1,2-cyclohexanediol was achieved with 97.4% yield, in the absence of a solvent using an aqueous solution of hydrogen peroxide, a phase-transfer-agent, and a tungstic acid/phosphoric acid catalytic system. One drawback of the synthesis was the difficulty in the recovery and reuse of the homogeneous catalyst and of the PTA.

The alternative route investigated is the direct hydrogenation of catechol to a mixture of *cis* and *trans*-1,2-cyclohexanediol, carried out in a water solvent, using a $Ru(OH)_x$-alumina heterogeneous catalyst. Glycol was obtained with 90% yield; furthermore, the catalyst could be recovered by filtration and reused, without any regeneration. The reactivity of the Ru-based catalyst was influenced by the Ru content; in fact, the in situ generation of metallic Ru during the hydrogenation reaction led to a greater intrinsic activity for the catalyst containing the greater Ru content. A comparison of the two processes allowed to show the lower environmental impact of the catechol hydrogenation route.

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References

[1] K.B. Sharpless, K. Akashi, J. Am. Chem. Soc. 98 (1976) 1986–1987.
[2] H.C. Kolb, M.S. VanNieuwenhze, K.B. Sharpless, Chem. Rev. 94 (1994) 2483–2547.
[3] M. Schröder, Chem. Rev. 80 (1980) 187–213.
[4] K. Bergstad, S.Y. Jonsson, J.E. Bäckvall, J. Am. Chem. Soc. 121 (1999) 10424–10425.
[5] F. Cavani, J.H. Teles, ChemSusChem 2 (2009) 508–534.
[6] V. Nardello, J.-M. Aubry, D.E. De Vos, R. Neumann, W. Adam, R. Zhang, J.E. ten Elshof, P.T. Witte, P.L. Alsters, J. Mol. Catal. A 251 (2006) 185–193.
[7] I.W.C.E. Arends, R.A. Sheldon, Appl. Catal. A 212 (2001) 175–187.
[8] V. Singh, P.T. Deota, Synth. Commun. 18 (1988) 617–624.
[9] M. Schwegler, M. Floor, H. Van Bekkum, Tetrahedron Lett. 29 (1988) 823–826.
[10] T. Oguchi, T. Ura, Y. Ishii, M. Ogawa, Chem. Lett. 18 (1989) 857–860.
[11] C. Venturello, M. Gambaro, Synthesis 4 (1989) 295–297.
[12] W.A. Herrmann, R.W. Fischer, D.W. Marz, Angew. Chem. Int. Ed. 30 (1991) 1638–1641.
[13] R. Noyori, M. Aoki, K. Sato, J. Chem. Soc. Chem. Commun. 16 (2003) 1977–1986.
[14] T. Tatsumi, K. Yamamoto, H. Tajima, H. Tominaga, Chem. Lett. 21 (1992) 815–818.
[15] A. Corma, M.A. Camblor, P. Esteve, A. Martinez, J. Perez-Pariente, J. Catal. 145 (1994) 151–158.
[16] Q.-H. Xia, X. Chen, T. Tatsumi, J. Molec Catal. A 176 (2001) 179–193.
[17] A. Corma, M.T. Navarro, J. Perez-Pariente, J. Chem. Soc. Chem. Commun. 147 (1994).
[18] T. Tatsumi, K.A. Noyano, N. Igarashi, J. Chem. Soc. Chem. Commun. 3 (1998) 325–326.
[19] J. Xin, J. Suo, X. Zhang, Z. Zhang, New J. Chem. 24 (2000) 569–570.
[20] T. Blasco, A. Corma, M.T. Navarro, J. Perez Pariente, J. Catal. 156 (1995) 65–74.
[21] D.C. Dutoit, M. Schneider, R. Hutter, A. Baiker, J. Catal. 161 (1996) 651–658.
[22] J.M. Fraile, J.I. Garcia, J.A. Mayoral, E. Vispe, J. Catal. 189 (2000) 40–51.
[23] P. Wu, T. Tatsumi, T. Komatsu, T. Yashima, J. Catal. 202 (2001) 245–255.
[24] M. Guidotti, C. Pirovano, N. Ravasio, B. Lázaro, J.M. Fraile, J.A. Mayoral, B. Coq, A. Galarneau, Green Chem. 11 (2009) 1421–1427.
[25] O.A. Kholdeeva, A.Yu. Derevyankin, A.N. Shmakov, N.N. Trukhan, E.A. Paukshtis, A. Tuel, V.N. Romannikov, J. Mol. Catal. A 158 (2000) 417–421.
[26] N.N. Trukhan, A.Yu. Derevyankin, A.N. Shmakov, E.A. Paukshtis, O.A. Kholdeeva, V.N. Romannikov, Microporous Mesoporous Mater. 44–45 (2001) 603–608.
[27] O.A. Kholdeeva, T.A. Trubitsina, M.N. Timofeeva, G.M. Maksimov, R.I. Maksimovskaya, V.A. Rogov, J. Mol. Catal. A 232 (2005) 173–178.
[28] N.V. Maksimchuk, K.A. Kovalenko, S.S. Arzumanov, Y.A. Chesalov, M.S. Melgunov, A.G. Stepanov, V.P. Fedin, O.A. Kholdeeva, Inorg. Chem. 49 (2010) 2920–2930.
[29] T. Yamase, E. Ishikawa, Y. Asai, S. Kanai, J. Mol. Catal. A 114 (1996) 237–245.
[30] F. Chiker, F. Launay, J.P. Nogier, J.L. Bonardet, Green Chem. 5 (2003) 318–322.
[31] A.C. Dengel, W.P. Griffith, B.C. Parkin, J. Chem. Soc. Dalton Trans. 18 (1993) 2683–2688.
[32] Y. Usui, K. Sato, M. Tanaka, Angew. Chem. Int. Ed. 42 (2003) 5623–5625.
[33] M.N. Timofeeva, O.A. Kholdeeva, S.H. Jhung, J.-S. Chang, Appl. Catal. A 345 (2008) 195–200.
[34] B.S. Lane, K. Burgess, Chem. Rev. 103 (2003) 2457–2474.
[35] C. Venturello, E. Alneri, M. Ricci, J. Org. Chem. 48 (1983) 3831–3833.
[36] C. Venturello, R. D'Aloisio, J.C. Bart, M. Ricci, J. Mol. Catal. 32 (1985) 107–110.
[37] C. Venturello, M. Ricci, J. Org. Chem. 51 (1986) 1599–1602.
[38] C. Venturello, R. D'Aloisio, J. Org. Chem. 53 (1988) 1553–1557.
[39] Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida, M. Ogawa, J. Org. Chem. 53 (1988) 3587–3593.
[40] Y. Ishii, Y. Sakata, J. Org. Chem. 55 (1990) 5545–5547.
[41] S. Sakagucchi, Y. Nishiyama, Y. Ishii, J. Org. Chem. 61 (1996) 5307–5311.
[42] K. Sato, M. Aoki, R. Noyori, Science 281 (1998) 1646–1647.
[43] K. Sato, M. Aoki, R. Noyori, J. Org. Chem. 61 (1996) 8310–8311.
[44] C. Aubry, G. Chottard, N. Platzer, J.M. Brégeault, R. Thouvenot, F. Chauveau, C. Huet, H. Ledon, Inorg. Chem. 30 (1991) 4409–4415.
[45] L. Salle, C. Aubry, R. Thouvenot, F. Robert, C. Doremieux-Morin, G. Chottard, H. Ledon, Y. Jeanin, J.M. Bregeault, Inorg. Chem. 33 (1994) 871–878.
[46] L. Salle, J.Y. Piquemal, R. Thouvenot, C. Minot, J.M. Bregeault, J. Mol. Catal. A 117 (1997) 375–387.
[47] C. Bolm, O. Beckmann, O.A.G. Dabard, Angew. Chem. Int. Ed. 38 (1999) 907–909.
[48] D.C. Duncan, R.C. Chambers, E. Hecht, C.L. Hill, J. Am. Chem. Soc. 117 (1995) 681–691.
[49] L.J. Csanyi, K. Jaky, J. Catal. 127 (1991) 42–50.
[50] G. Gelbard, F. Raison, E. Roditi-Lachter, R. Thouvenot, L. Ouahab, D. Grandjean, J. Mol. Catal. 114 (1996) 77–85.
[51] M. Quenard, V. Bonmarin, G. Gelbard, Tetrahedron Lett. 28 (1987) 2237–2238.
[52] D. Prat, R. Lett, Tetrahedron Lett. 27 (1986) 707–710.
[53] F. Gao, T. Yamase, H. Suzuki, J. Mol. Catal. A 180 (2002) 97–108.
[54] C.L. Hill, C.M. Prosser-McCartha, Coord. Chem. Rev. 143 (1995) 407–455.
[55] R. Neumann, Prog. Inorg. Chem. 47 (1998) 317–370.
[56] O.A. Kholdeeva, R.I. Maksimovskaya, J. Mol. Catal. A 262 (2007) 7–24.
[57] E. Antonelli, R. D'Aloisio, M. Gambaro, T. Fiorani, C. Venturello, J. Org. Chem. 63 (1998) 7190–7206.
[58] A. Lambert, P. Plucinshi, I.V. Kozhevnikov, Chem. Commun. 6 (2003) 714–715.
[59] J. Kaur, I.V. Kozhevnikov, Catal. Commun. 5 (2004) 709–713.
[60] R. Neumann, A.M. Khenkin, J. Org. Chem. 59 (1994) 7577–7579.
[61] W. Zhu, H. Li, X. He, Q. Zhang, H. Shu, Y. Yan, Catal. Commun. 9 (2008) 551–555.
[62] T. Sakamoto, C. Pac, Tetrahedron Lett. 41 (2000) 10009–10012.
[63] Z. Xi, N. Zhou, Y. Sun, K. Li, Science 292 (2001) 1139–1141.
[64] K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikicchi, N. Mizuno, Science 300 (2003) 964–966.
[65] R. Neumann, M. Cohen, Angew. Chem. Int. Ed. 36 (1997) 1738–1740.
[66] H. Nagahara, M. Ono, M. Konishi, Y. Fukuoka, Appl. Surf. Sci. 121 (1997) 448–451.
[67] P.N. Rylander (Ed.), Catalytic Hydrogenation in Organic Synthesis, Academic Press, New York, 1979, p. 175.
[68] S. Nishimura (Ed.), Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis, Wiley, New York, 2001, p. 414.
[69] E.L. Muetterties, J.R. Bleeke, Acc. Chem. Res. 12 (1979) 324–331.

[70] A.F. Borowski, S. Sabo-Etienne, B. Chaudret, J. Mol. Catal. A 174 (2001) 69–79.
[71] H. Yang, H. Gao, R.J. Angelici, Organometallics 19 (2000) 622–629.
[72] M. Takasaki, Y. Motoyama, K. Higashi, S.-H. Yoon, I. Mochida, H. Nagashima, Chem. Asian J. 2 (2007) 1524–1533.
[73] A.M. Raspolli Galletti, C. Antonetti, I. Longo, G. Capannelli, A.M. Venezia, Appl. Catal. A 350 (2008) 46–52.
[74] S. Velu, M.P. Kapoor, Appl. Catal. A 245 (2003) 317–331.
[75] K.V.R. Chary, D. Naresh, V. Vishwanathan, M. Sadakane, W. Ueda, Catal. Commun. 8 (2007) 471–477.
[76] N. Mahata, K.V. Raghavan, V. Vishwanathan, C. Park, M.A. Keane, Phys. Chem. Chem. Phys. 3 (2001) 2712–2719.
[77] H.A. Smith, B.L. Stump, J. Am. Chem. Soc. 83 (1961) 2739–2743.
[78] T. Maegawa, A. Akashi, K. Yaguchi, Y. Iwasaki, M. Shigetsura, Y. Monguchi, H. Sajiki, Chem. Eur. J. 15 (2009) 6953–6963.
[79] J.W. Kim, T. Koike, M. Kotani, K. Yamaguchi, N. Mizuno, Chem. Eur. J. 14 (2008) 4104–4109.
[80] K. Yamaguchi, T. Koike, J.W. Kim, Y. Ogasawara, N. Mizuno, Chem. Eur. J. 14 (2008) 11480–11487.
[81] K. Yamaguchi, J.W. Kim, J. He, N. Mizuno, J. Catal. 268 (2009) 343–349.
[82] N. Mizuno, K. Yamaguchi, Chem. Eur. J. 9 (2003) 4353–4361.
[83] N. Mizuno, K. Yamaguchi, Catal. Today 132 (2008) 18–26.
[84] T. Oishi, K. Yamaguchi, N. Mizuno, Angew. Chem. Int. Ed. 48 (2009) 6286–6288.
[85] J.W. Kim, K. Yamaguchi, N. Mizuno, J. Catal. 263 (2009) 205–208.
[86] F. Cavani, Catal. Today 157 (2010) 8–15.
[87] F. Cavani, J. Chem. Technol. Biotechnol. 85 (2010) 1175–1183.
[88] S. Sakaguchi, D. Kikuchi, Y. Ishii, Bull. Chem. Soc. Jpn. 70 (1997) 2561–2566.
[89] X. Zuwei, Z. Ning, S. Yu, L. Kunlan, Science 292 (2001) 1139–1141.
[90] J.M. Fraile, J.I. García, J.A. Mayoral, E. Vispe, J. Catal. 204 (2001) 146–156.
[91] O.A. Kholdeeva, B.G. Donoeva, T.A. Trubitsina, G. Al-Kadamany, U. Kortz, Eur. J. Inorg. Chem. 34 (2009) 5134–5141.
[92] K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, D. Panyella, R. Noyori, Bull. Chem. Soc. Jpn. 70 (1997) 905–915.
[93] M. Huang, C.Y. Chen, J. Chin. Chem. Soc. 27 (1980) 151–159.
[94] M. Zawadzki, J. Okal, Mater. Res. Bull. 43 (1991) 3111–3121.
[95] M. Lenarda, L. Storaro, R. Ganzerla, R. Bertoncello, J. Mol. Catal. A 144 (1999) 151–158.
[96] B. Varughese, S. Chellamma, M. Lieberman, Langmuir 18 (2002) 7964–7970.
[97] B. Faroldi, C. Carrara, E.A. Lombardo, L.M. Cornaglia, Appl. Catal. A 319 (2007) 38–46.
[98] H. Chan, C.G. Takoudis, M.J. Weaver, J. Catal. 172 (1997) 336–345.
[99] G.G. Yan, T. Wu, W. Weng, H. Toghiani, R.K. Toghiani, H.L. Wan, C.U. Pittman, J. Catal. 226 (2004) 247–259.
[100] W. Li, H. Liu, E. Iglesia, J. Phys. Chem. B 110 (2006) 23337–23342.
[101] E. Rozhko, K. Raabova, F. Macchia, A. Malmusi, P. Accorinti, S. Alini, P. Babini, G. Cerrato, M. Manzoli, F. Cavani, ChemCatChem 5 (2013) 1998–2008.
[102] Y. Wen, X. Wang, H. Wei, B. Li, P. Jin, L. Li, Green Chem. 14 (2012) 2868–2875.
[103] Z. Bohström, I. Rico-Lattes, K. Holmberg, Green Chem. 12 (2010) 1861–1869.
[104] M. Eissen, J.O. Metzger, Chem. Eur. J. 8 (2002) 3580–3585.
[105] R.A. Sheldon, Chem. Soc. Rev. 41 (2012) 1437–1451.