Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Molecular Catalysis A: Chemical 246 (2006) 85–99

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Ru-catalyzed oxidation of primary alcohols

A. Köckritz[a,∗,1], M. Sebek[a,1], A. Dittmar[a,1], J. Radnik[a,1], A. Brückner[a,1], U. Bentrup[a,1], M.-M. Pohl[a,1], H. Hugl[b], W. Mägerlein[b]

[a] *Institute for Applied Chemistry Berlin-Adlershof e.V. (ACA), Richard-Willstaetter-Str. 12, D-12489 Berlin, Germany*
[b] *Lanxess Deutschland GmbH, Gebäude Q 18, D-51368 Leverkusen, Germany*

Received 15 July 2005; received in revised form 4 October 2005; accepted 13 October 2005
Available online 28 November 2005

Abstract

Primary alcohols were transfered into the corresponding aldehydes by catalytic oxidation with heterogeneous ruthenium catalysts. Ru(III) and Ru(0) species were deposited on titania and zirconia supports by wet chemical and plasmachemical methods. The dispersion of the catalytically active centres influenced significantly the catalytic activity. The doping of the Ru catalysts with promoter metals such as Fe, Cu, Mn, Co, and Mo was also investigated. The Ru/Co and Ru/Mn catalysts **13** and **14** led to an increase in the conversion of benzyl alcohol and 1-octanol in the oxidation with molecular oxygen. With bleach and TBHP as oxidants the promoter metals had a detrimental effect. Wet chemically prepared Ru/TiO_2(P25) catalysts showed the highest aldehyde selectivities in these oxidations.

Keywords: Catalytic oxidation; Ruthenium; Promoter; Molecular oxygen; Titania; Aldehydes

1. Introduction

Aldehydes represent an important class of products and intermediates in the field of fine chemicals and specialities. A commonly used method for their preparation is the oxidation of the respective alcohols (Scheme 1). Instead of conventional waste-producing oxidation procedures such as the stoichiometric application of toxic inorganic salts selective catalytic oxidation with environmentally benign oxidants has gained the preference in the past years [1–8]. Among those “green” oxidants, molecular oxygen is especially attractive. Suitable active metals for both homogeneously and heterogeneously catalyzed oxidations with molecular oxygen include ruthenium and other group VIII metals like palladium [9–15], cobalt [16–18], iron [19], nickel and osmium [20–22] and also the groups I, V, VI, and VII metals such as copper [23–29], vanadium [30,31], molybdenum [32], and manganese [33,34]. Ruthenium catalysts are known to oxidize alcohols and other substrates according to different reaction mechanisms such as hydridometal or oxometal pathways and even radical mechanism, depending on the oxidation states of ruthenium, oxidant and cocatalysts or additives [23–35]. Various homogeneous Ru catalysts, like $RuCl_3$ [36], perruthenate [37,38] or Ru complexes [20,39,40] preferentially with salen [41], amine [42–44,50] or phosphine [45–51] ligands, also in combination with bases and TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl) as cocatalyst were successfully employed in the aerobic oxidation. Bäckvall and co-workers [52] developed methods for the oxidation of alcohols via biomimetic multi-stage electron transfers. Furthermore, Ru species immobilized on different supports [53–60] such as charcoal, oxidic materials or organic polymers were applied just as Ru-incorporated hydrotalcites [61], hydroxyapatites [62,63], and RuO_2 [64]. Some Ru-catalyzed oxidations of alcohols in ionic liquids have been reported in the last years [65].

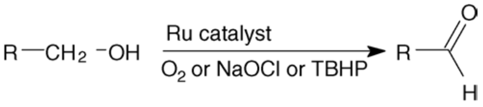
A drawback for a wider use of these methods is that they are often applicable only for benzylic or allylic alcohols, additional functional groups hamper the catalytic activity or the attainable catalytic activities and selectivities do not meet the needs of a technical application. In certain cases, additives have to be employed which must be disposed or can only be recycled in a complicated way [2]. Heterogeneous catalysts or immobilized complexes have the advantage of a better separation

---

[∗] Corresponding author.
E-mail address: koeck@aca-berlin.de (A. Köckritz).

[1] Members of the EU-funded Coordination Action of Nanostructured Catalytic Oxide Research and Development in Europe (CONCORDE).

1381-1169/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2005.10.020



Scheme 1.

from the product. Disadvantages are the possible leaching of the active metal, the oxidative degradation of an organic support or a decrease in the activity upon recycling.

Recently, Mizuno and Yamaguchi [66,67] developed a robust, recyclable and widely applicable Ru/Al_2O_3 catalyst. This promising system inspired us to check, if an increase of the catalyst activity can be enabled by the preparation of Ru catalysts using other supports or by the addition of promoter metals. Moreover, in addition to molecular oxygen other oxidants like NaOCl and *tert*-BuOOH (TBHP), which have advantages regarding safety on a technical scale and a minor detrimental potential from an ecological point of view, were investigated.

2. Experimental

2.1. General methods

The oxidations using molecular oxygen were carried out either in a SPR 16 multibatch reactor (amtec GmbH Chemnitz) or in a 100 ml Buechi glas reactor equipped with a stirrer (at 1300 rpm), a heating bath, a contact thermometer and a manometer. Oxidation reactions with bleach or *tert*-BuOOH were done on a Variomag Telesystem remote-controlled multiple point stirrer. The MPECVD (microwave plasma-enhanced chemical vapour deposition) process for the synthesis of supported catalysts was carried out in a microwave plasma apparatus Ilmplac 1200. Gas chromatograms were recorded on a Hewlett Packard HP 5890 equipped with a HP5 column and a HP 5971A mass selective detector. Diethyleneglycol *n*-butylether was used as internal standard. In order to test the reaction mixture for carboxylic acids trimethylsulfoniumhydroxide (TMSH) was added to 1 ml of the mixture before GC analysis. Elemental analyses were determined by the ICP-OES method using an Optima 3000 XL (Perkin-Elmer) and a EA 1110 (CE Instruments). TEM images were obtained with a CM-20 Phillips at 200 kW acceleration voltage. XPS measurements were done on a VG ESCALAB 220 i XL with Al Kα radiation ($E = 1486.6$ eV). For the determination of the electron binding energy the spectra were referred to the C 1s peak at 284.8 eV. For the FTIR investigations the samples were pressed into self-supporting disks (50 mg, Ø 20 mm). The spectra were recorded on a Bruker IFS-66 spectrometer after evacuation at ambient temperature and after heating up to 300 °C under vacuum and subsequent cooling down to room temperature. EPR measurements were performed in X-band ($\nu \approx 9.5$ GHz) by a cw-spectrometer ELEXSYS 500-10/12 (Bruker) using a microwave power of 6.3 mW, a modulation frequency of 100 kHz and a modulation amplitude of 0.5 mT. Spectra were recorded at 77 K using a finger dewar filled with liquid nitrogen. The magnetic field was measured with respect to the standard 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH). For the determination of the BET surface at 77 °C an ASAP 2000-Mg was used as adsorption system.

2.2. Preparation of catalysts

Deionized water was used for all relevant operations. TiO_2(P25) was obtained from Degussa (S_{BET} 50 $m^2/g \pm 15$). TiO_2(Kronos) with S_{BET} 307 m^2/g was received from Kronos International Inc. and $Zr(OH)_4$ MELCAT XZ0631/01 was supplied from MEL Chemicals (S_{BET} 459 m^2/g). The abbreviations of the catalysts were formed as follows: *W* (wet chemical preparation) or *P* (plasma chemical preparation) – active metal(s) (wt.%)/support.

2.2.1. General procedure for the preparation of Ru catalysts by impregnation

The procedure was done by modifying a literature method for the preparation of Ru/Al_2O_3 [66]. Definite amounts of $RuCl_3$ (or $RuCl_3{\cdot}H_2O$) (Table 1) and, in some cases, of a promoter precursor were dissolved in deionized water and under vigorous stirring the support was added. The slurry was stirred for 15 min and then centrifugated at 7000 rpm. The liquid was decanted and the solid residue was washed with water and centrifugated again. This procedure was repeated twice until the washing solution was colourless. The solid material was dried at r.t. in a vacuum oven for 24–48 h and then crushed in a mortar. It was suspended

Table 1
Catalysts prepared according to a wet chemical procedure

No.	Composition	Used amount of $RuCl_3$ or promoter precursor [mg]	Support [g]	Solvent H_2O [ml]	Received catalyst [g]
1	*W* – Ru0.83/TiO_2(Kronos)	103	2	60	1.87
2	*W* – Ru0.50/TiO_2(P25)[a]	152	10	180	8.12
3	*W* – Ru0.71/TiO_2(P25)[a]	304	10	180	8.07
4	*W* – Ru1.02/TiO_2(P25)	516	10	300	7.93
5	*W* – Ru1.2/TiO_2(P25)	103	2	60	1.48
6	*W* – Ru1.36/TiO_2(P25)[a]	304	10	180	7.99
7	*W* – Ru-1.57/TiO_2(P25)	516	10	180	8.20
8	*W* – Ru1.9/TiO_2(P25)	516	10	300	7.33
9	*W* – Ru2.13/ZrO_2	310	6	180	4.87
10	*W* – Ru1.85/Cu0.18/TiO_2(P25)	103 CuCl: 10	2	60	1.85
11	*W* – Ru1.1/Fe0.30/TiO_2(P25)	103 $FeSO_4{\cdot}7H_2O$: 32	2	60	1.49
12	*W* – Ru2.66Co0.18/TiO_2(P25)	311 $CoCl_2$:194	4.8	180	3.46

[a] $RuCI_3{\cdot}xH_2O$.

in 90–180 ml H_2O, the aqueous slurry was adjusted with 1 M NaOH to a pH value of 13.2 and stirred for 24 h. Then the mixture was centrifugated and the solid residue was washed three times with water. It was dried at r.t. for 24 h and additionally at 50 °C for 4 h in a vacuum oven.

2.2.2. *Special impregnation methods forRu/TiO_2 catalysts with promoters*

2.2.2.1. Preparation of $W-Ru0.45Co-0.36/TiO_2(P25)$ ***13***. 0.292 g $Co(OAc)_2{\cdot}4H_2O$ (1.17 mmol) was dissolved in deionized water and under vigorous stirring 4 g of $W-$Ru0.50/TiO_2(P25) was added. The slurry was stirred at r.t. for 24 h and then centrifugated at 7000 rpm. The liquid was decanted and the solid residue was washed with 90 ml water and centrifugated again. This procedure was repeated twice. The solid material was dried at r.t. in a vacuum oven for 25 h and then crushed in a mortar. It was suspended in 90 ml H_2O, the aqueous slurry was adjusted with 1 M NaOH to a pH value of 13.2 and stirred for 24 h. Then the mixture was centrifugated and the solid residue was washed three times with 90 ml H_2O. It was dried at r.t. in a vacuum oven for 24 h, yield 3.47 g.

2.2.2.2. Preparation of $W-Ru0.44Mn0.35/TiO_2(P25)$ ***14***. It was prepared according to the above procedure for **13** unless 0.288 g $Mn(OAc)_2{\cdot}4H_2O$ (1.18 mmol) was used and dissolved in 180 ml H_2O, yield 3.34 g.

2.2.2.3. Preparation of $W-Ru0.02/Mo0.64/TiO_2(P25)$ ***15***. 0.151 g $MoCl_3$ (0.75 mmol) was dissolved in 60 ml H_2O and 30 ml concentrated HCl and heated under vigorous stirring to 70 °C for 30 min. The suspension was filtered and 3 g TiO_2(P25) was added to the filtrate at r.t. The slurry was stirred for 15 min and then centrifugated. A solution of 0.155 g $RuCl_3{\cdot}xH_2O$ in 90 ml H_2O was added to the solid residue and stirred for additional 15 min. The slurry was centrifugated again and the solid residue was washed three times with 100 ml H_2O. The solid was dried in a vacuum oven for 24 h, crushed in a mortar and suspended in 60 ml H_2O. The pH value of the suspension was adjusted with 1 M NaOH to 13.2, the mixture was stirred for 24 h and then centrifugated. The solid residue was washed four times with 100 ml H_2O and dried in the vacuum oven at r.t. for 24 h and at 50 °C for 4 h.

2.2.2.4. Preparation of $W-Co0.12/TiO_2(P25)$ ***16***. It was prepared according to the above procedure for **13** unless 0.548 g $Co(OAc)_2{\cdot}4H_2O$ (2.2 mmol) and 5 g TiO_2(P25) were used and suspended in 180 ml H_2O. The solid residue was washed with 150 ml H_2O. The finished catalyst was dried at 50 °C for 24 h at r.t. and for 4 h in the vacuum oven, yield 4.64 g.

2.2.3. *General procedure for the preparation of Ru catalysts by MPECVD*

A definite amount of Ru(III) acetylacetonate (Table 2) and, in the case of catalyst **21**, Co(II) acetylacetonate was filled into the MPECVD apparatus together with 3 g TiO_2. Then it was evacuated to 10 Pa. The plasma was ignited at an oxygen flow of 300 cm^3/min and a microwave power of 300 W. The catalyst **20** was additionally treated with a hydrogen plasma.

Table 2
Catalysts prepared according to MPECVD procedures

No.	Catalyst	Used amount of $M(acac)_x$ precursor [mg]
17	$P-$Ru0.2/TiO_2(P25)	84
18	$P-$Ru0.34/TiO_2(P25)	167
19	$P-$Ru0.62/TiO_2(P25)	110
20	$P-$Ru1.57/TiO_2(P25)	240
21	$P-$Ru0.32/Co0.51/TiO_2(P25)	$Ru(acac)_3$: 120 $Co(acac)_2$: 77

2.3. *Oxidations with molecular oxygen*

Experiments in a SPR 16 multibatch reactor: The reactors were charged with 7 ml solvent, the catalyst and with 1 mmol of the alcohol. In some cases, additives were added. The reactors were closed and an Excel-based automatic schedule was started. After the termination of the reaction the yield and conversion were determined by GC-MS.

Experiments in a Buechi 100 ml glass reactor: the reactor was charged with 30 ml solvent, 1 mmol alcohol and the appropriate amount of catalyst and closed. Then it was rinsed five times with argon and heated to the reaction temperature. At this temperature the reactor was rinsed five times with oxygen. The pressure was adjusted. With the start of the stirrer the reaction time began. After the reaction the reactor was depressurized and cooled down to room temperature using an ice bath.

The content of the reactor was filtered over kieselguhr and the filter cake was washed three times with dichloromethane. The filtrate was transferred to the GC system to determine conversion and yield.

During some special runs samples of the reaction solutions were taken for the detection of the reaction course in definite time intervals.

2.3.1. *Experimental test to the question: heterogeneous or homogeneous catalysis?*

The experiment was carried out in a Buechi glass reactor according to the procedure described above with 1 mmol benzylalcohol, 71.2 mg catalyst **3** (0.005 mmol) in 30 ml dichloroethane at 80 °C and a pressure of 4 bar oxygen. After 20 min, the stirrer was stopped, the reactor was cooled down, the catalyst was filtered off and a sample for GC analysis was taken. The reactor was refilled with the filtrate. It was pressurized, heated and stirred again for an additional hour. A second sample for GC analysis was taken after cooling down.

2.3.2. *Recycling and regeneration of the catalysts*

In order to recycle the catalysts the reaction mixture was not filtrated but centrifugated. The solid catalysts were washed with 35–50 ml dichloromethane and dried in an argon stream.

Used catalysts were tried to regenerate by washing with 1 M NaOH. They were stirred in 10 ml of the NaOH solution at r.t.

for 1 h. Then the solid catalysts were separated by filtration, washed three times with H_2O, and dried in the vacuum oven at r.t. for 24 h. Alternatively, regeneration was attempted in an oxygen atmosphere by elutriating the used catalysts with 30 ml dichloromethane and stirring under 6 bar O_2 pressure at a stirrer velocity of 1300 rpm for 3 h. The catalyst was centrifugated and dried in a vacuum oven at r.t. for 24 h.

2.4. General procedure for oxidations with NaOCl and tert-BuOOH

One millimole alcohol, 7 ml solvent, 1.1 mmol of the oxidant and the appropriate catalyst were filled in a reaction flask and stirred for 1 h (unless otherwise noted). Alternatively, the oxidant was added via a syringe pump over a period of 1 h and the mixture was stirred for additional 10 min. Then the organic components were extracted with three portions of dichloroethane. This solution was dried with Na_2SO_4 and used for GC-MS analysis.

3. Results and discussion

3.1. Catalyst preparation and characterization

Catalysts with ruthenium as the single active metal and with ruthenium and a second metal such as Fe, Cu, Co, Mn, and Mo were prepared according to wet chemical procedures and also to plasma supported methods. Two titania modifications, Kronos (100% anatase) and P25 (25% rutile, 75% anatase), as well as zirconia were used as support. During the wet chemical procedure metal salts were adsorbed on the surface of the support and in a second step metal hydroxy species created via an alkaline hydrolysis were bond to hydroxy groups on the surface. In certain cases different ruthenium loadings of the catalysts were obtained, even if completely the same preparation procedure was applied (Table 1). Regarding this observation there was no difference between the use of $RuCl_3$ or $RuCl_3 \cdot xH_2O$. Possible reasons may be different batches of ruthenium chlorides or an inhomogeneity of the support. Possibly, the reaction time in the first adsorption step should be extended. The preferred procedure for the doping with a second metal was to deposit ruthenium on the support first and add the promoter metal afterwards (catalysts **13** and **14**). A simultaneous deposition led to a significantly higher Ru content compared with the promoter metal (catalysts **10–12**). The preparation of a Ru/Mo catalyst failed. $MoCl_3$ was only soluble in acids and therefore it was deposited first but only traces of Ru could be introduced in a second step (catalyst **15**). The plasma chemical procedure comprised evaporation, adsorption and decomposition of metal acetylacetonates in a low-pressure oxygen plasma in the presence of the support. The organic ligands were completely decomposed and metal oxides were deposited on the surface of the support.

After the preparation of the catalysts no significant change in the BET surface was found compared with the pure support (Table 3). Only the reflections of crystalline rutile and anatase phases of TiO_2(P25) could be observed in the XRD spectra even in the case of the catalysts with a higher Ru loading ($W-$Ru1.57/TiO_2(P25) **7**, $W-$Ru2.66Co0.18/TiO_2(P25) **12**). That points to a high dispersion of the Ru species. The size of the

Table 3
Characterization of the prepared catalysts

No.	Composition	Theoretical loading with active metals [%]	Diameter of Ru particles [nm]	Ru dispersion on surface of support	S_{BET} [m^2/g]	Binding energy E_B [eV]
1	$W-$Ru0.83/TiO_2(Kronos)	2.45	≤1	Homogeneously dispersed	253.8	[Ru 3$d_{5/2}$] 282.5
2	$W-$Ru0.50/TiO_2(P25)	0.73	≤2	Homogeneously dispersed	55.4	[Ru 3$d_{5/2}$] 282.1
3	$W-$Ru0.71/TiO_2(P25)	1.46	≤1	Homogeneously dispersed	54.6	[Ru 3$d_{5/2}$] 281.5
4	$W-$Ru1.02/TiO_2(P25)	2.45	≤1-2	Slightly inhomogeneous	45.5	[Ru 3$d_{5/2}$] 281.3
5	$W-$Ru1.2/TiO_2(P25)	2.45	≤1	Homogeneously dispersed	44.3	[Ru 3$d_{5/2}$] 281.1
6	$W-$Ru1.36/TiO_2(P25)	1.46	n.d	n.d	53.6	n.d.
7	$W-$Ru1.57/TiO_2(P25)	2.45	1–5	Inhomogeneous	57.9	[Ru 3$d_{5/2}$] 282.1
8	$W-$Ru1.9/TiO_2(P25)	2.45	≤1-2	Slightly inhomogeneous	62.8	[Ru 3$d_{5/2}$] 281.5
9	$W-$Ru2.13/ZrO_2	2.45	≤2	Slightly inhomogeneous	433.5	[Ru 3$d_{5/2}$] 281.8
10	$W-$Ru1.85/Cu0.18/TiO_2(P25)	Ru:2.46; Cu:0.31	n.d	n.d	57.2	[Ru 3$d_{5/2}$] 281.8; [Cu 2$p_{3/2}$] 929.7
11	$W-$Ru1.1/Fe0.30/TiO_2(P25)	Ru:2.45; Fe:0.31	n.d	n.d	55.0	n.d.
12	$W-$Ru2.66Co0.18/TiO_2(P25)	Ru:3.01; Co:1.75	1–300	Inhomogeneous	49.6	[Ru 3$d_{5/2}$]281.6
13	$W-$Ru0.45Co0.36/TiO_2(P25)	Ru:0.50; Co:1.72	≤2	Homogeneously dispersed	52.9	[Ru 3$d_{5/2}$] 282.1; [Co 2$p_{3/2}$] 780.5
14	$W-$Ru0.44Mn0.35/TiO_2(P25)	Ru:0.50; Mn:1.61	≤2	Homogeneously dispersed	58.5	[Ru 3$d_{5/2}$] 282.2; [Mn 2$p_{3/2}$] 640.9
15	$W-$Ru0.02/Mo0.64/TiO_2(P25)	Ru:2.40; Mo:2.28	1–2	Homogeneously dispersed	56.2	[Ru 3$d_{5/2}$] 281.8
16	$W-$Co0.12/TiO_2(P25)	2.53	n.d	n.d	n.d.	n.d.
17	$P-$Ru0.2/TiO_2(P25)	0.71	≤5	Inhomogeneous with crust formation	60.2	[Ru 3$d_{5/2}$] 280.6
18	$P-$Ru0.34/TiO_2(P25)	1.39	1 to >10	Inhomogeneous with crust formation	59.4	[Ru 3$d_{5/2}$] 280.3
19	$P-$Ru0.62/TiO_2(P25)	0.92	2 to >13	Inhomogeneous	62.4	[Ru 3$d_{5/2}$] 280.4
20	$P-$Ru1.57/TiO_2(P25)	2.00	1.5 to >10	Inhomogeneous with crust formation	58.7	[Ru 3$d_{5/2}$] 280.7
21	$P-$Ru0.32/Co0.51/TiO_2(P25)	Ru:1.00; Co:0.58	1 to >10	Inhomogeneous with crust formation	59.6	[Ru 3$d_{5/2}$] 282.3; [Co 2$p_{3/2}$] 780.5

n.d, not determined.

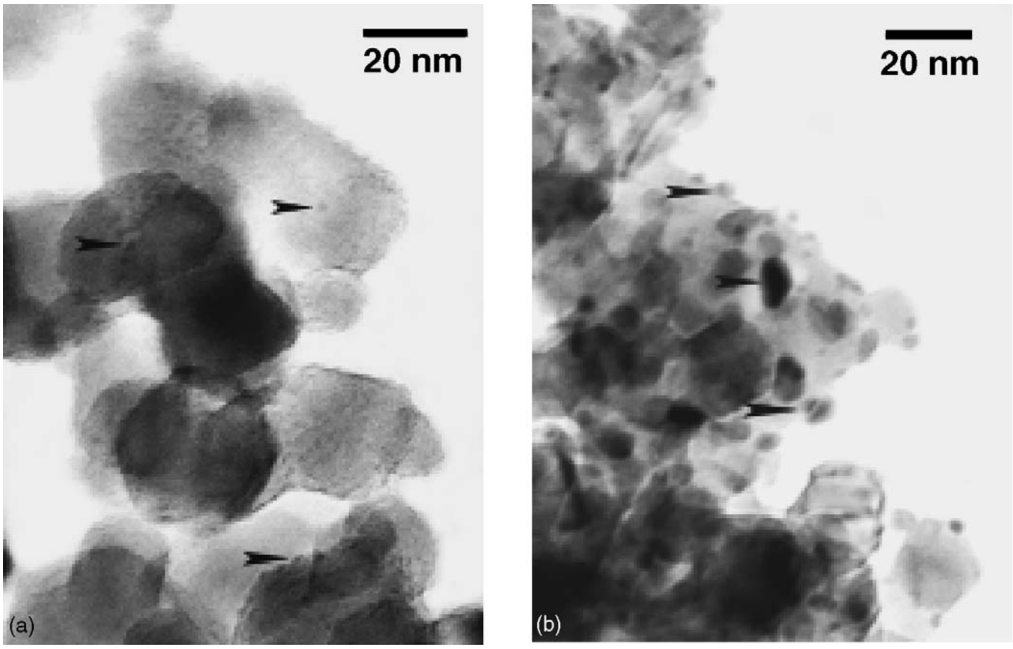


Fig. 1. (a) TEM image of catalyst $W-\mathrm{Ru}0.50/\mathrm{TiO_2}$(P25) **2**; (b) TEM image of catalyst $P-\mathrm{Ru}0.62/\mathrm{TiO_2}$(P25) **19**.

particles of the active metals could be well derived from TEM images. Their average size ranged between ≤ 1 and 10 nm with some outliers up to 300 nm (Table 3).

The catalysts generated by wet chemical methods showed a higher and more homogeneous dispersion of ruthenium species at a lower loading (Fig. 1a). The plasma chemically prepared catalysts showed generally bigger particles, often they had the shape of crusts or layers or agglomerations as shown in Fig. 1b.

The oxidation state of ruthenium was determined by XPS. The binding energy of the [Ru $3d_{5/2}$] level of all wet chemically prepared catalysts was found in the characteristic range of $\mathrm{Ru^{3+}/Ru^{4+}}$ species. Due to the same position of signals for both species a serious discrimination is impossible. The binding energy of the plasma chemically prepared catalysts **17**–**21** was with one exception lower than these of **1**–**15**. These values were slightly higher as the characteristic value of Ru(0) (280.1 eV). As main component metallic Ru can be proposed, the small shift to higher energies can be explained with proportions of oxidized Ru. The presence of the promoter metal Co may be the reason for the higher value of 282.3 eV (catalyst **21**).

Representative EPR spectra of the catalysts $W-\mathrm{Ru}0.50/\mathrm{TiO_2}$(P25) **2**, $W-\mathrm{Ru}0.71/\mathrm{TiO_2}$(P25) **3** and $W-\mathrm{Ru}1.57/\mathrm{TiO_2}$(P25) **7** are plotted in Fig. 2. Ru tends to form low-spin complexes. Thus, potential EPR active species are $\mathrm{Ru^{3+}}$ and $\mathrm{Ru^{+}}$ both with a spin of 1/2. $\mathrm{Ru^{4+}}$ ($S = 1$) is not detectable under these conditions due to short relaxation times. The spectra in Fig. 2 show a signal with rhombic g tensor which is assigned to isolated low spin $[\mathrm{Ru^{3+}(H_2O)}_m(\mathrm{O_{support}})_n]$ species ($S = 1/2$), in agreement with the XPS results that point to the presence of $\mathrm{Ru^{3+}}$ for these catalysts. Similar signals were observed for isolated $\mathrm{Ru^{3+}}$ centres in different zeolite matrices [68]. Besides, a broad more or less isotropic line is also superimposed on the EPR spectrum of isolated $\mathrm{Ru^{3+}}$, which is most obvious for catalyst **7** with the highest Ru content. This signal arises from neighbouring $\mathrm{Ru^{3+}}$ species in which the g anisotropy is averaged out by dipolar magnetic interactions. It points to a decreasing dispersion with rising Ru loading.

The room temperature FTIR spectrum of the fresh catalyst **3** shows (Fig. 3c) among the vibrations of the support only the bands of adsorbed H_2O and CO_2, which disappeared after the treatment at 300 °C (Fig. 3b). Compared to the titania support spectrum (Fig. 3a) the positions of the OH-bands were shifted to higher wavenumbers (3716/3668 $\mathrm{cm^{-1}}$) indicating the interaction with Ru species and the possible formation of Ru–OH bands. The band at 1860 can be correlated to $\mathrm{Ru^{4+}{=}O}$ species [69], which were formed due to the thermal treatment (Fig. 4).

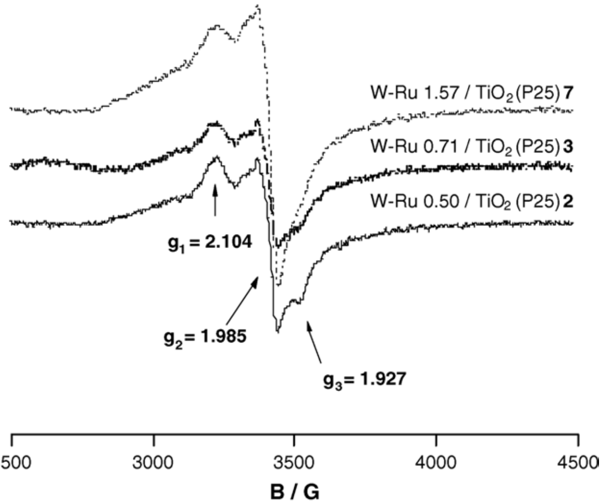


Fig. 2. EPR spectra of Ru/$\mathrm{TiO_2}$(P25) catalysts.

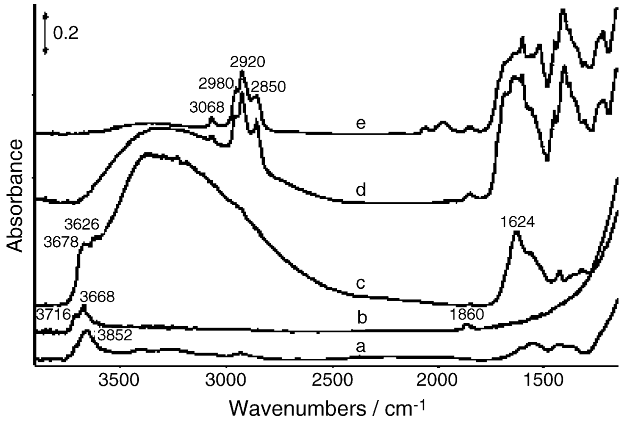


Fig. 3. FTIR spectra of fresh and used catalyst **3** ((a) titania support; (b) fresh **3**, after evacuation at 300 °C; (c) fresh **3**, r.t.; (d) used **3**, r.t.; (e) used **3** after evacuation at 300 °C) (used catalysts are discussed in a below-mentioned paragraph).

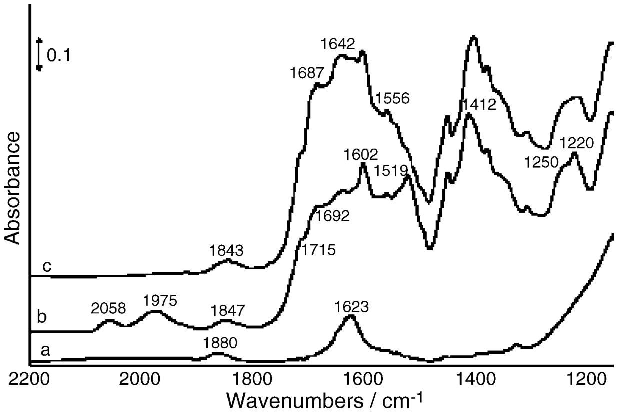


Fig. 4. Cut-out of Fig. 3 ((a) fresh **3** after evacuation at 300 °C; (b) used **3** after treatment at 300 °C; (c) used **3** r.t.).

3.2. *Catalytic oxidations with molecular oxygen*

At first, a screening of Ru catalysts was carried out in terms of pressure, temperature, solvent, substrate/catalyst (*S*/*C*) ratio, promoters and additives in the SPR 16 multibatch reactor (Table 4). A working pressure of at least 10 bar is required for this apparatus. For safety reasons a mixture of 5% oxygen and 95% argon was used instead of pure oxygen. In all reactions with molecular oxygen and Ru catalysts only the aldehydes could be found as products. The screening was accomplished with benzyl alcohol as used model substrate. At a total pressure of 30 bar

Table 4
Influences of reaction parameters on the oxidation of benzylic alcohol to benzaldehyde

Run	Catalyst	Ru [mmol]	Additive	*P* [bar]	Solvent	Yield [%][a]	$n_{\text{aldehyde}}/n_{\text{Ru}}$
1	**1**	0.0083	–	30	Dichloroethane	26	32
2	**1**	0.0083	CuCl[b]	30	Dichloroethane	37	45
3	**1**	0.0083	$FeSO_4 \cdot 7H_2O$[b]	30	Dichloroethane	32	38
4	**5**	0.012	–	30	Dichloroethane	66	56
5	**5**	0.012	CuCl[b]	30	Dichloroethane	70	59
6	**5**	0.012	$FeSO_4 \cdot 7H_2O$[b]	30	Dichloroethane	55	46
7	**9**	0.01	–	30	Dichloroethane	46	46
8	**9**	0.01	CuCl[b]	30	Dichloroethane	53	53
9	**9**	0.01	$FeSO_4 \cdot 7H_2O$[b]	30	Dichloroethane	49	49
10	**4**	0.01	CuCl[b]	80	Dichloroethane	85	85
11	**4**	0.01	$FeSO_4 \cdot 7H_2O$[b]	80	Dichloroethane	74	74
12	**9**	0.01	–	80	Dichloroethane	94	94
13	**9**	0.01	CuCl[b]	80	Dichloroethane	81	81
14	**9**	0.01	$FeSO_4 \cdot 7H_2O$[b]	80	Dichloroethane	77	77
15	**4**	0.01	–	60	Dichloroethane	86	86
16	**4**	0.01	–	70	Dichloroethane	88	88
17	**4**	0.01	–	80	Dichloroethane	96	96
18	**4**	0.01	–	90	Dichloroethane	93	93
19	**4**	0.01	–	30	Trifluorotoluene	59	59
20	**4**	0.01	–	30	Chlorobenzene	64	64
21	**4**	0.01	–	30	1.2-Dichlorobenzene	100	100
22	**10**	0.01	–	80	Dichloroethane	31	31
23	**10**	0.01	Molecular sieve 4A[c]	80	Dichloroethane	26	26
24	**10**	0.01	DBAD[b]	80	Dichloroethane	33	33
25	**10**	0.01	–	80	Trifluorotoluene	51	51
26	**10**	0.01	K_2CO_3[b]	80	*tert*-BuOH	45	45
27	**11**	0.01	–	80	Dichloroethane	46	46
28	**11**	0.01	Molecular sieve 4A[c]	80	Dichloroethane	47	47
29	**11**	0.01	K_2CO_3, DBAD[b]	80	Dichloroethane	61	61
30	**11**	0.01	–	80	Trifluorotoluene	60	60
31	**11**	0.01	K_2CO_3[b]	80	*tert*-BuOH	56	56

Reaction conditions: 1 mmol benzyl alcohol, 80 °C, 1 h, 7 ml solvent, 5% O_2/95% argon.

[a] Selectivity towards benzaldehyde >99% in each run.

[b] 5 mol%, DBAD = dibenzylazodicarboxylate.

[c] Molecular sieve 4 Å 400 mg.

(pO_2 1.5 bar) the addition of Cu(I) and Fe(II) salts increased the conversion (runs 2,3,5,8,9), but this effect could not be verified at 80 bar (pO_2 4 bar). At this pressure the pure Ru/titania or Ru/zirconia catalysts showed the best results.

As an optimal pressure 80 bar was identified (run 17) and the best solvent was 1.2-dichlorobenzene (run 21), but for practical reasons we carried out the further experiments with 1,2-dichloroethane. The direct simultaneous deposition of Cu and Fe species together with Ru (catalysts **10** and **11**) did not led to more active catalysts compared with the pure Ru catalysts even if bases, hydrogen acceptors or molecular sieves were added.

In the course of the optimization of the reaction conditions and in order to achieve good catalyst productivities alcohol/catalyst ratios of 100:1 and 200:1 were applied (Table 5). In several cases, catalyst amounts of 2.5–5 mol% were reported in the scientific literature [3]. Ru/TiO_2(P25) (**4**) and Ru/ZrO_2 (**9**) were the most active combinations at a catalyst concentration of 1 mol%, whereas, 0.5 mol% of **4** effected a higher conversion than 0.5 mol% **9** at 100 °C (run 15).

The optimized reaction conditions were applied to other benzylic alcohols and hydroxymethyl pyridines (Table 6). Nearly all of them reacted to the appropriate aldehydes in an excellent selectivity, no other products could be detected by GC. The methyl group with a positive inductive effect increased the aldehyde yield compared with benzaldehyde, whereas, electron-accepting groups led to a decrease. The highest decelerating effect was observed with strong electron accepting nitro substituents or with the hydroxymethyl pyridines, whereas, halogen substituents cause medium yields. This result corresponds with the mechanism of an oxidative dehydrogenation, which is accepted for comparable Ru-catalyzed reactions. An electron-donating substituent facilitates the β-hydride elimination in the reaction cyclus. The alcohol oxidation was not hampered by addition of 5 mol% of hydroquinone as a radical scavenger so that a radical mechanism is not likely. The only substrate that displayed a lower selectivity was 3-methoxy-

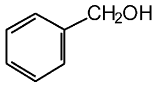
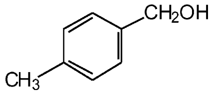
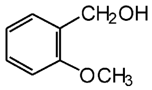
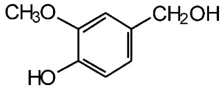
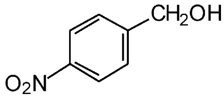
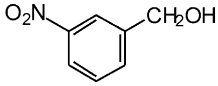
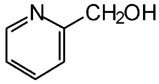
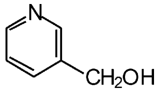
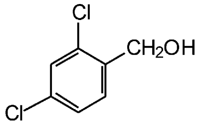
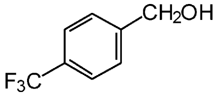
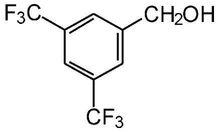
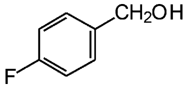
Table 5
Screening of Ru catalysts at different temperatures and S/C ratios

Run	Catalyst	Ru [mmol]	Temperature [°C]	Yield[a] [%]	$n_{aldehyde}/n_{Ru}$
1	**1**	0.01	80	61	61
2	**4**	0.01	80	91	91
3	**9**	0.01	80	94	94
4	**10**	0.01	80	40	40
5	**11**	0.01	80	54	54
6	**1**	0.01	100	72	72
7	**4**	0.01	100	97	97
8	**9**	0.01	100	97	97
9	**10**	0.01	100	64	64
10	**11**	0.01	100	32	32
11	**1**	0.005	80	27	53
12	**4**	0.005	80	60	121
13	**9**	0.005	80	62	125
14	**1**	0.005	100	41	81
15	**4**	0.005	100	94	188
16	**9**	0.005	100	62	124

Reaction conditions: 1 mmol benzyl alcohol, 80 bar (5% O_2/95% argon), 2 h, 7 ml dichloroethane.

[a] Selectivity towards benzaldehyde >99% in each run.

Table 6
Oxidation of substituted benzyl alcohols and hydroxymethyl pyridines

Run	Alcohol	$Yield_{aldehyde}$ [%]	Selectivity [%]	$n_{aldehyde}/n_{Ru}$
1		85	>99	86
2		93	>99	93
3		74	>99	75
4		46	55[a]	21
5		40	>99	39
6		26	>99	23
7		38	>99	23
8		2	>99	1
9		56	>99	50
10		74	>99	78
11		40	>99	37
12		85	>99	79

Reaction conditions: 1 mmol alcohol, 0.01 mmol Ru (**4**), 80 °C, 80 bar 5% O_2/95% argon, 2 h, 7 ml dichloroethane.

[a] 17% benzoic acid.

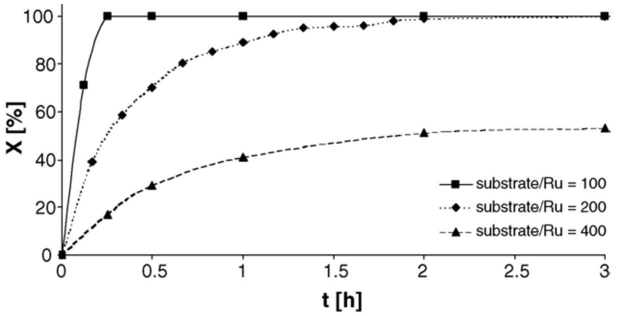


Fig. 5. Oxidation of benzyl alcohol at different substrate/catalyst ratios (reaction conditions 1 mmol benzyl alcohol, 1, 0.5 or 0.25 mol% Ru (catalyst **3**), 80 °C, $pO_2 = 4$ bar, 30 ml $C_2H_4Cl_2$, $S_{\text{benzaldehyde}} > 99\%$).

4-hydroxybenzyl alcohol. Beside the aldehyde also 17% of 3-methoxy-4-hydroxybenzoic acid was found but in this case, the participation of another reaction mechanism via a quinone methide is conceivable.

In a second experimental series the oxidations were operated in 100 ml glass autoclaves using molecular oxygen up to 4 bar. Different Ru/TiO_2(P25) catalysts which were prepared according to wet and plasma chemical methods as well as Ru catalysts with cobalt and manganese as promoter metals were investigated. As expected for such low molar Ru amounts, the conversion X increased with the Ru concentration (Fig. 5). Applying a catalyst concentration of 1 mol% complete conversion to benzaldehyde was observed after 15 min.

Similiarly, catalysts with higher Ru loading induce higher conversions (Fig. 6) but only to a certain level. By correlating catalytic results to particle size and dispersion of the Ru particles on the surface of the support (Table 3), being related to the number of the active catalytic centres, the less active catalyst **12** showed an inhomogeneous distribution of Ru species and particles up to 300 nm. That permits the conclusion of a lower number of active catalytic centres compared with the other investigated catalysts. **12** was included in these experiments with the undoped Ru catalysts, because the Co content was very small and, as the results confirm, did not have any beneficial effect on the conversion.

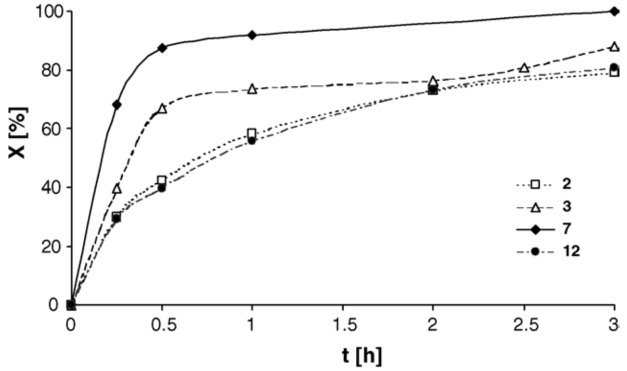


Fig. 6. Oxidation of benzyl alcohol with same masses of differently loaded catalysts (reaction conditions: 1 mmol benzyl alcohol, $T = 80$ °C, $pO_2 = 4$ bar, 30 ml $C_2H_4Cl_2$, $m_{\text{cat}} = 64.5$ mg, $S_{\text{benzaldehyde}} > 99\%$).

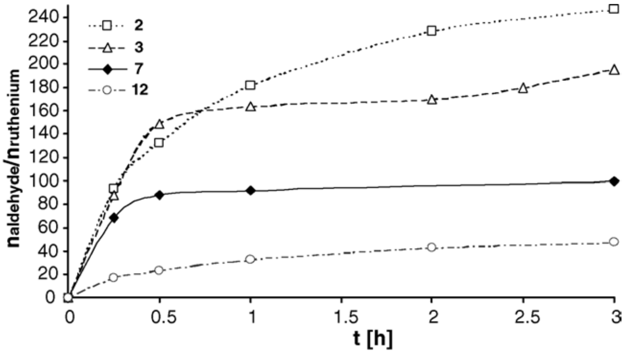


Fig. 7. Productivity of different Ru catalysts as $n_{\text{aldehyde}}/n_{\text{ruthenium}}$ ratio (reaction conditions: 1 mmol benzyl alcohol, $T = 80$ °C, pO_2 4 bar, 30 ml $C_2H_4Cl_2$, $m_{\text{cat}} = 64.5$ mg, $S_{\text{benzaldehyde}} > 99\%$).

The catalysts **2** and **3**, in which very small Ru hydroxyl species are homogeneously distributed, displayed the highest $n_{\text{aldehyde}}/n_{\text{Ru}}$ ratios, this means the highest catalyst productivity, in the oxidation of benzylic alcohol (Fig. 7). Catalyst **2** with a Ru amount of 3.2×10^{-3} mmol and a $n_{\text{aldehyde}}/n_{\text{Ru}}$ ratio of 247 generates two and a half times more benzaldehyde per mmol Ru than catalyst **7** with a ratio of 100 and five times more than **12** with a ratio of 48. Catalyst **2** with almost molecularly disperse Ru species exposes more catalytically active centres than the higher loaded catalysts **7** and **12**. However, the number of accessible Ru species cannot be exactly quantified since a suitable chemisorption method for its determination does not exist.

The plasma chemically prepared catalysts (Fig. 8) were less active than the catalysts synthesized according to wet chemical procedures. This is not surprising since the TEM images showed bigger Ru particles and layer or crust formations. Moreover, ruthenium exists predominantly in the Ru(0) oxidation state with some parts of oxidized Ru in the catalytically active species. This result can be also a reason for the lower activity. Merely catalyst **17** with the lowest Ru loading of 0.2% possessed a similar activity as catalysts **2** and **3** and led to a complete conversion of benzyl alcohol to benzaldehyde within 30 min.

Higher oxygen pressure enhances the oxygen concentration in the reaction solution and at the catalytically active centres. As a result increasing conversions per time unit could be observed

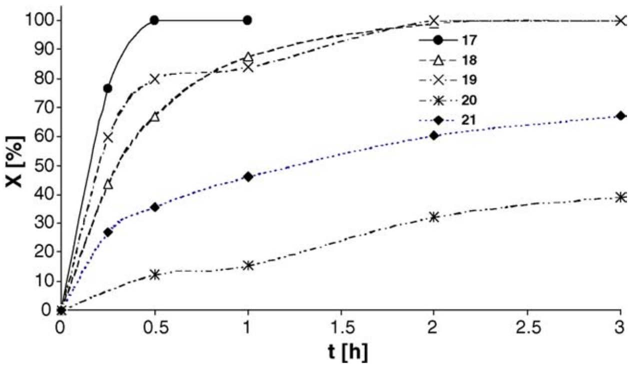


Fig. 8. Oxidation of benzyl alcohol with catalysts prepared by plasma chemical methods (reaction conditions: 1 mol% Ru, 1 mmol benzylalcohol, 80 °C, pO_2 4 bar, 30 ml $C_2H_4Cl_2$, $S_{\text{benzaldehyde}} > 99\%$).

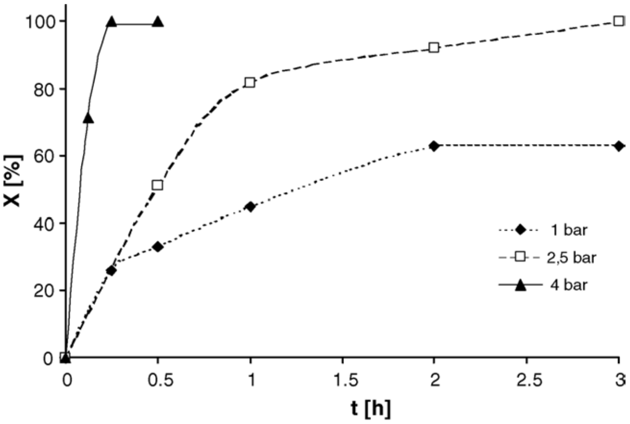


Fig. 9. Oxidation of benzyl alcohol at different oxygen pressures (reaction conditions 1 mol% Ru (**3**), 1 mmol benzyl alcohol, 80 °C, 30 ml $C_2H_4Cl_2$, $S_{benzaldehyde} > 99\%$).

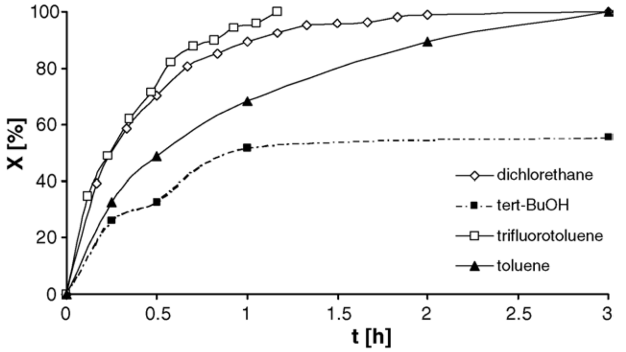


Fig. 10. Oxidation of benzyl alcohol in different solvents (reaction conditions: 0.5 mol% Ru (**3**), 1 mmol benzyl alcohol, 80 °C, pO_2 4 bar, 30 ml solvent, $S_{benzaidehyde} > 99\%$).

(Fig. 9). A high stirring velocity of 1300 rpm was chosen to avoid diffusion-controlled processes.

The most suitable solvents for these oxidations were halogenated hydrocarbons as observed in comparable catalytic oxidations (Fig. 10). It is known that the solubility of oxygen decreases in the sequence halogenated hydrocarbons > hydrocarbons > aqueous systems [70]. Toluene as solvent led to the same degree of conversion albeit in a longer reaction time, whereas, reactions in *tert*-BuOH did not lead to full conversion (max. 56%) and apparently deactivated the catalyst. Apart from the different oxygen concentrations in the investigated solvents the interaction of the solvent with the Ru centres and the varying ability to stabilize catalytic transition states have influence on the catalyst activity.

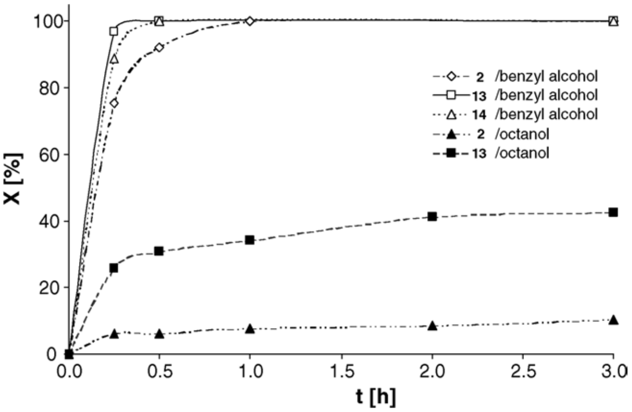


Fig. 11. Oxidation of benzyl alcohol and octanol applying catalysts with Co and Mn promoters (reaction conditions: 1 mol% Ru, 1 mmol alcohol, 80 °C, pO_2 4 bar, 30 ml $C_2H_4Cl_2$, $S_{benzaldehyde} > 99\%$).

Table 7
Reuse of catalysts **2**, **3** and **7**

Run	**2**/conversion [%]	**3**/conversion [%]	**7**/conversion [%]
1	77.1	100.0	76.0
2	18.0	38.7	12.2
3	11.2	7.5	5.2

Reaction conditions: 1 mol% Ru, 1 mmol benzyl alcohol, pO_2 4 bar, $T = 80\,°C$, 30 ml dichloroethane, 15 min, $S_{benzaldehyde} > 99\%$.

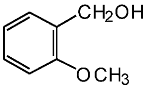
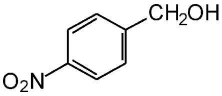
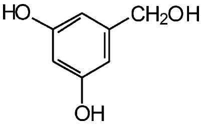
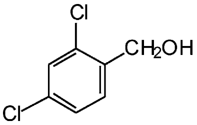
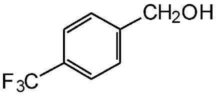
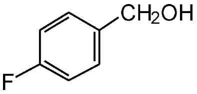
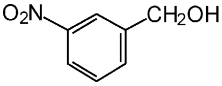
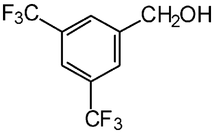
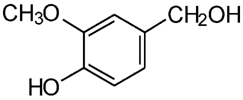
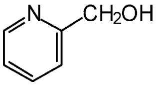
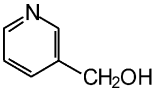
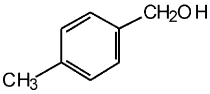
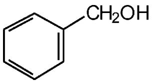
A simple experiment was performed to check if the catalysis is really heterogeneous. For these purposes, the oxidation of benzyl alcohol with catalyst **3** was stopped after 20 min, the catalyst was filtered off and a sample of the filtrate was taken to determine analytically the conversion. The reactor was refilled with the reaction solution, pressurized with oxygen, heated and stirred for an additional hour. The conversion of benzyl alcohol was analyzed again. The values of the measurements were

Table 8
Variation of solvent and molar amount of TBHP in the oxidation of benzyl alcohol

Run	Solvent	TBHP [mmol]	Conversion [%]	$Yield_{aldehyde}$ [%]	$Yield_{acid}$ [%]	$Selectivity_{aldehyde}$ [%]
1	Dichloroethane	1.1	50	20	30	40
2	Dichloroethane	1.1[a]	36	32	4	89
3	Dichloroethane	1.1[a,b]	52	39	13	75
4	*tert*-BuOH	1.1[a]	21	21	–	>99
5	Toluene	1.1[a]	24	24	–	>99
6	Toluene	1.5[a]	30	25	5	82
7	Toluene	2[a]	28	23	5	84
8	Toluene	1.1[a,b]	64	38	26	60
9	Toluene	1.1[a,c]	61	38	23	63

Reaction conditions: 1 mol% Ru (**8**), 1 mmol benzyl alcohol, 7 ml solvent, r.t., 1 h.
[a] Added via syringe pump.
[b] 70 °C.
[c] 70 °C, 2 h.

Table 9
Oxidation of other primary alcohols with TBHP

Run	Alcohol	Conversion [%]	Yield$_{\text{aldehyde}}$ [%]	Yield$_{\text{acid}}$ [%]	Selectivity [%]
1		26	22	4	84
2		7	7	–	>99
3		0		–	
4		47	46	1	97
5		44	44	–	>99
6		46	46	–	>99
7		2	2	–	>99
8		38	38	–	>99
9		4	4	–	>99
10		8	8		>99
11		2	2	–	>99
12		45	39	6	87
13		52	38	–	74
14	1-Octanol	29	7	16	24
15	Cinnamic alcohol	17	17		>99

Reaction conditions: 1 mol% Ru (**7**), 1 mmol alcohol, 1.1 mmol TBHP added via syringe pump, 70 min, 70 °C, 7 ml dichloroethane.

exactly the same after 20 min and 1 h 20 min. The reaction could not be continued after the removal of the solid catalyst. This result serves as proof of truly heterogeneous catalysts.

Doping of the catalyst $W-$Ru0.50/TiO_2(P25) **2** with Co(II) and Mn(II) species led to more active catalysts **13** and **14** in the oxidation of benzyl alcohol even though the Ru content was slightly diminished during the preparation procedure. The complete conversion of the alcohol was observed after 30 min, whereas, catalyst **2** required 1 h (Fig. 11). A more pronounced influence of the Co doping was found in the oxidation of 1-octanol. Whereas, with **2** only 11% of 1-octanal were obtained the yield could be increased with **13** up to 43%. A catalyst $W-$Co0.12/TiO_2(P25) **16** without ruthenium did not exhibit any catalytic activity. In a very recent paper Kozhevnikov and co-workers [71] discuss the cause for the promoting effect of Co in a RuO_2/CoO(OH) catalyst in the facilitation of the catalyst regeneration.

Preparation of a Ru/Mo catalyst by simultaneous or two-step procedures failed. Besides molybdenum only traces of ruthenium could be deposited on titania. The catalyst $W-$Ru0.02/Mo0.64/TiO_2(P25) **15** (0.01 mmol Mo) converted 1 mmol benzyl alcohol in 30 ml dichloroethane to 59% benzaldehyde and 41% benzoic acid at 80 °C and 4 bar oxygen within 3 h.

During the reuse of the Ru catalysts a dramatic decrease of the conversion was observed (Table 7). Since, the leaching of Ru was low (0 to max. 4% of the used Ru, possibly introduced by incomplete separation of the finely powdered catalyst) this drop could not be explained by Ru loss. Treatment with 1 M NaOH or with molecular oxygen did not improve the catalyst performance. Therefore, the used catalysts were examined with analytical methods. A change in the particle size of the Ru species in the used catalysts could not be detected by TEM. The oxidation state of Ru in the used catalysts **2** and **3** remained unchanged at +3. The most informative result was obtained by FTIR spectroscopy (Figs. 3 and 4). The used catalyst shows intensive bands in the C–H stretch and the finger print region (Fig. 3d,e), which point to the formation of organic adsorbates. The bands at 1750–1687 cm^{-1} can be assigned to carbonyl vibrations (Fig. 4b,c), the bands around 1600 cm^{-1} result from C=C vibrations and the bands around 1412 cm^{-1} from C–H deformation vibrations. After evacuation at 300 °C, water (band around 1642 cm^{-1}) is removed, whereas, the adsorbates remain. These results refer to a deactivation and blocking of the active centres by irreversible deposition of either the aldehyde or of oligomeric or polymeric products formed from the aldehyde and alcohol by consecutive reactions [72]. The additional bands at 2058/1975 cm^{-1} (Fig. 4b) are assigned to CO, adsorbed on Ru sites, possibly formed upon decomposition of the adsorbates at 300 °C.

3.3. *Oxidations with TBHP and NaOCl*

From a practical point of view other technically significant oxidants such as *tert*-BuOOH (TBHP) and NaOCl were also

Table 10
Oxidation of benzyl alcohol with bleach as oxidant

Run	Catalyst	Ru [mmol]	Solvent	NaOCl [mmol]	Conversion [%]	$Yield_{aldehyde}$ [%]	$Yield_{benzoic\ acid}$ [%]	$Selectivity_{aldehyde}$ [%]
1	–	–	3.5 ml H_2O/3.5 ml dichloroethane	1.1[a]	20	20	–	>99
2	**8**	0.01	3.5 ml H_2O/3.5 ml *tert*-BuOH	1.1	44	44	–	>99
3	**8**	0.01	3.5 ml H_2O/3.5 ml *tert*-BuOH	1.1[a]	66	66	–	>99
4	**8**	0.01	7 ml *tert*-BuOH	1.1[a]	42	38	4	90
5	**8**	0.01	3.5 ml H_2O/3.5 ml dichloroethane	1.1[a]	83	83	–	>99
6	**8**	0.01	3.5 ml H_2O/3.5 ml dichloroethane	1.1[a,b]	76	73	3	97
7	**8**	0.005	3.5 ml H_2O/3.5 ml dichloroethane	1.1[a,b]	77	77	–	>99
8	**1**	0.01	3.5 ml H_2O/3.5 ml dichloroethane	1.1[a]	74	73	1	98
9	**9**	0.01	3.5 ml H_2O/3.5 ml dichloroethane	1.1[a]	77	76	1	98
10	**17**	0.005	3.5 ml H_2O/3.5 ml dichloroethane	1.1[a]	92	36	56	39
11	**18**	0.005	3.5 ml H_2O/3.5 ml dichloroethane	1.1[a]	47	24	23	50
12	**10**	0.01	3.5 ml H_2O/3.5 ml dichloroethane	1.1[a]	75	73	2	97
13	**11**	0.01	3.5 ml H_2O/3.5 ml dichloroethane	1.1[a]	72	70	2	97
14	**13**	0.005	3.5 ml H_2O/3.5 ml dichloroethane	1.1[a]	38	19	19	50
15	**14**	0.005	3.5 ml H_2O/3.5 ml dichloroethane	1.1[a]	85	74	11	87
16	**15**	0.005[c]	3.5 ml H_2O/3.5 ml dichloroethane	1.1[a]	39	9	30	23
17	**21**	0.005	3.5 ml H_2O/3.5 ml dichloroethane	1.1[a]	100	0	100	0
18	**8**	0.01	3.5 ml H_2O/3.5 ml dichloroethane	1.3[a]	85	81	4	95
19	**8**	0.01	3.5 ml H_2O/3.5 ml dichloroethane	1.5[a]	100	86	14	86
20	**8**	0.01	3.5 ml H_2O/3.5 ml dichloroethane	2[a]	100	74	26	74
21	**1**	0.01	3.5 ml H_2O/3.5 ml dichloroethane	1.5[a]	80	78	2	97
22	**9**	0.01	3.5 ml H_2O/3.5 ml dichloroethane	1.5[a]	90	88	2	98
23	**10**	0.01	3.5 ml H_2O/3.5 ml dichloroethane	1.5[a]	97	91	6	94

Reaction conditions: 1 mmol benzyl alcohol, r.t., 70 min.

[a] Added via syringe pump.

[b] 130 min.

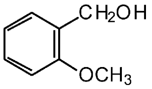
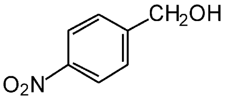
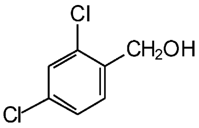
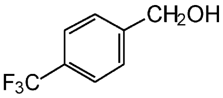
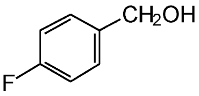
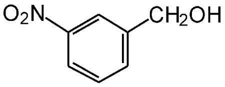
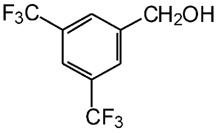
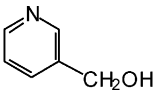
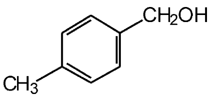
[c] 0.005 mmol Mo.

Table 11
Oxidation of benzyl alcohol at different pH values

Catalyst	Solvent	pH	NaOCl [mmol]	Conversion [%]	Yield$_{\text{aldehyde}}$ [%]	Yield$_{\text{benzoic acid}}$ [%]	Selectivity$_{\text{aldehyde}}$ [%]
8	3.5 ml buffer/3.5 ml dichloroethane	9	1.1	65	61	4	95
8	3.5 ml buffer/3.5 ml dichloroethane	10	1.1	65	62	3	96
8	3.5 ml buffer/3.5 ml dichloroethane	11	1.1	73	69	4	95
8	3.5 ml buffer/3.5 ml dichloroethane	12	1.1	67	64	3	96
8	3.5 ml buffer/3.5 ml dichloroethane	13	1.1	64	60	4	95

Reaction conditions: 0.005 mmol Ru, 1 mmol benzyl alcohol, r.t, 70 min; NaOCl added via syringe pump.

Table 12
Oxidation of other primary alcohols

Run	Alcohol	Conversion [%]	Yield$_{\text{aldehyde}}$ [%]	Yield$_{\text{acid}}$ [%]	Selectivity$_{\text{aldehyde}}$ [%]
1		62	61	1	98
2		100	99	1	99
3		62	49	13	80
4		55	50	5	91
5		67	66	1	99
6		35	34	1	96
7		58	58	–	>99
8		0	–	–	–
9		73	72	1	98
10	1-Octanol	36	28	8	77
11	Cinnamic alcohol	20	7; 13%benzaldehyde	37	
12	*N*-Boc-D-leucinol	2	2	–	>99
13	2-Phenoxyethanol	31	7	24	23

Reaction conditions: (**8**) 1 mmol alcohol, 3.5 ml H_2O/3.5 ml dichloroethane, r.t., 70 min; NaOCl added via syringe pump.

Table 13
Upscaling and solvent-free oxidation of benzyl alcohol with bleach

Catalyst	Ru [mmol]	Benzyl alcohol [mmol]	Solvent [ml]	NaOCl [mmol]	Conversion [%]	Yield$_{aldehyde}$ [%]	Yield$_{acid}$ [%]	Select$_{aldehyde}$ [%]
7[a]	0.5	50	175 H_2O/175 dichloroethane	51	77	74	4	95
6[b]	1.0	100	99.4 NaOCl sol./50 dichloroethane	110	74	73	1	99
8[c]	0.01	1	3.5 H_2O	1.1	64	55	9	85

Reaction conditions: r.t., 70 min, NaOCl added via a syringe pump or a dropping funnel; Ru leaching: [a]0 wt.% referring to the applied Ru amount. [b]0.1 wt.% referring to the applied Ru amount. [c]Not determined.

tested in oxidations with the new Ru catalysts. Homogeneous and immobilized Ru complexes as well as heterogeneous Ru catalysts with ruthenium in different oxidation states are known to oxidize alcohols to aldehydes or ketones with these types of oxidants [73–79]. Therefore, it was interesting to investigate the scope and limitations of the newly prepared catalysts. Attempts of oxidation with H_2O_2 failed due to the catalase activity of ruthenium.

3.4. TBHP

The conversion of benzyl alcohol with TBHP succeeded only with moderate performance (Table 8). The addition of 1.1 equivalent of TBHP was carried out via a syringe pump at room temperature to avoid overoxidation to benzoic acid. The most suitable solvent was dichloroethane.

Substituted benzyl alcohols as well as other primary alcohols could be oxidized with low or medium yields to the corresponding aldehydes (Table 9). Benzyl alcohols with electron withdrawing groups (e.g. runs 2, 5–8) showed high selectivities towards the aldehydes.

Beside ruthenium the TEMPO/NaOCl combination, especially in the presence of NaBr (formation of NaOBr), was described as a well-suited catalytic system for alcohol oxidation [5,80,81]. Other successful “green” attempts represent the metal-free phase transfer oxidation of alcohols with hypochlorites [82–85] and the oxidation in room temperature ionic liquids [86].

The advantage of our heterogeneous catalysts should be the easy separation from the products and the oxidative stability in the presence of NaOCl. A conversion of 20% within 70 min was found under the two-phase reaction conditions (Table 10, run 1) without any catalyst. Using catalyst **8**, the conversion could be increased to 83% with an excellent selectivity of 99% (run 5). At longer reaction times (130 min), overoxidation to benzoic acid was observed (run 6). The biphasic solvent system H_2O/dichloroethane was superior to *tert*-BuOH. The addition of bleach via a syringe pump was indispensable (run 2 versus run 3). Also with other supports high selectivities and good aldehyde yields could be achieved (runs 8 and 9). Oxidant/substrate ratios higher than 1.1 led to higher proportions of acid even if the conversion and aldehyde yield increased (runs 18–23). The application of plasma chemical prepared catalysts provoked clearly unselective oxidations with high acid yields although only 0.5 mol% catalyst was used (runs 10 and 11). Doping of the Ru catalysts with a second metal, such as Cu, Fe, Co, and Mn, worsened the aldehyde selectivity (runs 12–17). Catalyst **15** containing mainly Mo as the catalytically active metal and only traces of Ru showed a low aldehyde selectivity of 23% (run 16). With the plasma chemically prepared catalyst **21** containing Ru and Co the selective oxidation to benzoic acid was observed (run 17). Probably, a radical oxidation to benzoic acid was caused or facilitated by the dopants.

The variation of the pH value in the basic range did not have any significant influence on the yield and catalyst selectivity (Table 11). In all batches small amounts of benzoic acid were found.

The oxidation of other primary alcohols with bleach brought about different results (Table 12). Most of the substituted benzyl alcohols reacted in 55–100% conversion and 80 to >99% selectivity to the aldehydes. Only 3-nitrobenzyl alcohol and 3-hydroxymethyl pyridine were less reactive or non-reactive, respectively. The investigated aliphatic alcohols could be converted to the aldehydes only with minor yields. Overoxidation to the aliphatic acid or, as in the case of cinnamic alcohol, Ru-catalyzed C=C cleavage [87] took place.

The upscaling and increase of substrate concentration (Table 13, runs 1 and 2) were feasible without lowering the benzaldehyde selectivity. However, in the absence of an organic solvent, a decrease in conversion and aldehyde selectivity (run 3) was observed. Probably, the diffusion of the oxidant through the phase interfaces and thus the oxidation to the aldehyde were hampered in comparison with the H_2O/dichloroethane system. With regard to the Ru concentration of 1 ppm in the product solution (run 2) one should have in mind that the separation of the catalysts from the product was carried out by centrifugation. Therefore, it cannot be excluded that traces of catalyst remained in the product.

4. Conclusions

Wet chemically prepared Ru/TiO_2(P25) catalysts with a Ru loading of 0.5–0.7 wt.% were found to be highly active in the oxidation of benzyl alcohol and substituted benzyl alcohols with molecular oxygen. Not only the Ru loading but also the size of the catalytically active particles have a strong influence on the catalytic activity. Catalysts with homogeneously dispersed Ru species with particle sizes of $\leq$1–2 nm showed the best results. Using the microwave plasma-enhanced CVD preparation method, an analogous dispersion with small Ru particles could not be generated on the surface of the support. In this case, Ru was shown to exist predominantly in the oxidation state 0, as compared with +3 in the wet chemically prepared catalysts. These findings should account for the inferior activity of the MPECVD catalysts. As an exception to these results a catalyst with a very low Ru loading of 0.2% and particle sizes $\leq$5 nm converted benzyl alcohol completely to benzaldehyde in a rather short reaction time of 30 min. Halogenated solvents and an oxygen pressure of 4 bar were found to be the optimal reaction conditions. The addition of promoter metals such as Co and Mn improved the conversion, e.g. in the oxidation of the aliphatic alcohol 1-octanol. Further investigations have to be carried out in order to identify more effective combinations and loadings of such promoter metals. With bleach and TBHP as oxidants, lower aldehyde yields were obtained in general, however the Ru amount could not be increased due to overoxidation. Promoter metals had a detrimental effect on conversion and selectivity with these oxidants.

Acknowledgements

The authors acknowledge gratefully the financial support of the German Federal Ministry of Education and Research (BMBF) (project CTCH03036801) and Lanxess Deutschland GmbH. Thanks are dedicated to Mrs. S. Ziemann, Mrs. C. Domke and Mr. R. Eckelt for their technical assistance.

References

[1] J.-E. Bäckvall (Ed.), Modern Oxidation Methods, Wiley-VCH, 2004.

[2] R.A. Sheldon, I.W.C.E. Arends, A. Dijksman, Catal. Today 57 (2000) 157.

[3] T. Mallat, A. Baiker, Chem. Rev. 104 (2004) 3037;
T. Mallat, A. Baiker, Cheminform 35 (36) (2004).

[4] I.E. Marko, P.R. Giles, M. Tsukazaki, I. Chellé-Regnaut, A. Gautier, R. Dumeunier, F. Philippart, K. Doda, J.-L. Mutonkole, S.M. Brown, C.J. Urch, Adv. Inorg. Chem. 56 (2004) 211.

[5] R.A. Sheldon, I.W.C.E. Arends, G.-J. Ten Brink, A. Dijksman, Ace. Chem. Res. 35 (2002) 774.

[6] I.W.C.E. Arends, R.A. Sheldon, Appl. Catal. A: Gen. 212 (2001) 175.

[7] M.S. Sigman, D.R. Jensen, S. Rajaram, Curr. Op. Drug Disc. Dev. 6 (2002) 860.

[8] B.-Z. Zhan, A. Thompson, Tetrahedron 60 (2004) 2917.

[9] J. Muzart, Tetrahedron 59 (2003) 5789.

[10] G.J. Ten Brink, I.W.C.E. Arends, R.A. Sheldon, Science 287 (2000) 1636.

[11] M. Caravati, J.-D. Grunwaldt, A. Baiker, Catal. Today 91/92 (2004) 1.

[12] U.R. Pillai, E. Sahle-Demessie, Green Chem. 6 (2004) 161.

[13] C. Keresszegi, T. Bürgi, T. Mallat, A. Baiker, J. Catal. 211 (2002) 244.

[14] M. Caravati, J.-D. Grunwaldt, A. Baiker, Phys. Chem. Chem. Phys. 7 (2005) 278.

[15] B.P. Buffin, J.P. Clarkson, N.L. Belitz, A. Kundu, J. Mol. Catal. A: Chem. 225 (2005) 111.

[16] V.B. Sharma, S.L. Jain, B. Sain, Tetrahedron Lett. 44 (2003) 383.

[17] M. Gilhespy, M. Lok, X. Baucherel, Chem. Commun. (2005) 1085.

[18] F. Rajabi, B. Karimi, J. Mol. Catal. A: Chem. 232 (2005) 95.

[19] S.E. Martin, D.F. Suarez, Tetrahedron Lett. 43 (2002) 4475.

[20] P.A. Shapley, N. Zhang, J.L. Allen, D.H. Pool, H.-C. Liang, J. Am. Chem. Soc. 122 (2000) 1079.

[21] K.S. Coleman, M. Coppe, C. Thomas, J.A. Osborn, Tetrahedron Lett. 40 (1999) 3723.

[22] C. Döbler, G.M. Mehltretter, U. Sundermeier, M. Eckert, H.-C. Militzer, M. Beller, Tetrahedron Lett. 42 (2001) 8447.

[23] I.W.C.E. Arends, R.A. Sheldon, in: J.-E. Bäckvall (Ed.), Modern Oxidation Methods, Wiley-VCH, 2004, p. 83.

[24] R. Naik, P. Joshi, R.K. Deshpande, Catal. Commun. 5 (2004) 195.

[25] P. Gamez, I.W.C.E. Arends, J. Reedijk, R.A. Sheldon, Chem. Commun. (2003) 2414.

[26] G. Ragagnin, B. Betzemeier, S. Quici, P. Knochel, Tetrahedron 58 (2002) 3985.

[27] P. Lahtinen, H. Korpi, E. Haavisto, M. Leskelä, T. Repo, J. Comb. Chem. 6 (2004) 967.

[28] W. Tsai, Y.-H. Liu, S.-M. Peng, S.-T. Liu, J. Organomet. Chem. 60 (2005) 415.

[29] I.E. Marko, A. Gautier, R. Dumeunier, K. Doda, F. Philippart, S.M. Brown, C.J. Urch, Angew. Chem. 116 (2004) 1614.

[30] S. Velusamy, T. Punniyamurthy, Org. Lett. 6 (2004) 217.

[31] S.R. Reddy, S. Das, T. Punniyarmurthy, Tetrahedron Lett. 45 (2004) 3561.

[32] S. Velusamy, M. Ahamed, T. Punniyamurthy, Org. Lett. 6 (2004) 4821.

[33] P.V. Prabhakaran, S. Venkatachalam, K.N. Ninan, Eur. Polym. J. 35 (1999) 1743.

[34] Y.-C. Son, V.D. Makwana, A.R. Howell, S.L. Suib, Angew. Chem. 113 (2001) 4410.

[35] S.-I. Murahashi, N. Komiya, in: J.-E. Bäckvall (Ed.), Modern Oxidation Methods, Wiley-VCH, 2004, p. 165.

[36] R. Tang, S.E. Diamond, N. Neary, F. Mares, J. Chem. Soc. Chem. Commun. 562 (1978).

[37] I.E. Marko, P.R. Giles, M. Tsukazaki, I. Chellé-Regnaut, C.J. Urch, S.M. Brown, J. Am. Chem. Soc. 119 (1997) 12661.

[38] M. Hasan, M. Musawir, P.N. Davey, I.V. Kozhevnikov, J. Mol. Catal. A: Chem. 180 (2002) 77.

[39] A.M. Khenkin, L.J.W. Shimon, R. Neumann, Inorg. Chem. 42 (2003) 3331.

[40] M. Lee, S. Chang, Tetrahedron Lett. 7507 (2000).

[41] A. Miyata, M. Muratami, R. Irie, T. Katsuki, Tetrahedron Lett. 42 (2001) 7067;
A. Miyata, M. Furukawa, R. Irie, T. Katsuki, Tetrahedron Lett. 43 (2002) 3481;
K. Masutani, T. Uchida, R. Irie, T. Katsuki, Tetrahedron Lett. 41 (2000) 5119;
A. Tashiro, A. Mitsuishi, T. Katsuki, SynLett. 12 (2003) 1868;
R. Irie, T. Katsuki, Chem. Rec. 4 (2004) 96.

[42] M. Rodriguez, I. Romero, A. Llobet, A. Deronzier, M. Biner, T. Parella, H. Stoeckli-Evans, Inorg. Chem. 40 (2001) 4150.

[43] R. Lenz, S.V. Ley, J. Chem. Soc. Perkin Trans. 1 (1997) 3291.

[44] P. Langer, J. Prakt. Chem. 342 (2000) 728.

[45] E. Takezawa, S. Sakaguchi, Y. Ishii, Organic Lett. 1 (1999) 713, 4.

[46] M. Matsumoto, S. Ito, Chem. Commun. 907 (1981).

[47] A. Hanyu, E. Takezawa, S. Sakaguchi, Y. Ishii, Tetrahedron Lett. 39 (1998) 5557.

[48] R.H. Meijer, G.B.W.L. Ligthart, J. Meuldijk, J.A.J.M. Vekemans, L.A. Hulshof, A.M. Mills, H. Kooijman, A.L. Spek, Tetrahedron 60 (2004) 1065.

[49] A. Dijksman, I.W.C.E. Arends, R.A. Sheldon, Chem. Commun. 1591 (1999);
A. Dijksman, A. Martino-Gonzalez, A. Mairata, I. Payeras, I.W.C.E. Arends, R.A. Sheldon, J. Am. Chem. Soc. 123 (2001) 6823.

[50] A.J.M. Elzinga, Y.-X. Li, I.W.C.E. Arends, R.A. Sheldon, Tetrahedron: Asymmetry 13 (2002) 879.

[51] M. Takahashi, K. Oshima, S. Matsubara, Tetrahedron Lett. 44 (2003) 9201.

[52] J.-E. Bäckvall, R.L. Chowdhury, U. Karisson, J. Chem. Soc. Chem. Commun. 473 (1991);
A. Zsigmond, F. Notheisz, G. Csjemyik, J.-E. Bäckvall, Topics Catal. 19 (2002) 119;
G. Csjemyik, A.H. Ėll, L. Fadini, B. Pugin, J.-E. Bäckvall, J. Org. Chem. 67 (2002) 1657;

J.-E. Bäckvall, A.K. Awasthi, Z.D. Renko, J. Am. Chem. Soc. 109 (1987) 4750;
J.-E. Bäckvall, R. Bruce, H. Grennberg, M.M. Mader, A.K. Awasthi, J. Am. Chem. Soc. 112 (1990) 5160.
[53] R.A. Sheldon, I.W.C.E. Arends, A. Dijksman, Catal. Today 57 (2000) 157.
[54] H. Ji, T. Mizugaki, K. Ebitani, K. Kaneda, Tetrahedron Lett. 43 (2002) 7179;
H. Ji, K. Ebitani, T. Mizugaki, K. Kaneda, React. Kinet. Catal. Lett. 78 (2003) 73;
K. Ebitani, H.-B. Ji, T. Mizugaki, K. Kaneda, J. Mol. Catal. A: Chem. 212 (2004) 161.
[55] A.M.J. Joma, A.E.M. Boelrijk, H.J. Hoorn, J. Reedijk, React. Funct. Polym. 29 (1996) 101.
[56] A. Bleloch, B.F.G. Johnson, S.V. Ley, A.J. Price, D.S. Shephard, A.W. Thomas, Chem. Commun. (1999) 1907.
[57] M.K. Dalai, R.N. Ram, J. Mol. Catal. A: Chem. 159 (2000) 285.
[58] M.K. Dalai, M.J. Upadhyay, R.N. Ram, J. Mol. Catal. A: Chem. 142 (1999) 325.
[59] M. Magliaro, R. Ciriminna, Tetrahedron Lett. 42 (2001) 4511.
[60] H.B. Friedrich, N. Singh, Tetrahedron Lett. 41 (2000) 3971.
[61] T. Matsushita, K. Ebitani, K. Kaneda, Chem. Commun. (1999) 265;
K. Kaneda, T. Yamashita, T. Matsushita, K. Ebitani, J. Org. Chem. 63 (1998) 1750.
[62] K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, J. Am. Chem. Soc. 122 (2000) 7144.
[63] Z. Opre, J.-D. Grunwaldt, M. Maciejewski, D. Ferri, T. Mallat, A. Baiker, J. Catal. 230 (2005) 406.
[64] M. Matsumoto, N. Watanabe, J. Org. Chem. 49 (1984) 3436.
[65] A. Wolfson, S. Wuyts, D.E. De Vos, I.F.J. Vankelecom, P.A. Jacobs, Tetrahedron Lett. 43 (2002) 8107.
[66] K. Yamaguchi, N. Mizuno, Angew. Chem. 114 (2002) 4720.
[67] K. Yamaguchi, N. Mizuno, Chem. Eur. J. 9 (2003) 4353.
[68] P.J. Carl, S.C. Larsen, J. Catal. 196 (2000) 352.
[69] K. Hadjivanov, J.-C. Lavalley, J. Lamette, F. Mauge, J. Saint-Just, M. Che, J. Catal. 176 (1998) 415.
[70] N.J. Turro, http://turroserver.chem.columbia.edu/courses/MMPChapterUpdates/Chapter14current.pdf.
[71] T.L. Stuchinskaya, M. Musawir, E.F. Kozhevnikova, I.V. Kozhevnikov, J. Catal. 231 (2005) 41.
[72] M. Besson, P. Gallezot, in: R. Sheldon, H. van Bekkum (Eds.), Fine Chemicals through Heterogeneous Catalysis, Wiley-VCH, 2000, p. 491.
[73] H.B. Friedrich, Plat. Met. Rev. 43 (1999) 94.
[74] C.-M. Che, K.-W. Cheng, M.C.W. Chan, T.-C. Lau, C.-K. Mak, J. Org. Chem. 65 (2000) 7996.
[75] W.-H. Cheung, W.-Y. Yu, W.-P. Yip, N.-Y. Zhu, C.-M. Che, J. Org. Chem. 67 (2002) 7716.
[76] D. Chatterjeea, A. Mitra, B.C. Roy, J. Mol. Catal. A: Chem. 161 (2000) 17.
[77] L. Gonsalvi, I.W.C. Arends, R.A. Sheldon, Org. Lett. 4 (2002) 1659.
[78] L. Gonsalvi, I.W.C. Arends, P. Moilanen, R.A. Sheldon, Adv. Synth. Catal. 345 (2003) 1321.
[79] G. Balavoine, C. Eskenazi, F. Meunier, J. Mol. Catal. 30 (1985) 125.
[80] G. Pozzi, M. Cavazzini, O. Holczknecht, S. Quici, I. Shepperson, Tetrahedron Lett. 45 (2004) 4249.
[81] C. Fraschini, M.R. Mignon, Carbohydr. Res. 328 (2000) 585.
[82] M. Schneider, J.-V. Weber, P. Faller, J. Org. Chem. 47 (1982) 364.
[83] G.A. Mirafzal, A.M. Lozeva, Tetrahedron Lett. 39 (1998) 7263.
[84] J.-S. Do, T.-C. Chou, Ind. Emg. Chem. Res. 29 (1990) 1095.
[85] G.A. Lee, H.H. Freedman, Tetrahedron Lett. 17 (1976) 1641.
[86] H. Xie, S. Zjang, H. Duan, Tetrahedron Lett. 45 (2004) 2013.
[87] K. Kaneda, S. Haruna, T. Imanaka, K. Kawamoto, J. Chem. Soc. Chem. Commun. 1467 (1990).