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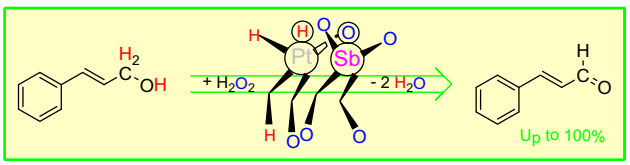
Antimony-Modified Platinum Catalysts for the Selective and Stable Oxidation of Cinnamyl Alcohol with Hydrogen Peroxide

Sandile Langa[1] · Benias C. Nyamunda[1] · Josef Heveling[1,2]

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Abstract Platinum-antimony and platinum-bismuth deposited on activated carbon were prepared by various methods. The materials were characterized by nitrogen physisorption, X-ray diffraction and high-resolution transmission electron microscopy. The samples were tested as catalysts for the selective oxidation of cinnamyl alcohol to cinnamaldehyde, using H_2O_2 as the oxidant. 5%Pt–5%Sb/C shows selectivities in excess of 98 % in both water and toluene as the reaction medium. In comparison, state-of-the art bismuth catalysts give selectivities of 73–95 % (in water) and 84 % (in toluene).

Graphical Abstract



Keywords Selective oxidation · Hydrogen peroxide · Platinum · Antimony · Sonication · Cinnamyl alcohol · Cinnamaldehyde

✉ Josef Heveling
hevelingj@tut.ac.za

[1] Department of Chemistry, Tshwane University of Technology, Pretoria 0001, South Africa

[2] Institute for NanoEngineering Research, Tshwane University of Technology, Pretoria 0001, South Africa

1 Introduction

The selective oxidation of primary alcohols to aldehydes is an important transformation in organic synthesis. Aldehydes are used in carbon–carbon bond forming reactions such as Aldol, Grignard, Wittig and Michael reactions for the synthesis of fine chemicals. For environmental reasons, the use of stoichiometric oxidizing agents should be avoided. There is therefore a need to develop catalytic methods that use clean oxidants, such as molecular oxygen or hydrogen peroxide [1]. The oxidation of alcohols, aldehydes and carbohydrates with oxygen occurs over Pd or Pt catalysts under mild conditions, that is temperatures of 293–353 K and atmospheric pressure [2, 3]. A possible weakness of unmodified Pd and Pt catalysts is their deactivation caused by over-oxidation of the metal surface and by poisoning via the formation of strongly adsorbing side-products [2–4]. Many research groups have shown that the presence of a second metal component (containing Bi or Pb) is advantageous in terms of improving the catalytic activity and selectivity and in prolonging catalyst lifetime [3, 5–9]. Bismuth-modified platinum catalysts are commercially available from several precious-metal-catalyst producers.

This study compares carbon-supported antimony-modified platinum with bismuth-modified systems. The oxidation of cinnamyl alcohol is used as the test reaction. Apart from our recent patent application [10], we could not find any evidence in the literature that platinum–antimony catalysts have already been used for liquid-phase oxidation reactions. However, Pt–Sb catalysts were reported for fuel-cell applications [11], more precisely for formic acid [12, 13] and methanol [14] electro-oxidation reactions. Chemically Sb resembles Bi. It can therefore be expected that antimony also acts as a catalyst modifier.

2 Experimental

2.1 Chemicals and Commercial Catalysts

Trans-cinnamaldehyde (>98.5 % purity), cinnamyl alcohol (>98 %) and *trans*-cinnamic acid (>99.5 %) were purchased from Alfa Aesar. $H_2PtCl_6{\cdot}6H_2O$ (>99.9 %), $SbCl_3$ (>98 %), $Bi(NO_3)_3{\cdot}5H_2O$ (>98 %), hydrazine monohydrate (64–65 % hydrazine in water) and activated carbon (Darco KB-G) were purchased from Sigma-Aldrich, Triton X-100 [4-(1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol] (>98 %) and methanol (99.8 %) from BDH-Merck, aqueous hydrogen peroxide (30 %), $NaBH_4$ (>98.5 %), biphenyl (>98 %) and CH_2Cl_2 (>99 %) from SMM Instruments, and toluene (99.8 %) from Rochelle Chemicals. A commercial 5%Pt–5%Bi/C catalyst (CF105RA/W, containing 53.9 % water) was obtained from Evonik.

2.2 Synthesis of Carbon-Supported Pt–Sb and Pt–Bi Catalysts

Synthesis of carbon-supported Pt and Pt–Sb catalysts by deposition of pre-reduced nanoparticles: a carbon-supported 5%Pt–5%Sb catalyst was prepared by dissolving 0.105 g of $H_2PtCl_6{\cdot}6H_2O$ in 30 ml deionized water, to which 6 ml of Triton X-100 was added. To this, 30 ml of 0.05 M aqueous $NaBH_4$ was added dropwise under stirring to reduce the coordinated platinum ions. After addition of a solution of 0.0935 g $SbCl_3$ in 50 ml deionized water, another 50 ml of 0.05 M aqueous $NaBH_4$ was added dropwise to reduce the antimony ions. Finally, 0.9 g of activated carbon was added and the mixture was stirred for 6 h to give metal nanoparticles supported on activated carbon. The mixture was filtered, washed several times with 100 ml deionized water, and the residue was dried. A 5%Pt/C catalyst and catalysts with varying antimony to platinum loadings were prepared accordingly by adjusting the stoichiometry of the ingredients.

Synthesis of carbon-supported Pt–Bi catalysts by reductive deposition: a carbon-supported 5%Pt–5%Bi catalyst was prepared by dissolving 0.105 g $H_2PtCl_6{\cdot}6H_2O$ and 0.116 g $Bi(NO_3)_3{\cdot}5H_2O$ in a mixture of methanol (50 ml) and water (50 ml), to which 6 ml of Triton X-100 and 0.9 g of activated carbon were added. Under vigorous stirring 3 ml of a solution of hydrazine monohydrate in water (64–65 % hydrazine) was added. The mixture was stirred for 6 h to give metal nanoparticles supported on activated carbon. The mixture was filtered, washed several times with 100 ml deionized water, and the residue was dried. Catalysts with varying platinum to bismuth loadings were prepared accordingly by adjusting the stoichiometry of the ingredients.

Synthesis of carbon-supported 5%Pt–5%Sb and 5%Pt–5%Bi catalysts by reductive deposition under sonication: $H_2PtCl_6{\cdot}6H_2O$ (0.113 g) and $SbCl_3$ (0.0935 g) or $Bi(NO_3)_3{\cdot}5H_2O$ (0.116 g) were added to a mixture of methanol (50 ml) and water (50 ml). The solution was sonicated for 6 h at autogenic temperature ($\leq$64 °C) using a Hielscher UP50H ultrasonic processor (sonication amplitude 100 %, wave cycle: 1). Triton X-100 (3 ml) and 0.9 g of activated carbon were added. Under continued sonication 0.2 ml of hydrazine monohydrate (64–65 % hydrazine in water) was added to reduce the metal ions and to precipitate the metals onto the support. The mixture was sonicated for another 4 h. The slurry was filtered, and the catalysts were washed thoroughly with deionized water. All catalysts prepared under sonication are designated with an "s", e.g. 5%Pt–5%Sb/C–s.

2.3 Oxidation Reactions

Cinnamyl alcohol (0.013 mol), 20 ml of deionized water and 0.2 g of the catalyst were added to a 3-necked flask, equipped with a condenser and a peristaltic pump. The reaction mixture was refluxed at 60 °C and vigorously stirred. H_2O_2 (0.015 mol) was pumped over 2 h as an aqueous solution directly into the reaction mixture. If not otherwise indicated, solutions containing 30 % H_2O_2 were used. During the course of the reaction, samples were withdrawn at regular time intervals, while stirring was continued. The same procedure was used when suspending the catalyst in 20 ml toluene instead of deionized water. After the runs, the catalyst was filtered off with a membrane filter and dried. For the testing of recycled catalysts the molar ratio of all active ingredients was kept constant, but the amount of solvent was not changed. (Recycled catalysts carry the appendix "r", e.g. 5%Pt–5%Sb/C–r.)

2.4 Characterization of the In-House Made Catalysts and of the Carbon Support

The mass% of platinum, antimony and bismuth deposited on the activated carbon were determined by inductively coupled plasma optical emission spectrometry (ICP-OES), using a Spectro Arcos instrument. X-ray powder diffraction (XRD) of the catalysts was performed on a Bruker D8 Advance X-ray diffractometer, using nickel-filtered Cu K_α radiation (40 kV, 40 mA). Phases were identified with the help of Bruker's DIFFRAC^{plus} evaluation software (EVA) in combination with the ICDD powder diffraction database (International Centre for Diffraction Data). The Scherrer equation [15] was used to determine the crystallite size of the supported platinum. For transmission electron microscopy and scanning transmission electron microscopy a

Jeol 2100F HRTEM was employed; particle-size distributions were determined with the help of the ImageJ software. Physisorption measurements (BET) were carried out using a Micromeritics ASAP 2020 surface area and porosity analyzer.

2.5 Analysis of the Reaction Mixtures

The reaction mixtures were diluted with methanol and analyzed on an Agilent 1200 reversed phase high-performance liquid chromatography (HPLC) system, equipped with a diode array detector (DAD) and a Phenomenex C18 column (150 mm × 4.6 mm × 5 μm). The following conditions were used: column temperature: 20 °C, mobile phase: water/acetonitrile (gradient 5–95), flow rate: 1.0 ml/min, detection wavelength: 210 nm. Alternatively, samples were analyzed on a Varian Chromapack CP-3800 gas chromatograph, equipped with a Hewlett Packard Phenomenex Zebron ZB-5 column (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector (FID). Before GC analysis, the reaction mixtures were extracted with dichloromethane (for reactions carried out in water) or diluted with dichloromethane (reactions carried out in toluene). In both cases (HPLC and GC), the detector response was calibrated using pure compounds as standards. Biphenyl was used as the internal standard.

Product selectivity is expressed as the mole percentage of the desired product in the converted starting material.

3 Results

3.1 Catalyst Preparation and Characterization

Differences in availability and solubility of antimony and bismuth salts make it difficult to use exactly the same preparation method for Sb- and Bi-modified catalysts. Considering a possible influence of the synthesis procedure on catalyst performance, several different methods were used (see Sect. 2).

The chemical compositions and some physical properties of the prepared carbon-supported catalysts are given in Table 1. The metal content found by ICP-OES is generally close to the values targeted during catalyst preparation, except for antimony, for which somewhat lower values were recorded. The surface area of the unloaded carbon support is always higher than the surface areas found for the metal-loaded catalysts. The average crystallite sizes of platinum (estimated by XRD line broadening) are in a narrow range between 4.4 and 5.4 nm and appear to be slightly lower for the Bi-modified catalysts than for the unmodified and Sb-modified catalysts. For the 5%Pt catalysts modified with 5 % Sb or Bi fairly narrow particle-size distributions are found by HRTEM. There is a shift to smaller particle sizes for Bi-modified catalysts and for catalysts prepared under sonication. The images shown in Fig. 1 for the catalysts prepared under sonication illustrate the high dispersion of the catalytically active components, which appear as circular dots before the lighter background of the carbon support.

Table 1 Chemical composition and some physical properties of the carbon carrier and the in-house made platinum catalysts

Catalyst[a]	Metal content (mass%)			Crystallite size[b] (nm)	Particle size[c] (nm)	BET surface area (m^2/g)
	Pt	Sb	Bi	Pt	Range (average)	
Activated C	–	–	–	–		865
5%Pt/C	4.8	–	–	5.0		700
5%Pt–1%Sb/C	4.4	0.7	–	5.3		680
5%Pt–3%Sb/C	4.6	2.3	–	5.4		660
5%Pt–5%Sb/C	4.7	4.1	–	5.1	3–13 (10.2)	645
5%Pt–5%Sb/C–s	4.9	4.4	–	5.1	1.5–5 (3.1)	725
5%Pt–5%Sb/C–s–r	4.7	4.2	–	–[d]	–[d]	–[d]
5%Pt–1%Bi/C	4.9	–	0.9	4.5		745
5%Pt–3%Bi/C	4.8	–	2.8	4.4		730
5%Pt–5%Bi/C	4.9	–	4.9	4.7	2–12 (7.3)	725
5%Pt–5%Bi/C–s	4.9	–	4.7	4.8	0.5–4 (2.1)	645
5%Pt–5%Bi/C–s–r	4.6	–	4.6	–[d]	–[d]	–[d]

[a] Suffix "–s" stands for catalysts prepared under sonication, "–r" for recycled catalysts

[b] Average determined by XRD

[c] Determined by HRTEM (for catalysts containing 5 % modifier)

[d] Not measured (too little sample)

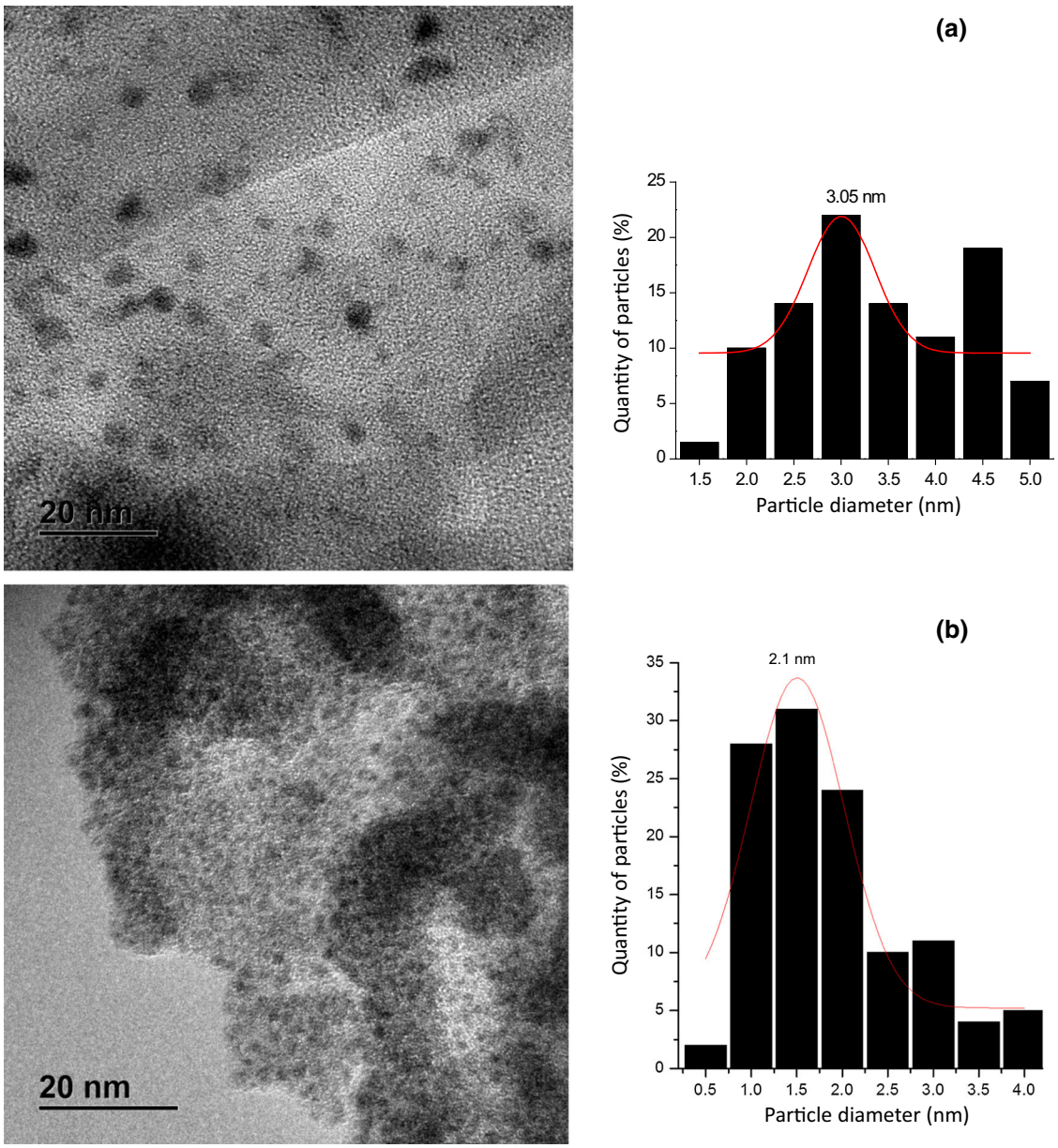


Fig. 1 Representative HRTEM images and the corresponding histograms of the particle-size distribution for as-prepared 5%Pt–5%Sb/C–s (**a**) and 5%Pt–5%Bi/C–s (**b**)

In Fig. 2 STEM combined with elemental mapping reveals a close association of platinum with antimony.

Figure 3 shows the wide-angle XRD pattern of the 5%Pt–5%Sb/C–s catalyst. As on all the other catalysts, platinum is present in its face-centered cubic phase, corresponding to the powder diffraction file (PDF) 03-065-2868. The broad peaks confirm the presence of small nanometer-size platinum crystals (compare Table 1). A broad feature in the region of $2\theta = 20°–22°$ is commonly attributed to amorphous carbon [16, 17]. The intensities and location of all other peaks corresponds to the valentinite phase of Sb_2O_3 (PDF 03-065-2426). The presence of different, but intimately associated phases seen by XRD and elemental mapping would be in line with the concept of a bifunctional catalyst, as further discussed in Sect. 4.

3.2 Catalyst Testing

The selective oxidation of cinnamyl alcohol to cinnamaldehyde with hydrogen peroxide is used as the test reaction (Scheme 1). Ideally, the addition rate of the oxidant should match the rate of its consumption [8], as any excess of H_2O_2 can be expected to decompose on the catalyst surface [18, 19] and may lead to the over-oxidation

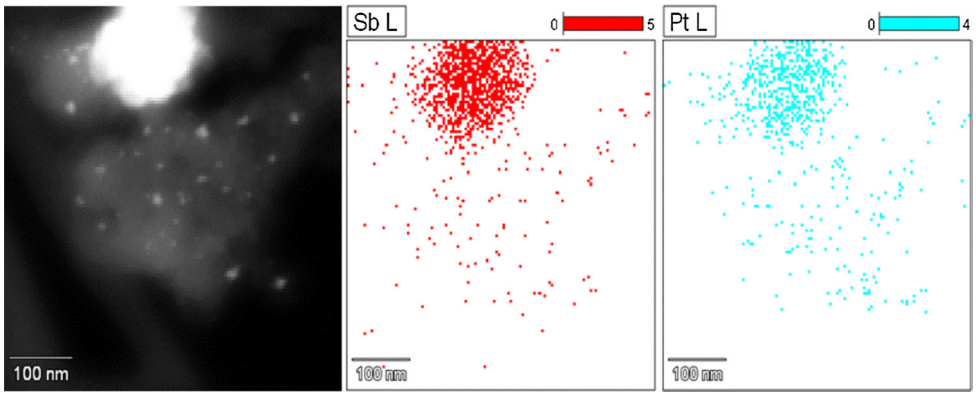


Fig. 2 STEM image and elemental mapping of the 5%Pt–5%Sb/C–s catalyst

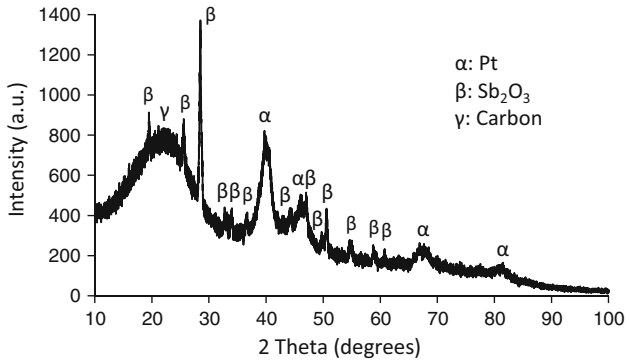


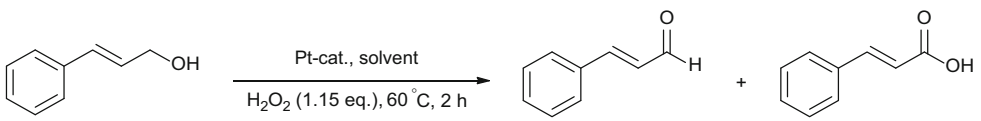
Fig. 3 X-ray diffraction pattern of the as-prepared antimony-modified 5%Pt–5%Sb/C–s catalyst

of the catalytically active metal (Pt) [3]. For each test only 1.15 equivalents of the oxidant were added in a dropwise manner over 2 h. Under these conditions total conversion of the substrate cannot be expected; for example, Anderson et al. [8] needed more than five equivalents of H_2O_2 to completely convert 1-octanol over a 5%Pt–1%Bi/C catalyst. Our conditions of limited conversion allow, however, for the meaningful comparison of different catalysts. (The need for excess H_2O_2 is not a particularity of precious metal catalysts, e.g. Kholdeeva et al. [20] used a 2.5-fold excess for an oxidation reaction catalyzed by Ti-silicate.)

Figure 4 demonstrates that our 5%Pt–5%Bi/C catalyst compares favorably with a commercial catalyst of the same nominal composition. This test was carried out at two different H_2O_2 concentrations. As is to be expected, the H_2O_2 concentration has an effect on the reaction rate, and lower concentrations lead to lower conversions.

Figure 5 shows that over the whole conversion range bismuth- and antimony-modified catalysts are considerably more selective than unmodified platinum. The graph also indicates that the catalysts prepared under sonication (5%Pt–5%Sb–s and 5%Pt–5%Bi–s) are more selective than those prepared by conventional methods. All antimony containing catalysts are more selective than bismuth-modified catalysts; that is, for the sonicated Pt–Sb catalyst over-oxidation to cinnamic acid is totally absent, while over the unsonicated Sb catalyst a selectivity to the aldehyde of >98 % is maintained throughout the reaction.

For the experiments shown in Fig. 5 the catalyst was suspended in water. At least at room temperature the organic compounds shown in Scheme 1 have a limited solubility in water [21]. In order to alleviate the perceived problem, Mallat et al. [7], using air as the oxidant, recommended the addition of an anionic surfactant. Anderson et al. [8] reported that toluene and xylene are the most effective solvents for the selective oxidation of primary and secondary alcohols with air. Others found that complete solubility is not a prerequisite for high conversion, and observed increasing reactivities with increasing water content in the solvent system [22]. Likewise, in our case (aq. H_2O_2 as the oxidant) all catalysts are more active in water (Fig. 5) than in toluene (Fig. 6). For each catalyst, the highest conversions seen in Figs. 5 and 6 are the conversions reached within 2 h, and these are always higher in water than in toluene. As in water, the selectivity in toluene increases in the order Pt < Pt–Bi < Pt–Sb < Pt–Sb–s. Again, no over-oxidation to cinnamic acid is seen for the sonicated Pt–Sb catalyst.



Scheme 1 Oxidation of cinnamyl alcohol to cinnamaldehyde and cinnamic acid

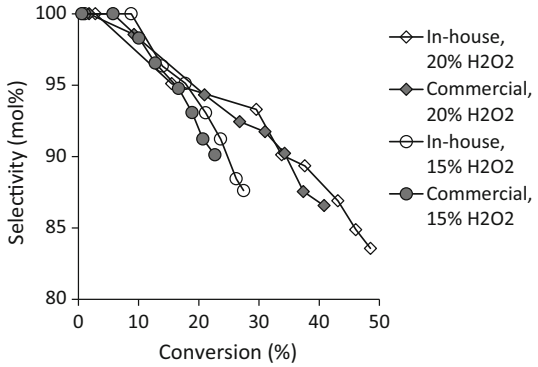


Fig. 4 Oxidation of cinnamyl alcohol: selectivity to the aldehyde as a function of conversion. Comparison of the in-house prepared 5%Pt–5%Bi/C catalyst with a commercial catalyst of identical metal loading (reaction time: 2 h, reaction medium: water)

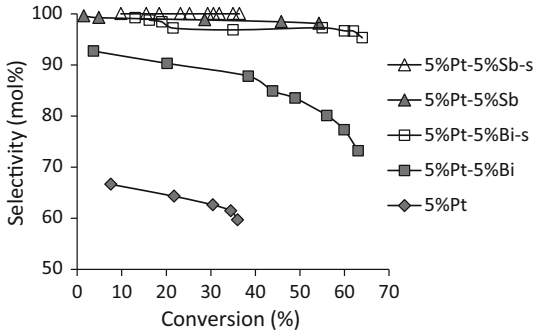


Fig. 5 Oxidation of cinnamyl alcohol: selectivity to the aldehyde as a function of conversion over various carbon-supported platinum catalysts (reaction time: 2 h, reaction medium: water)

In summary, Figs. 5 and 6 demonstrate that Sb-modified catalysts are more selective for the formation of cinnamaldehyde than Bi-modified and unmodified catalysts. The 5%Pt–5%Sb/C catalysts give selectivities in excess of 98 % in both water and toluene. Selectivity is lowest over the unmodified Pt/C catalyst (60 and 78 % after 2 h in water and toluene, respectively). The corresponding numbers for the unsonicated Bi-modified catalyst are 73 and 84 %, while 95 % was observed for the Bi catalyst prepared under sonication. Selectivities are always higher in toluene than in water.

Remarkably, the conversion improves when the catalysts are reused for a second run. This is demonstrated in Fig. 7. Furthermore, there is almost no deterioration in selectivity (Fig. 8). In particular, the selectivity remains above 99.6 % for the reused Sb-modified system. For all catalysts little metal leaching (Pt, Sb and Bi) is detected during the first run (2–6 mass%, compare Table 1).

Figure 9 illustrates that the selectivity to cinnamaldehyde increases with increasing antimony loading of the catalyst, while the catalyst activity (conversion) has a

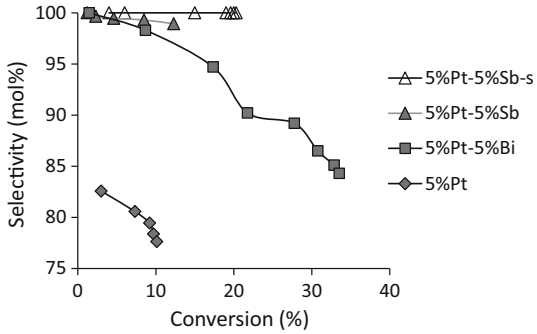


Fig. 6 Oxidation of cinnamyl alcohol: selectivity to the aldehyde as a function of conversion over various carbon-supported platinum catalysts (reaction time: 2 h, reaction medium: toluene)

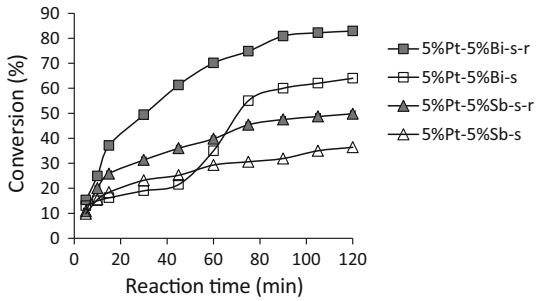


Fig. 7 Oxidation of cinnamyl alcohol: conversion as a function of reaction time for fresh and reused (–r) catalysts (reaction medium: water)

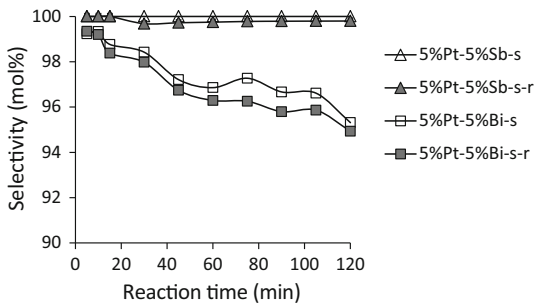


Fig. 8 Oxidation of cinnamyl alcohol: selectivity as a function of reaction time for fresh and reused (–r) catalysts (reaction medium: water)

maximum at around 1 % Sb loading. A similar trend is observed for bismuth-modified catalysts (not shown).

4 Discussion

Most literature reports favor the view that the mechanism of alcohol oxidation on palladium and platinum surfaces involves the dehydrogenation of the adsorbed alcohol to the aldehyde, and subsequently the chemisorbed hydrogen

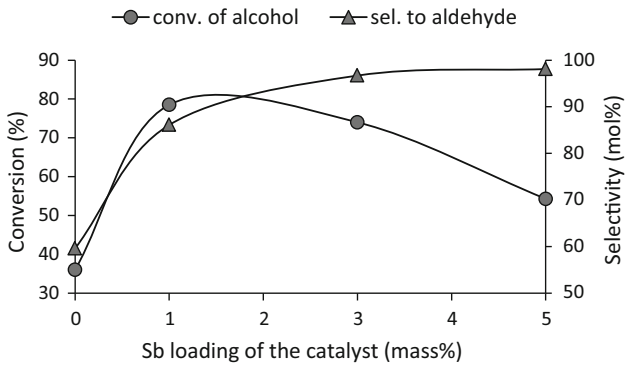


Fig. 9 Oxidation of cinnamyl alcohol: conversion and selectivity as a function of Sb addition to the 5%Pt/C catalyst (reaction time: 2 h, reaction medium: water)

is oxidized to water [2, 3]. The role of the "promoter" (e.g. bismuth) is still a matter of speculation. Besson et al. [23] suggested that it is bismuth oxide that converts the chemisorbed hydrogen to water, and the oxidizing agent used for the overall reaction (in their case O_2) reoxidizes the resulting lower-oxidation-state bismuth species. This would imply that the catalyst is essentially bifunctional: platinum dehydrogenates the substrate, and the base metal component oxidizes the hydrogen. In this way, bismuth keeps the precious metal surface free of excess oxygen and improves the catalyst activity, selectivity and life-time. The recommendation to work in a regime of limited oxygen supply [3] would be in line with this mechanism.

Our own results indicate that antimony is a better catalyst modifier than bismuth. A possible explanation for the difference observed between antimony and bismuth could be derived from the oxide chemistry of the two metals [24]. The only stable oxide of bismuth is Bi_2O_3. In contrast, antimony forms oxides in the oxidation states (III) and (V), namely Sb_2O_3, Sb_2O_4 and Sb_2O_5, whereby Sb_2O_4 constitutes a mixed oxide. It can be expected that this flexibility in oxidation states would make antimony a more favorable catalyst modifier than bismuth, provided the mechanism discussed above makes a significant contribution to the overall reaction. In any case, the mechanism would require an intimate association between platinum and the base-metal component. For the most selective catalyst (5%Pt–5%Sb/C–s) this is confirmed by the elemental mapping shown in Fig. 2.

The increase in selectivity with increasing antimony loading (Fig. 9) could be explained by the necessity to have a specific stoichiometric ratio of antimony to platinum present on the catalyst surface in order to ensure best possible bifunctionality. The maximized conversion at a Sb loading of approximately 1 % is explicable by a trade-off between the need for sufficient antimony oxide and the blocking of some of the platinum sites at higher antimony loadings (in analogy to the situation found with bismuth [7]). The improved activities of the recycled catalysts (Fig. 7) indicate that further chemical and/or physical optimization of the catalysts takes place under the reaction conditions. The sudden activity increase of the 5%Pt–5%Bi–s catalyst observed in Fig. 7 could also be explained along these lines.

Enhanced aldehyde selectivities in organic solvents (toluene in our case), as compared to water, are commonly observed [2, 3, 22]. The formation of carboxylic acid is regarded as a consecutive reaction; hydration of the aldehyde gives a geminal diol, which dehydrogenates further to form the acid [2, 25]. The presence of water can therefore be expected to lower the aldehyde selectivity. In our case, depending on the catalyst used, acid formation increases in the following order: Pt–Sb–s $\cong$ Pt–Sb < Pt–Bi–s < Pt–Bi < Pt. The unmodified platinum catalyst shows the lowest aldehyde selectivity. It is therefore not unlikely that acid formation takes place mainly on sections of the platinum surface that are not closely associated with antimony or bismuth.

At this stage, it can only be speculated that the difference in catalyst activity (conversion) observed in water and toluene is caused by solvation effects that alter the competitive chemisorption of the different species involved in the reaction. This was also suggested by Frassoldati et al. [22] for the reaction in dioxane/water. In addition, Balbuena et al. [26] found that the adsorption, dissociation and bonding strength of H_2O_2 on platinum is influenced by solvation.

5 Conclusion

Carbon-supported antimony- and bismuth-modified platinum catalysts for the oxidation of cinnamyl alcohol to cinnamaldehyde were prepared by several different methods. The catalysts were characterized by nitrogen physisorption (BET), XRD and HRTEM. Platinum nanocrystallites with diameters of 4.4–5.4 nm (XRD) were found on all catalysts. Catalyst modification with antimony significantly improves the selectivity to cinnamaldehyde in comparison to unmodified and bismuth-modified systems. The selectivity increases in the order 5%Pt/C < 5%Pt–5%Bi/C < 5%Pt–5%Sb/C. Over the antimony containing catalysts little over-oxidation to cinnamic acid takes place, and the fraction of the aldehyde in the product spectrum remains high (≥98 mol%). However, the Pt–Sb catalysts are less active than their Pt–Bi counterparts. Catalyst activities are generally higher in water than in toluene, but the organic solvent markedly increases the aldehyde selectivity in case of the Pt–Bi and the unmodified Pt catalyst, while it remains at a high level (≥99 %) for the

Pt–Sb catalysts. Catalysts prepared under sonication show higher selectivities. Recycled catalysts have enhanced activities, while the selectivity remains at a high level. The selectivity improves with increasing Sb or Bi loading ($\leq$5 %) of the catalyst, while the catalyst activity peaks at about 1 % base-metal loading. The experimental evidence obtained demonstrates that antimony is a very promising modifier for selective platinum oxidation catalysts. This work is currently being extended to air as the oxidant and to a variety of other substrates.

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