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Selective Oxidation of Cinnamyl Alcohol to Cinnamaldehyde with Air over Bi–Pt/Alumina Catalysts

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The partial oxidation of cinnamyl alcohol to cinnamaldehyde with air in an aqueous solution has been studied over a series of Bi–Pt/alumina catalysts. The bimetallic catalysts were prepared by selective Bi deposition onto supported Pt particles of 3–4 nm. XPS and electrochemical measurements indicated that an increase in Bi/Pt_s overall ratio results in higher Bi coverage and suppresses the hydrogen sorption on Pt, without any detectable influence on the electronic state of the noble metal. The bimetallic catalysts proved to be superior to 5 wt% Pt/alumina: an enhancement in initial rate by a factor of more than 26 was observed and the cinnamaldehyde yield increased by Bi promotion from 9 to 94–96% under otherwise identical conditions. Monitoring of catalyst potential during reaction, combined with cyclic voltammetric measurements, revealed that the low activity of Pt/alumina was due to the initial, destructive adsorption of the reactant ("self-poisoning"). The formation and irreversible adsorption of by-products were suppressed but not eliminated by Bi promotion. Even the bimetallic catalysts were in a partially oxidized state when conversion exceeded 10–15%. There was no sign of "oxygen poisoning." On the contrary, a partial oxygen coverage of active sites enhanced the oxidative removal of surface impurities and accelerated the desired reaction. The main role of Bi promotion is a geometric (blocking) effect which decreases the size of Pt ensembles. In addition, at higher conversions Bi adatoms might behave as new active centers which adsorb OH better than Pt (bifunctional catalysis). The good selectivity (up to 98.5%) is due to (i) the negligible hydration of cinnamaldehyde, and to (ii) Bi promotion which decreases the catalyst potential during alcohol oxidation and hinders the further oxidation of cinnamaldehyde. © 1995 Academic Press, Inc.

INTRODUCTION

An increasing number of papers have been published in the past decade on the partial oxidation of alcohols in aqueous solutions with molecular oxygen over bi- and trimetallic catalysts (1–6). It has been found that promotion of Pt or Pd (active components) by Bi, Pb, or other inactive metals increases the reaction rate or changes the selectivity of the reaction. Various interpretations have been suggested on the role of promoter metals:

(i) In the oxidation of D-gluconic acid to 2-keto-D-gluconic acid Pb^{2+}-complexation with the carboxyl- and α-OH functional groups of the reactant has been proposed, which accelerated the dehydrogenation reaction (2). A similar mechanism has been adopted for the electrocatalytic oxidation of D-glucose and sucrose on lead-modified Pt electrodes (7, 8).

(ii) Promotion by Cd or Co increases the resistance of Pd/C catalyst against over-oxidation and deactivation in the selective oxidation of 2,3;4,6-di-isopropylidene-α-L-sorbose by changing the adsorption properties of Pd (9).

(iii) A geometric blocking of Pt has been suggested as the main role of Bi adatoms in the oxidation of glycerol to dihydroxyacetone (10), and 1-phenylethanol to acetophenone (11). In the former case, promotion controlled the surface orientation of the reactant and improved the selectivity, while in the latter case, a decrease of the size of active site ensembles suppressed the formation and strong adsorption of poisoning intermediates and enhanced the reaction rate.

(iv) It has been proposed (12) that the geometry of active site ensembles are influenced by the size of the promoter-metal adatoms and by the number of surface-noble-metal atoms which they occupy. By this way the superior effect of Bi adatoms, compared to that of Pb or Sn, can be rationalized.

(v) Bi, Pb, and Sn adatoms can form new active centers, which adsorb the oxidizing species (OH_{ads}) better than Pt (12, 13). The reactant is adsorbed on Pt and the adsorbed OH radicals are donated by the promoter. The partially oxidized state of *X*/Pt/alumina-type bimetallic catalysts was proved by measuring the catalyst potential during the oxidation of 1-methoxy-2-propanol to methoxy-acetone. Note that several examples can be found in the electrocatalytic literature (13) on this type of combined action of promoter and Pt. A similar bifunctional mechanism has been proposed for the electrooxidation of methanol on Pt, according to which the promoter acts as a redox couple (M^{m+}/M^{n+}).

(vi) It has been observed (14) that Te inhibits the corro-

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sion of Pd/C during the oxidation of lactic acid to pyruvic acid. The formation of Pd_3Te intermetallic compound was assumed to be responsible for catalyst deactivation at high Te/Pd ratios (15).

(vii) It has been suggested (16) that the combination of Bi and Se promoters results in an optimum in the oxidation state of Pd/C during the oxidation of a nonionic surfactant. A much stronger synergic effect between Cd and Bi or Pb has been found earlier (1) in the oxidation of 2-phenoxy-ethanol to phenoxyacetic acid over Pd/C.

(viii) A possible role of promoters is the suppression of hydrogen sorption on the platinum metal (13). Hydrogen adsorbed on Pt may have an influence on the self-poisoning process. In the oxidation of 1-methoxy-2-propanol Bi, Pb, and Sn (which do not adsorb hydrogen) had higher influence on the reaction rate than Ru (which adsorb hydrogen excellently) (12).

Unfortunately, most of the above interpretations are rather hypothetical, mainly due to the lack of information about the surface structure and composition of the catalysts. We proposed recently (12) that the controlled and selective deposition of promoter-metal adatoms onto supported Pt or Pd is advantageous from a catalytic point of view. Moreover, the interpretation of the results is easier than in the case of catalysts prepared by simultaneous deposition and reduction of the metals.

There are several examples in the electrocatalytic literature on the selective adatom deposition onto Pt or Pd in the liquid phase, based on the "underpotential deposition" theory (17, 18). We have applied a nonelectrochemical method, which is a necessary prerequisite for the preparation of bimetallic particles supported on nonconductive materials. The basis of the method is our former observation (19) that a considerable decrease in Bi^{3+} concentration during the cyclic voltammetric study of Bi deposition onto Pt in acidic media suppressed bulk metal (i.e., multilayer) deposition, but did not influence the deposition of adatoms. That is, both adatom and bulk-metal deposition are possible thermodynamically, but at low Bi^{3+} concentrations the formation of adatoms is kinetically favored.

Application of very dilute ($\sim 10^{-6}$ *M*) solutions can easily be realized by a slow dosing of the metal salt solution. The method has been found to be excellent for the modification of dispersed, unsupported Pt: only Bi or Pb adatoms have been detected by cyclic voltammetry up to $\Theta = 0.5$ or 0.8, respectively (11, 12). In the present study an improved version of the method is used, by which Bi can be deposited selectively onto alumina-supported Pt particles.

The electrocatalytic study of Bi-modified Pt revealed the existence of "irreversibly" adsorbed Bi (Bi_{ad}), and also the influence of the surface coverage of Pt on the adsorption geometry and the redox behavior of Bi_{ad} (20–22). Bi does not adsorb hydrogen and one Bi adatom occupies three hydrogen sorption sites (surface Pt atoms) on polycrystalline Pt and on Pt(111), but only two sites are blocked on Pt(100) (21, 23). Bi adatoms have a strong influence on the electrocatalytic oxidation of small organic molecules. The rate enhancement observed in the oxidation of 1,2-propanediol and benzyl alcohol in alkaline medium was explained by a bifunctional mechanism, i.e., the adsorption of the organic molecule on Pt and that of the oxidizing species on Bi_{ad} (24, 25). In acid medium the rate acceleration in the oxidation of benzyl alcohol and methanol was attributed to Bi adatoms as inert site blockers (25, 26). In the latter case, deposition of Bi_{ad} onto a Pt(111) surface completely eliminated the formation of poisoning intermediates at coverages above 0.7, due to steric requirements of the poison formation reaction (26). Similarly, Bi adatoms eliminate CO formation from ethylene glycol and change the selectivity of the oxidation reaction by suppressing the partial oxidation of diol to oxalic acid, which reaction requires ensembles of several active sites (27).

Under ultrahigh vacuum conditions, Bi adatoms on Pt(111) mainly act as site blockers: they are inert in the chemisorption of hydrogen, CO or cyclic hydrocarbons, though the oxygen sorption on the bimetallic system is more complex (28–30). Bi adatoms at coverages less than 0.1–0.15 prevent the dehydrogenation of cyclohexane or benzene, which have reactions that require relatively large active site ensembles. The electronic influence of Bi_{ad} on the neighboring Pt atoms was found to be negligible.

In the primary alcohol → aldehyde transformation high selectivities have been reported for those reactants, in which the hydroxyl group is located next to an aromatic ring, e.g., 5-hydroxymethyl-furfural (31) or various substituted benzyl alcohols (32–34). In the synthesis of saturated aliphatic aldehydes acceptable yields were obtained only in apolar organic solvents, such as heptane; in aqueous alkaline solutions the main products are the corresponding carboxylic acids (35). In an early attempt (36) an unsaturated aliphatic alcohol, retinol [3,7-dimethyl-9-(2,6,6-trimethyl-1-cyclohexenyl)-2,4,6,8-nonatetraen-1-ol, vitamin-A] was oxidized to the corresponding unsaturated aldehyde, retinal. The oxidation was carried out in acetic acid over unsupported Pt at a very high Pt : reactant weight ratio of 0.4 and the yield was only 20%.

The aim of the present work was to elucidate the role of promoter in the partial oxidation of primary alcohols. We have chosen the oxidation of cinnamyl alcohol to cinnamaldehyde in aqueous solution, as an interesting test reaction:

$$\text{Ph-CH=CH-CH}_2\text{OH} \rightarrow \text{Ph-CH=CH-CHO}. \quad [1]$$

Both the reactant and product are water-insoluble and an anionic surfactant was used to enhance the reaction rate in the multiphase system (11, 12, 37).

EXPERIMENTAL

Catalyst Preparation

The symbol Bi/Pt in the text and figures represents the atomic ratio of the total amounts of Bi and Pt in the catalyst, while Bi/Pt_s indicates the atomic ratio of the total amount of Bi and the fraction of surface Pt atoms present.

Unsupported Pt powder catalyst was prepared from aqueous H_2PtCl_6 via hydroxide by hydrogen reduction (12). Metal dispersion was 0.052 as determined from the hydrogen region of a cyclic voltammogram (38).

Promoted catalysts have been prepared by modification of a 5 wt% Pt/alumina catalyst [Engelhard, No. 7004; dispersion = 0.30 determined by TEM (12)]. At first, the noble metal catalyst was prereduced with hydrogen at 25°C and 1 bar in water (50–100 cm^3/g catalyst). After 20 min the pH was decreased to 3 with perchloric acid (unsupported Pt) or acetic acid (alumina supported Pt, to minimize the corrosion of alumina) and the appropriate amount of bismuth nitrate in a dilute aqueous acetic acid solution (10^{-3}–10^{-4} *M*, pH 3) was added (in 15–20 min) to the thoroughly mixed slurry in a hydrogen atmosphere. At the end of the reduction 2-propanol was added (1 vol% of the mixture) and the catalyst was filtered off. After washing with 1 vol% aqueous 2-propanol, suspended with 0.05 *M* aqueous $NaHCO_3$, and washed with deionized water, the catalyst was dried in air. 2-Propanol was used to keep the catalyst in a reduced state and to avoid any corrosion–restructuring process during filtration, when acid and oxygen could be simultaneously present. The metal composition of the catalysts and the metal content of the filtrates were determined by inductive coupled plasma atomic emission spectroscopy (ICP–AES) and found that the Bi deposition onto Pt/alumina was complete.

Unsupported Bi_{ad}/Pt (Pt, covered by Bi adatoms; Bi/Pt_s = 0.14) catalyst was prepared by Bi deposition onto Pt powder as described above, but without using 2-propanol as a reducing agent in the second part of the method. A trimetallic 4 wt% Pd-1 wt% Pt-5 wt% Bi/C (Degussa, CEF 196 RA/W) catalyst was used as delivered.

Oxidation Procedure

The reactions were performed in a 200-ml flat-bottomed, thermostated glass reactor equipped with gas inlet and outlet, reflux condenser, thermometer and electrodes (see below). Before reaction 0.14 g catalyst was prereduced *in situ* under nitrogen atmosphere (20 min) with the alcohol reactant (3.5 g) in 30 cm^3 aqueous solution containing 0.14 g Li_2CO_3 and 0.14 g dodecylbenzenesulfonic acid sodium salt detergent. The reactions were performed with air as oxidant. During prereduction the slurry was slowly heated up to the reaction temperature (40–80°C). The oxidation of dodecanol (3.8 g) was carried out similarly, but at 85°C.

The reactor worked in a mass transfer limited regime, controlled by the air flow rate (10 cm^3 min^{-1}) and the mixing rate (1500 min^{-1}). This situation was necessary to avoid the over-oxidation of the active sites. The initial rates were determined with an air flow rate of 30 cm^3 min^{-1}.

Products were analyzed gas-chromatographically during and after reaction (12). The main products were cinnamaldehyde and cinnamic acid and the total amount of other detectable products was less than 0.1%.

Steady-State Catalyst Potential

All potentials denoted in the text and figures are referred to reversible hydrogen electrode in the same solution (RHE). A bright Pt rod collector electrode (Metrohm, geometric surface area 3.5 cm^2) and a Ag/AgCl/$KCl_{(sat)}$ reference electrode (Metrohm, E = 197 mV) were used. The reference electrode was separated from the reactor by two diaphragms in order to minimize the pollution of the catalyst by Cl^- ions.

The characteristics of the charge transfer between the collector electrode and the catalyst particles in suspension electrodes (39–41) and the application of the technique in studying hydrogenation reactions in slurry reactors (42–44) have been reported. During testing the method in alcohol oxidation we found that the best collector electrode material is Pt (37). A carbon paste electrode containing 10 wt% Pt/alumina was used as a reference in the same solution (not disguised by charge transfer problems) and under standard oxidation conditions (see above) Pt showed about the same value (±10 mV). Au indicated a positive deviation of at least 50 mV and Ag or glassy carbon were even less reliable. Note that the same material of catalyst and collector electrode has been recommended for slurry systems (40). Concerning the rate of charge transfer, Pt provided the shortest response time under identical conditions (catalyst concentration, mixing rate, solvent composition).

The lowest measurable catalyst (Pt/alumina) concentration was found to be 0.15 g l^{-1}; the actual concentration under standard conditions is 4.2 g l^{-1}. In the latter case, the ratio of the total Pt surface in the catalyst and on the collector electrode is 1500. This high value shows that the reactions, occurring on the surface of the bright Pt electrode, are negligible. Contamination of the electrode surface, frequently observed during the oxidation of α-tetralol (37), was absent in this case.

Electrochemical Polarization

The electrochemical cell and polarization method used for cyclic voltammetric measurements have been described previously (45). Pt rod counter electrode and $Ag/AgCl/KCl_{sat}$ reference electrode were used. The latter was separated from the main compartment of the cell by two diaphragms in order to minimize the pollution of the electrolyte by Cl^- ions. The polarizations were carried out in a nitrogen atmosphere at 25°C. 2 mg Pt or Bi–Pt powder on a carbon paste electrode was reduced electrochemically in aqueous 0.05 *M* K_2SO_4 (to avoid the corrosion of oxidized surface atoms), then the same volume of 0.5 *M* H_2SO_4 was added. Anodic polarization between 0.05 and 1 V was performed with 1 $mV.s^{-1}$ scan rate. The degree of coverage of platinum by Bi atoms ($\Theta_{Bi} \approx 0.4$) was determined from the hydrogen sorption on uncovered surface platinum atoms, assuming a H : Pt = 1 : 1 stoichiometry (38).

For the measurement of the influence of organic residues, the adsorption of cinnamyl alcohol on Pt was studied in the electrochemical cell, using the same aqueous alkaline solution and temperature (40°C) as applied in the standard oxidation procedure. Pt powder catalyst (2 mg) on the carbon paste was reduced cathodically by 12 $mV.s^{-1}$ sweep rate and its potential was kept at 150 mV for 5 min. Then 2.5 mg cinnamyl alcohol was added in 0.5 cm^3 base solution (final concentration: 4.6×10^{-4} *M*) and after 0.5–120 min the catalyst was polarized anodically with 2 $mV.s^{-1}$ up to 1.15 V. A new catalyst sample was used for each experiment. The polarization was repeated in the absence of cinnamyl alcohol, and the curve was taken as a reference. The speed of the rotating carbon paste electrode was 500 min^{-1}.

X-Ray Photoelectron Spectroscopy (XPS)

XP spectra were measured with a Kratos S-800 XPS instrument (Kratos, Manchester) using MgK_α (1253.6 eV) radiation. The samples were prepared by pressing the catalyst into an indium template. The base pressure of the apparatus was less than 10^{-9} mbar. The hemispherical analyzer was operated at a constant pass energy of 40 eV, the energy resolution being 1.0 eV (Ag $3d_{5/2}$). The energy scale was calibrated using Au $4f_{7/2}$ = 84.0 eV (46) and the peaks were corrected to the binding energy of Al $2p$ = 74.5 eV (47, 48) due to charging effect of Al_2O_3 support. The problem of inhomogeneous electrostatic charging and its effect on XPS measurements has been discussed in (49).

UV Spectroscopy

UV absorption spectra were taken with a Perkin Elmer Lambda 16 UV/VIS spectrometer at room temperature. Matched fused quartz cells (10 mm sample path) were used. The cinnamaldehyde concentration was 10^{-4} *M* with all measurements.

Transmission Electron Microscopy (TEM)

TEM measurements were performed using a Hitachi H-600 instrument operated at 100 kV, with a point resolution of about 0.5 nm. Samples were dispersed in acetone and loaded onto a holey carbon film supported on a copper grid.

RESULTS

Location and Structure of Bismuth Promoter on Platinum

During liquid-phase reduction the second metal may be deposited onto supported Pt or Pd as (i) a (sub)-monolayer, forming isolated adatoms or adatom islands and (ii) as bulk-metal particles (multilayer deposition) on the noble metal or on the support. (Alloy formation has not been considered as no evidence has been found yet under similar conditions.) The best performance of the bimetallic system is expected when the active metal is covered only by adatoms and the formation of bulk-metallic crystallites can be avoided.

The first and easier task is the selective deposition of Bi onto Pt particles avoiding promoter deposition on the support. When hydrogen is the reducing agent, Bi^{3+} ions are reduced on the surface of Pt particles via the ionization of adsorbed hydrogen. Bi^{3+} ions, adsorbed on the surface of nonconductive alumina which does not adsorb hydrogen, remain unchanged. Electron microscopic study of a Bi–Pt/alumina (Bi/Pt_s = 0.5) catalyst confirmed our expectation: the modified version of our preparation method (12) led to Bi deposition onto the 3–4 nm Pt particles and no detectable Bi crystal formation occurred on alumina.

Selective deposition of a Bi submonolayer onto Pt, even at high coverage, and minimizing the formation of multilayers proved to be more difficult. The best method known for investigation of the geometry of Bi deposition and for determining the ratio of the two energetically different structures is cyclic voltammetry (17, 18). However, this electrochemical method is limited to conductive materials. For the analysis of the structure of alumina-supported catalysts we used X-ray photoelectron spectroscopy. The measured binding energies, together with some reference data, are gathered in Table 1.

TABLE 1

X-Ray Photoelectron Spectroscopic Analysis of Pt and Bi–Pt Catalysts and Reference Binding Energies (in eV)

	Binding energies			
	Pt 4$d_{5/2}$	Bi 4$f_{7/2}$		
		Measured	Deconvoluted into	
Sample (atomic ratio)			2 peaks	3 peaks
	Our samples			
$\mathrm{Bi_{ad}}$/Pt	314.7	158.2		
Pt/alumina	314.6			
Bi–Pt/alumina (Bi/Pt$_s$ = 0.3)	314.6	≈158.2	157.5	157.0
			159.5	157.8
				159.0
Bi–Pt/alumina (Bi/Pt$_s$ = 0.4)	314.6	≈158.4	156.7	156.3
			158.5	158.1
				158.6
Bi–Pt/alumina (Bi/Pt$_s$ = 0.6)	314.7	≈158.4	156.4	156.4
			158.6	158.3
				158.9
	Literature data			
Pt (46, 48, 52)	314.4±0.2			
1–10 wt% Pt/alumina[a] (48, 51)	314.6±0.3			
1.4–10 wt% Pt/alumina[b] (48)	315.4±0.3			
0.7 wt% Pt/pumice (52)	314.8			
Bi (46, 50, 53)		156.9±0.1		
$\mathrm{Bi_2O_3}$ (54)		158.5		

[a] After *in situ* reduction by hydrogen at 400–450°C.

[b] Oxidized in air at 450°C, after reduction in hydrogen at 450°C.

The interpretation of Pt lines is complicated by the overlapping of Al 2p and Pt 4f lines. For analysis the less intensive Pt 4$d_{5/2}$ lines were used instead, as has been suggested earlier (48). Interestingly, the same Pt 4$d_{5/2}$ binding energies (within the experimental error of ±0.05 eV) were measured for unpromoted and Bi-promoted Pt/alumina catalysts. The samples were stored in air after preparation (reduction). The measured binding energies agree well with those reported for Pt/alumina after an *in situ* prereduction in flowing hydrogen at 400–450°C (48, 51). We can conclude that Pt is predominantly in a reduced state in the high-vacuum system and Bi deposition has no detectable influence on its electronic state. The latter conclusion is in agreement with the results obtained in ultrahigh vacuum on Bi-promoted Pt(111) (28–30). Note that a minor shift (≈0.15 eV) of Pt 4f lines toward higher binding energies has been observed for unsupported Pt–Bi alloys (53).

The intensity of the Pt 4$d_{5/2}$ lines decreased with increasing overall Bi : Pt ratio. This information, together with the TEM evidence of selective Bi deposition onto Pt, indicates that the higher the amount of Bi promoter, the higher is the coverage of Bi on Pt.

The 4$f_{7/2}$ lines were used for the analysis of the electronic state of Bi, but similar conclusions can be drawn from the 4$f_{5/2}$ maxima (Fig. 1). At the lowest Bi/Pt$_s$ atomic ratio the 4$f_{7/2}$ peak is rather diffuse and it is located at a binding energy which is clearly more negative than that of $\mathrm{Bi_2O_3}$. At the highest measured Bi/Pt$_s$ ratio the positions of the maximum and the shoulder are close to those characteristic of $\mathrm{Bi_2O_3}$ and metallic Bi (46, 50, 53, 54).

For the interpretation of the broad peaks, a similarly prepared but unsupported $\mathrm{Bi_{ad}}$/Pt catalyst powder was also analyzed. In this case no organic material was used during preparation and a relatively low Bi/Pt ratio was chosen in order to avoid multilayer Bi deposition (11). The electrochemical polarization of the Pt catalyst before and after Bi promotion (Fig. 2) confirms that there are only Bi adatoms on Pt, which are oxidized above 0.7 V. In this acidic solution the oxidation of bulk Bi to $\mathrm{BiO^+}$

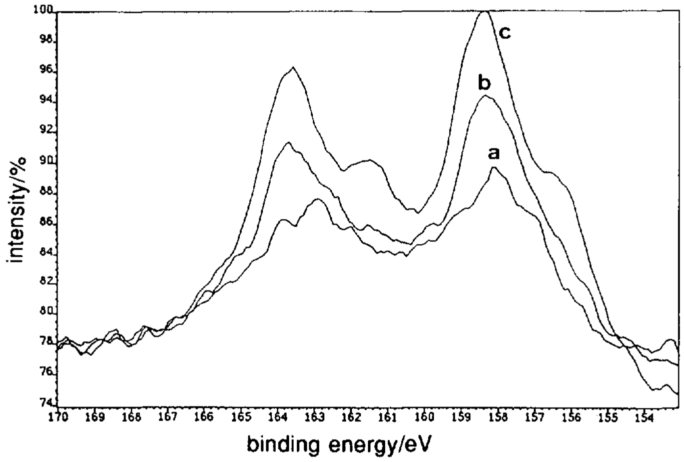

FIG. 1. Bi 4*f* XP spectra of Bi–Pt/alumina catalysts with different Bi/Pt$_s$ atomic ratios; a, Bi/Pt$_s$ = 0.3; b, Bi/Pt$_s$ = 0.4; and c, Bi/Pt$_s$ = 0.6.

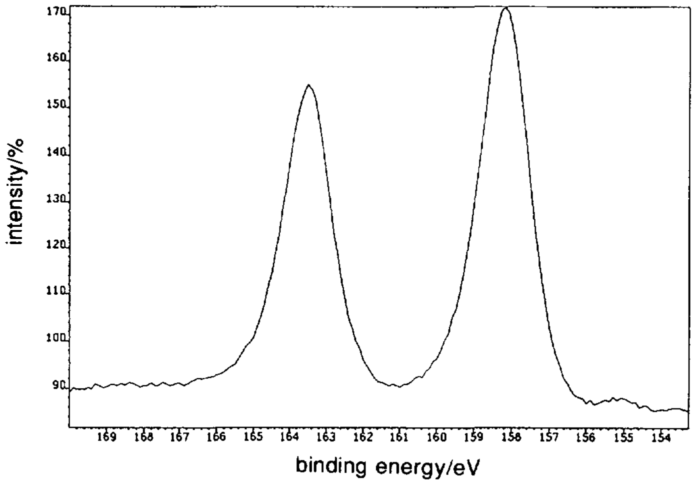

FIG. 3. Bi 4*f* XP spectra of Bi$_{ad}$/Pt catalyst (Bi/Pt$_s$ = 0.14 $\Theta_{Bi} \approx 0.4$).

occurs at around 0.3 V [E° = 0.32 V, (55)]. The potential shift of about 0.4 V is due to the different binding energies of Pt–Bi$_{ad}$ and Bi–Bi–Bi... structures (17, 18). Note, that similar results concerning the surface structure of the catalyst have been obtained in alkaline medium, using aqueous Na_2CO_3 or Li_2CO_3 electrolytes. The small wave at 0.5–0.6 V in Fig. 2 is due to the redox processes occurring on the carbon paste and it was found to be independent of the presence or absence of Bi.

Bismuth deposition suppresses the hydrogen adsorption on Pt, but does not influence the H$_{ad}$–Pt binding energy distribution: the two voltammograms in the hydrogen region (0–0.3 V in Fig. 2) are very similar. This is in accordance with the conclusion derived from XPS analysis of alumina-supported Pt, that Bi deposition has no detectable influence on the electronic state of Pt. $\Theta_{Bi} \approx 0.4$ was calculated from the difference in the amount of adsorbed hydrogen before and after Bi promotion.

The XP spectra of the unsupported Bi$_{ad}$/Pt catalyst powder is shown in Fig. 3. The Bi $4f_{7/2}$ maximum is located more negative by 0.3 eV than the value characteristic to bulk Bi_2O_3 (Table 1). The interpretation is that a Bi adatom and a Bi atom in multilayer deposition have different binding energies and this difference remains after exposure to air (oxidation).

We propose that Bi is located in (at least) three, energetically different states on the surface of alumina-supported Pt particles. The following species may be expected after catalyst preparation and exposure to air, as it is shown schematically in Fig. 4: (A) oxidized Bi adatoms (isolated or in clusters), (B) metallic Bi inside the bulk Bi deposits, covered by (C) a few layers of oxidized Bi with characteristics similar to those of bulk Bi_2O_3.

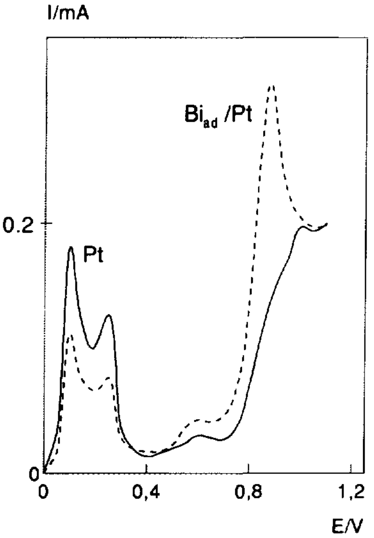

FIG. 2. Positive sweeps of the cyclic voltammograms of unsupported Pt and Bi$_{ad}$/Pt catalysts (Bi/Pt$_s$ = 0.14; 0.25 *M* H_2SO_4 + 0.025 *M* K_2SO_4, v = 1 mV.s^{-1} 25°C).

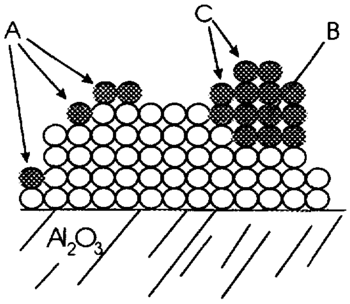

FIG. 4. Schematic representation of Bi deposition (filled circle) on supported Pt (empty circle) particles; A, Bi$_{ad}$; B, Bi atoms inside the bulk Bi deposit; and C, surface Bi atoms covering Bi deposits.

In order to determine the ratio of different structures we attempted to deconvolute the Bi 4*f* spectra to two or three composite peaks, as shown in Table 1. Unfortunately, neither of the approximations proved to be acceptable. Either the binding energies of the composite peaks (Gaussian peak fitting) were too far from the expected ones, or the fit (deviation between calculated and measured curves) was unsatisfactory. A likely explanation of the poor fitting is the presence of organic residues, originating from the decomposition of 2-propanol on Pt (see Experimental). Another possibility is that the real structure of Bi-covered Pt particles is more complicated than that suggested in Fig. 4. A recent study of Bi adsorption on Pt(111) surface proved the existence of both on-top and bridge-site adsorption (20). These two species are energetically different and the mode of adsorption is a function of coverage.

Due to the above difficulties, we can draw only a qualitative picture of Bi deposition on Pt/alumina. There are at least two energetically different Bi species and at high Bi/Pt ratio the fraction of Bi^0 (unexposed Bi atoms inside the multilayer deposits) increases and that of oxidized species decreases. This indicates that even at the lowest Bi/Pt_s ratio studied here (0.3) there is some bulk Bi deposition on Pt and the proportion of bulk deposition increases with increasing Bi/Pt_s ratio.

Catalytic Oxidation of Cinnamyl Alcohol

The optimum reaction conditions for the selective oxidation of cinnamyl alcohol to cinnamaldehyde were determined in preliminary experiments. Our aim was to minimize the amount of catalyst, base, and detergent, and to maximize the yield of cinnamaldehyde. Various promoted and unpromoted catalysts were compared under optimum conditions; the results are shown in Table 2. The 5 wt% Pt/alumina exhibited rather low activity and selectivity for this reaction. The initial rate and final conversion after 290 min increase dramatically by Bi promotion. Interestingly, the most active catalyst ($Bi/Pt_s = 0.5$) had the highest selectivity to cinnamaldehyde.

In order to obtain a more objective picture, we compared our catalysts to a commercial Bi–Pt–Pd/C catalyst, which has been found excellent for the selective oxidation of D-glucose to D-gluconic acid (3). This three-component catalyst had good selectivity, but the final conversion (reaction rate) was moderate. Likely reasons for this behavior are the inappropriate distribution of Bi promoter and/or the partial substitution of Pt by Pd.

The initial rates listed in Table 2 represent rough estimation. For oxidative dehydrogenation only the metallic sites (Pt^0) are active and consequently, the rate of oxygen supply from the gas phase to the catalyst surface should be lower than that of the surface chemical reaction, in order to avoid the over-oxidation and deactivation of the catalyst (56, 57). The oxidation reactions were performed in a transport-limited regime. For the determination of initial rates, a higher air flow rate (higher actual concentration of dissolved oxygen) has been chosen as a compromise. Under these conditions the oxygen transport had still some minor influence on the kinetics. The distortion is the highest in the case of the most active catalyst ($Bi/Pt_s = 0.5$). Note that working in the kinetic region resulted in a rapid deactivation due to surface oxide formation which hindered the reliable determination of initial rates.

The influence of reaction temperature is illustrated in Table 3. A considerable deactivation has been observed at 80°C, resulting in an increase of reaction time and decrease of selectivity. The formation of high molecular weight by-products was indicated by the yellow color of the liquid phase. Preliminary experiments indicated that not only the reaction temperature, but also the temperature during catalyst prereduction (by the alcohol reactant

TABLE 2

The Influence of Catalyst Composition on the Oxidation of Cinnamyl Alcohol to Cinnamaldehyde (40°C, Reaction Time: 290 min)

Catalyst	Bi/Pt_s (atomic ratio)	E_{red}[a] (V)	E_{10}[b] (V)	Initial rate ($mmol.min^{-1}g^{-1}$)	Conversion (%)	Selectivity (%)
Pt/Al_2O_3[c]	0	0.38	0.70	0.10	10.0	88.5
$Bi–Pt/Al_2O_3$	0.3	0.12	0.44	2.0	84.5	93.0
$Bi–Pt/Al_2O_3$	0.5	0.10	0.39	2.6	95.5	98.5
$Bi–Pt/Al_2O_3$	0.6	0.15	0.40	2.4	83.0	96.0
Bi–Pt-Pd/C[d]	—	0.34	0.65	—	38.5	97.0

[a] Catalyst potential measured after pre-reduction with cinnamyl alcohol in nitrogen.

[b] Catalyst potential measured after 10 min oxidation reaction.

[c] 5 wt% Pt.

[d] 5 wt% Bi-1 wt% Pt-4 wt% Pd/C.

TABLE 3

The Influence of Reaction Temperature on the Oxidation of Cinnamyl Alcohol to Cinnamaldehyde (Bi–Pt/Al$_2$O$_3$ Catalyst, Atomic Ratio Bi/Pt$_s$ = 0.5)

T (°C)	Reaction time (min)	Conversion (%)	Selectivity (%)
40	290	95.5	98.5
40	310	99.0	97.0
60	310	98.0	96.5
80	480	94.0	75.0

in a nitrogen atmosphere) influences the final yield. The highest yield (94–96%) was obtained, when cinnamyl alcohol had been added to the catalyst slurry at room temperature and the reaction temperature had been reached after 15–20 min (general procedure).

Oxidation State of Catalysts after Prereduction and during Reaction

The XPS study revealed the oxidation state of alumina-supported Pt and Bi–Pt catalysts before use. An electrochemical method, the measurement of catalyst potential (37, 41), was used to follow the oxidation state of the catalysts during alcohol oxidation. During prereduction under nitrogen atmosphere, the surface oxides (Pt^{4+} and Bi^{3+}) were reduced to metals on the expense of the oxidation of the reactant. This process was indicated by the 1–2% conversion of cinnamyl alcohol after catalyst prereduction and by the decrease of catalyst potential from around 1 to 0.1–0.4 V (E_{red} in Table 2).

For the interpretation of these potential values, the cyclic voltammograms of similarly prepared but unsupported Pt and Bi–Pt catalysts were measured. The same dilute aqueous Li$_2$CO$_3$ solution was chosen for polarization and for the catalytic oxidation measurements (except for the presence of detergent). The use of unsupported metals was necessary due to the conductivity requirements of the method. The voltammograms are similar to those measured in acidic medium (Fig. 2), but the strong adsorption of OH$^-$ results in overlapping of hydrogen and oxygen (OH) adsorption (58, 59). The positive sweep of the cyclic voltammogram of Pt powder catalyst is shown in Fig. 5, curve a. Several examples on the voltammograms of the Bi/Pt system in basic medium can be found in the literature (6, 11, 24, 25, 37, 59, 60). The borderline between reduced and oxidized surface is around 0.5 V in aqueous Li$_2$CO$_3$. The higher the potential above 0.5 V, the higher is the oxygen (OH) coverage on the bimetallic particles.

Neglecting any side reactions, the catalyst potential after prereduction in a nitrogen atmosphere is determined by the alcohol/aldehyde redox reaction (calculated standard potential is around 0.1 V). It is clear from Table 2 that the Bi-promoted catalysts are well reduced by cinnamyl alcohol, but the reduction of unpromoted Pt/alumina and that of the three-component commercial catalyst is incomplete. The relatively high potential after prereduction is an indication for the formation and strong adsorption of poisoning species on Pt, as will be discussed later.

After substituting nitrogen by air, the measured value is a mixed potential (61). When the side reactions can be neglected, the potential is determined by the alcohol oxidation and the oxygen reduction processes. In general, after introducing air into the reactor, the catalyst potential increased sharply by a few hundred mV in a few minutes, followed by a slow increase with conversion until full consumption of the reactant ("reducing agent"). The first transient period is finished within a few minutes. The catalyst potential measured after 10 min (E_{10}) are shown in Table 2. This value indicates the oxidation state of the catalyst at the beginning of the oxidation reaction.

All Bi-promoted catalysts are active, their potential during reaction is lower by 0.3–0.4 V than that of Pt/alumina at comparable conversions. The measured E_{10} = 0.39–0.44 V values correspond to a reduced state of Bi and Pt, with a minor hydrogen coverage on Pt. The borderline between reduced and oxidized surface (0.5 V) was reached at 10–15% conversion. From this point on, the Bi-promoted catalysts were in a partially oxidized state during reaction and the oxygen coverage increased monotonously with increasing conversion (or aldehyde/alcohol molar ratio). The final potential of the catalysts at

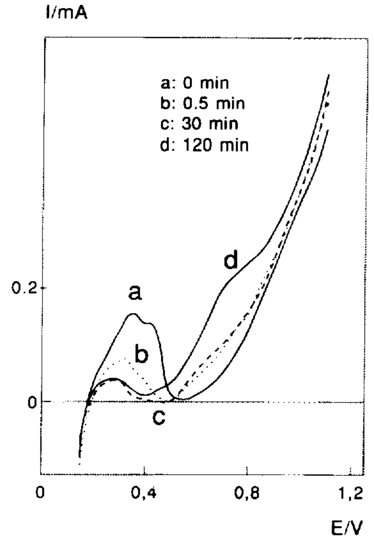

FIG. 5. Positive sweeps of the cyclic voltammograms of unsupported Pt in the absence (a) and in the presence of cinnamyl alcohol after 0.5 min (b), 30 min (c), and 120 min (d); (aqueous Li$_2$CO$_3$-dodecylbenzenesulfonic acid Na salt solution, 40°C, v = 2 mV.s^{-1}).

full conversion (>99%) was above 0.9 V. At this potential all Bi adatoms are in a fully oxidized state and the oxygen coverage on Pt is also high. (A typical catalyst potential–conversion curve is shown later, in Fig. 6.)

The unpromoted Pt/alumina behaved differently. Its potential was 0.55 V already after 1 min reaction time, i.e., the surface Pt atoms were in an oxidized state from the very beginning of the reaction. The behavior of the Bi–Pt–Pd/C reference catalyst was similar, but its deactivation was less pronounced than that of Pt/alumina.

Nature of Catalyst Deactivation

Some definite signals of catalyst deactivation have been observed during the partial oxidation of cinnamyl alcohol on Pt/alumina and Bi–Pt/alumina catalysts. The rather positive value of catalyst potential measured after prereduction (E_{red} in Table 2) is an indication of incomplete reduction of Pt/alumina, due to the formation of poisoning species during the initial adsorption of cinnamyl alcohol on surface Pt atoms. More details of the self-poisoning of Pt during alcohol adsorption, including the formation of CO and C_xH_y-type species can be found elsewhere (13, 62–64). A partial coverage of Pt by Bi suppressed this poisoning process and the prereduction by the reactant in a nitrogen atmosphere seemed to be complete within 15–20 min. There are numerous examples in the literature (25–30) on the elimination of poisoning side reactions by Bi adsorption, due to blocking a fraction of active sites on Pt.

In fact, Bi promotion suppressed but did not eliminate the formation of poisoning species. Following the catalyst potential during prereduction for a longer period revealed that after reaching a minimum in 15–20 min, its value increased again slowly and reached a plateau after 60–90 min. This behavior was characteristic for all catalysts, independent of the Bi/Pt ratio. Note that in the standard procedure the catalyst prereduction was interrupted after reaching the minimum potential value.

In order to prove the self-poisoning of Pt under our conditions, we studied the influence of cinnamyl alcohol adsorption on unsupported Pt powder as a model catalyst. Figure 5 shows the positive sweeps of the voltammograms. The amount of hydrogen adsorbed on Pt in dilute aqueous Li_2CO_3 decreases rapidly in the presence of cinnamyl alcohol (competitive adsorption). The change in hydrogen adsorption is negligible between 30 and 120 min, but the increase of the area under the broad wave between 0.5 and 0.9 V indicates the formation of further oxidizable species. We assume that the formation and strong adsorption of these species explain the unusual time-dependence of catalyst potential during prereduction. Similarly, the formation and transformation of these poisoning species may be the explanation of the higher rate and final yield obtained after prereduction at temperatures lower than that of the oxidation reaction.

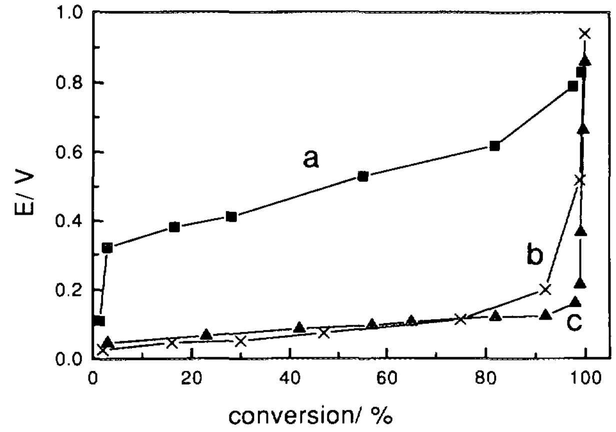

FIG. 6. Potential of a Bi–Pt/alumina catalyst (Bi/Pt_s = 0.5) as a function of conversion during the oxidation of cinnamyl alcohol at 60°C (a), 1-phenylethanol at 60°C (b), and diphenyl carbinol at 74°C (c).

The other source of deactivation is the by-product formation and catalyst poisoning during the oxidation reaction. The amount of products (besides cinnamaldehyde and cinnamic acid), detectable in the liquid phase at 40 and 60°C, was less than 0.1%. An unknown fraction of these by-products adsorbed on the active sites and decreased the rate of the surface chemical reaction, which is indicated by the continuous increase of catalyst potential with time. An important feature of deactivation during reaction is that Bi promotion had only a minor influence on it. Figure 6, curve a, shows the potential of the best catalyst (Bi/Pt_s = 0.5) as a function of conversion at 60°C. The increase of catalyst potential was substantially higher than that expected from the increase of alcohol : aldehyde ratio, according to the Nernst equation. For comparison, Fig. 6 shows the catalyst potential as a function of conversion of some secondary alcohols to ketones (11, 65). In the latter reactions the by-product formation was negligible and the increase of catalyst potential between 10 and 90% conversion was only 0.1–0.15 V. In the oxidation of cinnamyl alcohol, the corresponding potential increase was around 0.35 V. Note that all three reactions were catalyzed by the same Bi–Pt/alumina, and the reaction temperature (60–74°C) and solvent composition (aqueous Li_2CO_3 or Na_2CO_3, containing dodecylbenzenesulfonic acid sodium salt detergent) were similar.

It has been reported (9, 59, 66) for the oxidation of some primary alcohols to the corresponding acids that Pd or Pt as active components and Bi promoter can partially be leached out during reaction, resulting in irreversible catalyst deactivation. This corrosion process could be excluded in our case: the XPS analysis did not show any

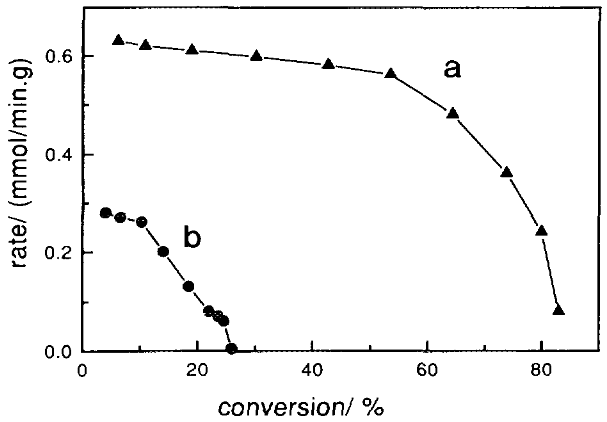

FIG. 7. Rate of the oxidation of cinnamyl alcohol with a Bi-Pt/Al_2O_3 ($Bi/Pt_s = 0.6$) catalyst at constant air flow rate (a) and at constant catalyst potential (b).

difference in the Bi/Pt ratio before and after reaction, and similarly, no metal ions could be detected by ICP–AES analysis in the reaction mixture.

A frequently proposed mechanism of catalyst deactivation is the so-called "oxygen poisoning" or over-oxidation of active sites (e.g., 2, 5, 67). The measurement of catalyst potential revealed that not only Pt/alumina of low activity, but even the Bi-promoted catalysts are in a partially oxidized state during reaction. In order to clarify the role of adsorbed oxygen [or rather OH_{ad} in the aqueous alkaline medium (58)], we repeated the oxidation reaction catalyzed by Bi–Pt/alumina ($Bi/Pt_s = 0.6$). During the reactions shown in Table 2, the air flow rate was kept constant, and the catalyst potential increased monotonously with time. In the second case the catalyst potential was kept in a potential range of 450 ±20 mV by controlling the oxygen partial pressure and the gas-flow rate. This potential range corresponds to a reduced state of the catalyst, with negligible hydrogen coverage. The observed reaction rates as a function of conversion are shown in Fig. 7. When the catalyst potential is low, due to the low and controlled oxygen concentration, the initial reaction rate is suppressed and the catalyst rapidly deactivates. The final conversion after 290 min was only 26%, whereas 83% was achieved when the catalyst was allowed to become oxidized during reaction. Similarly, when the unpromoted Pt/alumina was used at a controlled potential range of 450 ±20 mV, the reaction rate was much smaller, compared to that measured under standard conditions and the final conversion decreased to 2.8 from 10%, obtained in the presence of sufficient oxygen. These experiments demonstrate that a partial oxygen (OH) coverage of Pt is not detrimental to the activity. On the contrary, it is necessary for preserving the activity by an oxidative removal of poisoning species.

Interpretation of the Excellent Selectivity toward Cinnamaldehyde

We have proposed earlier (6) that good selectivity can be obtained in the partial oxidation of primary alcohols to aldehydes, when the hydration of the aldehyde intermediate is negligible. In this case the oxidation involves an oxygen insertion (Eq. [2]), which usually necessitates higher oxygen (OH) coverage on Pt than does the dehydrogenation of a geminal glycol (Eqs. [3], [4]):

$$\text{R-CHO}_{ad} + 1/2\ \text{O}_2 \rightarrow \text{R-COOH}_{ad} \qquad [2]$$

$$\text{R-CHO}_{ad} + \text{H}_2\text{O} \rightleftharpoons \text{R-CH(OH)}_{2,ad} \qquad [3]$$

$$\text{R-CH(OH)}_{2,ad} \rightarrow \text{R-COOH}_{ad} + 2\ \text{H}_{ad}. \qquad [4]$$

In the standard oxidation procedure the dilute Li_2CO_3 solution had a pH around 11 during reaction. At pH > 10 the addition of hydroxyl ion should be considered instead of reaction [3], as OH^- is a much stronger nucleophile than water (68):

$$\text{R-CHO}_{ad} + \text{OH}^- \rightleftharpoons \text{R-CH(OH)O}^-_{ad}. \qquad [5]$$

In other words, above a certain pH, which depends on the pK value of the geminal diol (hydrated form), the monoanion $R\text{-}CH(OH)O^-$ predominates in solution.

Due to a lack of literature data, some UV measurements were carried out to determine the extent of hydration of cinnamaldehyde. Dioxane–water mixtures were applied to obtain a homogeneous solution and NaOH was used to model the effect of base, as Li_2CO_3 does not dissolve in this medium. The spectra are shown in Fig. 8. The addition of water to dioxane causes a shift in the absorption maximum ($\pi \rightarrow \pi^*$) without influencing its in-

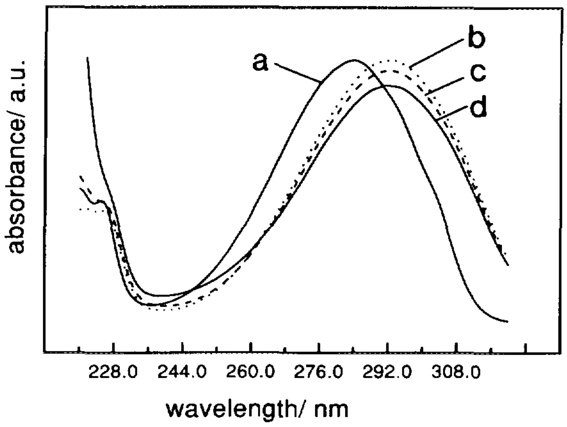

FIG. 8. UV absorption spectra of 10^{-4} M cinnamaldehyde in dioxane (a), in 25% dioxane + 75% water (b), in 25% dioxane + 75% 0.1 M aqueous NaOH (c), and in 25% dioxane + 75% 1.3 M aqueous NaOH (d); the last two spectra were taken 2 min after mixing.

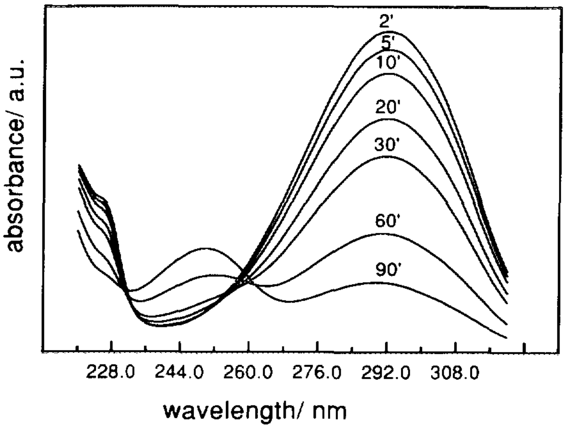

FIG. 9. UV absorption spectra of 10^{-4} M cinnamaldehyde in 25% dioxane + 75% 0.1 M aqueous NaOH measured after the indicated time in minutes.

tensity (curves *a* and *b*). Furthermore, no decrease of absorbance with time was observed, indicating that the hydration of cinnamaldehyde in neutral aqueous solutions can be excluded.

Addition of NaOH decreased the maximum absorbance at around 290 nm (curves *c* and *d*). These spectra were taken 2 min after mixing the solutions. Measuring the spectra repeatedly (Fig. 9) revealed the time-dependence of the disappearance of the carbonyl band. It has been found earlier (69–71) that the hydration of aldehydes is fast; the equilibrium is reached within a minute at pH of around 5 and the rate of addition reaction increases with increasing pH. We can conclude that the slow reaction shown in Fig. 9, which is not complete in 90 min, cannot be the hydroxyl addition to the carbonyl group. It is likely that the disappearance of the band at 290 nm and the emergence of a new band at around 250 nm is due to the aldol reaction in the presence of a strong base. This is in accordance with our observation during preliminary experiments that when applying a stronger base than Li_2CO_3 (pH of 12–13, instead of 11), both reaction rate and selectivity decrease with the simultaneous formation of polymeric by-products.

The negligible hydration of cinnamaldehyde is obviously due to the extra resonance stabilization of the unhydrated aldehyde in the presence of the C=C double bond and the aromatic ring. In order to gain further evidence on the correlation between the selectivity in the oxidation of alcohols to aldehydes and the hydration of aldehydes in aqueous medium, the partial oxidation of 1-dodecanol (lauryl alcohol) to dodecanal (laurinaldehyde) was also studied. It is known (71) that simple aliphatic aldehydes are hydrated to a considerable extent and, accordingly, low selectivities are reported for these cases (35). The same Bi–Pt/Al_2O_3 (Bi/Pt_s = 0.5) catalyst was used for dodecanol oxidation which proved to be the best in the oxidation of cinnamyl alcohol. The selectivity was close to 80% at low conversion, but decreased monotonously with increasing conversion, as shown in Fig. 10. Similar or even lower selectivities have been achieved when weaker or stronger bases ($NaHCO_3$ or NaOH, respectively), were applied.

We can conclude that the negligible hydration of the cinnamaldehyde product is the main reason for the excellent oxidation selectivity. A further factor is the catalyst composition. Interestingly, the most active catalyst has the highest selectivity (Table 2), which is not usual in catalysis. The explanation is that promoting Pt with Bi suppressed deactivation and decreased the catalyst potential during reaction. The oxidation of unhydrated aldehyde requires considerably higher oxygen coverage (catalyst potential) than the alcohol dehydrogenation. That is, the lower the catalyst potential during alcohol oxidation, the better is the separation of the two processes, and the formation of cinnamic acid becomes considerable only at the end of alcohol oxidation, when the reactant ("reducing agent") has been consumed.

DISCUSSION

Structural Aspects

According to electron microscopic, XPS, and electrochemical analysis, Bi has been deposited selectively onto the Pt particles, without any detectable influence on the electronic state of Pt. The higher the Bi/Pt_s ratio, the higher the Bi coverage of Pt and the fraction of multilayer Bi deposition. The electrochemical study of Bi deposition on unsupported model catalyst (11) showed that with our method selective adatom deposition on Pt can be expected only below Θ_{Bi} = 0.5. One Bi adatom blocks 2–3 hydrogen adsorption sites, depending on the crystallo-

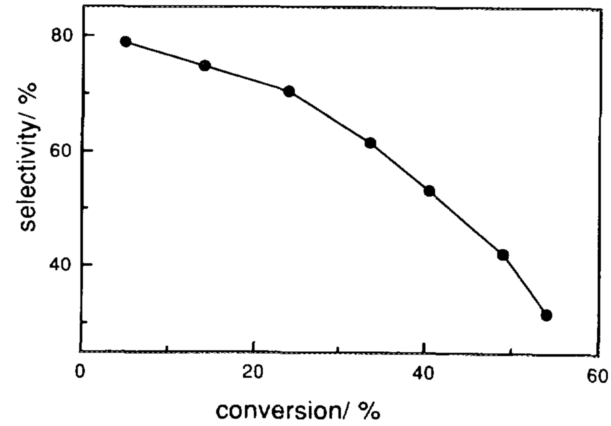

FIG. 10. Oxidation of dodecanol to dodecanal at 85°C with a Bi–Pt/Al_2O_3 (Bi/Pt_s = 0.5) catalyst.

graphic face and surface coverage of Pt (21, 56, 72). Accordingly, the limit of our method for depositing Bi submonolayers onto Pt is $Bi/Pt_s = 0.17–0.25$. However, the optimization of catalyst composition revealed that a Bi/Pt_s ratio of about 0.5 was necessary for high reaction rate and good selectivity to cinnamaldehyde.

The application of 2-propanol as a reducing agent during the separation and washing steps of catalyst preparation was successful: it prevented the corrosion of surface Bi species and the subsequent formation of bulk Bi deposition on the alumina support, around the Pt particles (12). It also shows that there is a limit in the application of these type of catalysts, as the simultaneous presence of an acid and oxygen during the oxidation reaction results in some corrosion and restructuring of the bimetallic system, as has been reported recently (59).

The Role of Bi Promotion

The 5 wt% Pt/alumina catalyst showed rather poor performance in the partial oxidation of cinnamyl alcohol to cinnamaldehyde. Deposition of Bi onto the surface of Pt particles enhanced the initial reaction rate by more than a factor of 26 and improved the selectivity toward cinnamaldehyde. Following the catalyst potential during prereduction and during the oxidation reaction and combining these results with those of cyclic voltammetric measurements on unsupported Pt and Bi–Pt model catalysts (in the presence and absence of cinnamyl alcohol) revealed that the unpromoted Pt rapidly deactivates. The loss of activity is mainly due to the initial, destructive adsorption of cinnamyl alcohol on the noble metal. This explains why the Pt/alumina catalyst cannot be completely reduced by the reactant in a nitrogen atmosphere (but can be reduced easily with gaseous hydrogen). The formation and chemisorption of by-products diminishes the number of free Pt^0 active sites, which results in a rapid oxidation of the Pt surface after introducing air into the reactor. The Pt/alumina catalyst is in a considerably oxidized state throughout the reaction.

A partial coverage of Pt by Bi suppresses but does not eliminate the deactivation of Pt during the initial alcohol adsorption. Moreover, Bi deposition has only a minor influence on the by-product formation and catalyst poisoning during the oxidation reaction. Accordingly, the oxidation reaction starts on reduced Bi–Pt particles, but the active sites are successively oxidized when conversion exceeds 10–15%. We propose that the basic role of Bi promotion is a geometric (blocking) effect. A decrease of the size of active site ensembles suppresses the initial, destructive adsorption of cinnamyl alcohol and the chemisorption of bulky (polymeric) by-products formed during reaction. On the basis of XPS and electrochemical measurements, any electronic influence of Bi on Pt seems unlikely.

As soon as the Bi–Pt/alumina catalysts are partially oxidized, another role of surface Bi atoms can be assumed. From ca. 0.6 V on, Bi adatoms adsorb oxygen (OH) better than Pt in this dilute aqueous Li_2CO_3 solution. When the catalyst is partially oxidized, Bi adatoms can behave as new active centers which take part in the alcohol oxidation reaction. Bi_{ad}, which is characteristic at low catalyst potential, can reversibly be oxidized to BiO_{ad} or $Bi(OH)_{2,ad}$ at higher potential (OH coverage) via $BiOH_{ad}$ as an intermediate (21). This type of bifunctional mechanism has been proposed for the oxidation of 1-methoxy-2-propanol over X–Pt/alumina type bimetallic catalysts in a batch reactor (12) and in several cases for the electrocatalytic oxidation of various alcohols on Pt modified by foreign metal adatoms (13).

Unfortunately, we do not have unambiguous evidence for or against this contribution of Bi adatoms. It is clear from Fig. 7 that the presence of a sufficient amount of oxygen, resulting in the partial oxidation of surface Bi and Pt sites, is advantageous for the alcohol oxidation reaction and increases the reaction rate by a factor of 2 to 13, compared to the situation where the bimetallic catalyst was kept in a reduced state throughout the oxidation reaction. However, a similar rate enhancing effect of "sufficient oxygen" has been observed with unpromoted Pt/alumina, which queries the necessary involvement of Bi/Bi^{n+} redox couples.

Below 10–15% conversion the bimetallic catalysts are in a reduced state, when the contribution of Bi/Bi^{n+} redox systems can be excluded. The initial rates (extrapolated to zero time) correspond to a reduced surface and the big differences among unpromoted and promoted catalysts (up to a factor of 26 or more) can be explained only by the geometric effect of Bi.

Summarizing these considerations we propose that the main role of Bi promotion is a geometric blocking effect, but the involvement of Bi adatoms as new active centers cannot be excluded at higher conversions, when the bimetallic catalyst works in a partially oxidized state.

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