A simple discrimination of the promoter effect in alcohol oxidation and dehydrogenation over platinum and palladium

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Abstract

Several models have been suggested to interpret the positive effect of Bi, Pb, and other metal promoters in the oxidative dehydrogenation of alcohols over Pt-group metal catalysts, though the experimental proof to these models is mainly missing. Here we propose a new and simple approach for clarifying the promoter effect: the comparison of dehydrogenation in inert atmosphere and oxidative dehydrogenation in the presence of oxygen over promoted and unpromoted catalysts. As test reactions the transformations of 1-phenylethanol, 2-octanol, and cinnamyl alcohol to the corresponding carbonyl compounds in a slurry reactor are used. The observed promoter effects can be classified into three groups: (i) acceleration of the hydrogen abstraction (dehydrogenation) step, (ii) acceleration of a reaction involving the transfer of (chemisorbed) oxygen, e.g., oxidation of the coproduct hydrogen or a surface impurity, thus generating free active sites, and (iii) a combination of these two different processes. This discrimination revealed that the metal promoter may have a dual effect on the aerobic oxidation of alcohols, and this behavior may rationalize some former controversial interpretations. Besides, this study presents the first evidence for the promoting effect of Bi in alcohol dehydrogenation in the absence of oxygen.

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1. Introduction

Transformation of alcohols to carbonyl compounds or carboxylic acids with molecular oxygen over platinum-group metal catalysts has long been the topic of academic and industrial interest [1–5]. In some reactions, such as the oxidation of aromatic alcohols, very high reaction rates have been reported (e.g., [6,7]), whereas in other cases serious catalyst deactivation hinders the practical application of the method [8–10]. According to the most accepted model, the reaction obeys a dehydrogenation mechanism and the coproduct hydrogen reacts with adsorbed oxygen to form water [11]. Another important role of oxygen is the oxidative removal of surface impurities [12] formed in side reactions such as alcohol degradation on the Pt-group metal surface [13–16].

There are numerous reports on the improvement of the performance of supported Pt and Pd catalysts by promo-

tion with metals, oxides, phosphates, amines, or phosphines [17–21]. The promoter metals, such as Bi, Pb, Te, Sn, and others, have generated the most interest [22–26]. The promoter metals alone are inactive in alcohol oxidation under the mild conditions applied; still, they induce sometimes spectacular rate enhancement [27–29] or a shift in the product distribution [21,30,31]. Despite the intensive effort by several research groups, the real nature of the promoter effect is still debated. Several strategies have been applied to understand the behavior of the bi- and trimetallic catalysts, including the detailed kinetic analysis of the reaction [4,32,33], in situ study of the oxidation state of the metals by electrochemical methods [34–37] and X-ray absorption spectroscopy (XAS) [38–41], and the synthesis and catalytic test of intermetallic compounds [42,43].

Here we report a new approach to clarify this mechanistic point. We compare the performance of various promoted and unpromoted catalysts in the oxidation of aromatic, aliphatic, and allylic alcohols in the presence and absence of molecular oxygen. The bimetallic catalysts were prepared by preferential deposition of Bi onto the surface of alumina-supported

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Pt or Pd particles [12,44]. The advantage of this approach is that during the promotion step the original structure of supported Pt and Pd is dominantly preserved and thus a direct comparison of promoted and unpromoted catalysts is possible.

2. Experimental

2.1. Materials

1-Phenylethanol (Aldrich, 98%), 2-octanol (Fluka, $\geqslant$ 99.5%), toluene (J.T. Baker, > 99.5%), cyclohexane (Aldrich, > 99%), acetic acid (Fluka, $\geqslant$ 99.8%), acetophenone (Fluka, $\geqslant$ 99%), 2-propanol (J.T. Baker, > 99.5%), NaHCO$_3$ (Merck, $\geqslant$ 99.7%), Bi(NO$_3$)$_3 \cdot$ 5H$_2$O (Fluka, 99%), and high purity water (Merck) were used as received. *trans*-Cinnamyl alcohol (Acros, 98%) was purified by recrystallization from petroleum ether (99.3% by ^{1}H NMR and GC). Ethylene glycol diacetate (Aldrich, > 99%) was applied as internal standard and dodecylbenzenesulfonic acid sodium salt (Fluka, techn.) as surfactant. Cyclohexene (Merck, > 99%) and vinyl acetate (Aldrich, 99%) were used as H acceptor for transfer dehydrogenation reactions. Gases were of 99.999% purity (PANGAS).

The 5 wt% Pd/Al$_2$O$_3$ (Johnson Matthey 324) and 5 wt% Pt/Al$_2$O$_3$ (Engelhard 4759) catalysts were used as received. The bimetallic catalysts 0.75 wt% Bi–5 wt% Pd/Al$_2$O$_3$, 1.0 wt% Bi–5 wt% Pt/Al$_2$O$_3$, and 0.9 wt% Bi–5 wt% Pt/Al$_2$O$_3$ were prepared according to a former recipe [44]. At first, 2.5 g 5 wt% Pd/Al$_2$O$_3$ or 5 wt% Pt/Al$_2$O$_3$ was prereduced by hydrogen (40 ml min^{-1}) in 200 ml distilled water at room temperature under magnetic stirring. After 20 min the pH was set to 3 with 3 ml acetic acid and the appropriate amount of Bi(NO$_3$)$_3 \cdot$ 5H$_2$O in 2% aqueous acetic acid solution ($\sim 10^{-3}$ M Bi^{3+}) was dropped into the stirred slurry within 30 min under hydrogen atmosphere. After 5 min, 3 ml 2-propanol was added in order to keep the metals in a reduced state during filtration. The system was flushed with nitrogen; the catalyst was filtered off and washed to neutral with a 1% aqueous 2-propanol solution without contacting it with air, then suspended with a 0.05 M NaHCO$_3$ solution, and washed with water to neutral. The catalyst was dried under vacuum at room temperature.

2.2. Methods for catalyst characterization: XPS, XAS, and TEM

The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Leybold Heraeus LHS11 MCD instrument using MgK$_\alpha$ (1253.6 eV) radiation [45]. The powdered sample was pressed into a sample holder, evacuated in the load lock at room temperature to 10^{-6} mbar and transferred to the analysis chamber at a typical pressure of 10^{-9} mbar. The peaks were energy-shifted to the binding energy of Al $2p$ (74.7 eV) to correct for the charging of the

Al$_2$O$_3$ support. Reduction of the catalyst was performed in the load lock, for 15 min in a hydrogen atmosphere at room temperature, in a similar way as described previously [45]. The surface ratio of Bi^{3+} to Bi^0 was determined by peak fitting (after correction for background and energy shifting), using the SPECSLAB program (Specs, Berlin). In order to limit the number of fit parameters, the tabulated energy differences between Bi $4f_{7/2}$ and Bi $4f_{5/2}$ (5.39 eV) were kept constant. In addition, the full width at half-maximum (FWHM) was constrained to one value.

The Bi/Pt and Bi/Pd mass ratios in the bimetallic catalysts were calculated from the edge jumps (absorption step, i.e., difference in X-ray absorption coefficients times pathlength; $\Delta\mu \cdot d$) of X-ray absorption near-edge structure (XANES) spectra using pellets of 13 mm diameter by comparison to reference pellets with known Bi, Pd, and Pt concentrations.

X-ray absorption spectroscopy (XAS) experiments at the Pd K, Pt L_3, and Bi L_3 edges were recorded at beamline X1 at HASYLAB (DESY in Hamburg) in the transmission mode using Si(311) and Si(111) double-crystal monochromators. The raw data were energy-calibrated with the respective metal foil (Pd K, Pt L_3 edges), background-corrected, and normalized using the WINXAS 2.1 program package [46]. For exact determination of the X-ray absorption step ($\Delta\mu \cdot d$), all spectra were treated in the same way using a linear background subtraction before the edge and a parabolic correction above the edge.

For transmission electron microscopy (TEM), the samples were dispersed in ethanol and deposited onto a perforated carbon foil supported on a copper grid. The measurements were performed on a CM30 microscope (Philips; LaB6 cathode, operated at 300 kV). For determination of the metal particle size (surface average diameter), different areas were examined and about 700 particles were counted. Metal dispersion was calculated from the metal particle size [47].

2.3. Alcohol dehydrogenation

Oxidation and dehydrogenation of 1-phenylethanol, *trans*-cinnamyl alcohol and 2-octanol were carried out in a flat-bottomed, magnetically stirred 100-ml glass reactor at 1 bar. Gases (argon, nitrogen, hydrogen, oxygen, and air) were saturated with the corresponding solvent before entering the reactor. The air (oxygen) flow rate (20–60 ml min^{-1}) and stirring speed (500–1000 min^{-1}) were set to ensure working in the mass-transport-limited regime and avoid overoxidation of the catalyst [2,4,48].

Method I

One hundred milligrams catalyst (without any pretreatment), 1.0 g 1-phenylethanol or 2-octanol, and 30 ml solvent (cyclohexane or toluene) were given into the reactor. Air was replaced by Ar, the reactor was immersed into a preheated oil bath (reaction temperature: 80 °C), and stirring started (750 min^{-1}).

Method II

One hundred milligrams catalyst was prereduced at room temperature by flowing hydrogen for 10 min in 30 ml water containing 10 mg surfactant (dodecylbenzenesulfonic acid sodium salt). Then the reactor was purged with nitrogen (5 min), and the catalyst was reoxidized with air (10 min). Air was replaced by Ar and the reactor was immersed into a preheated oil bath (reaction temperature: 55 °C). The 1.0 g 1-phenylethanol or 2-octanol was injected to the reaction mixture through a septum and stirring started (750 min^{-1}).

Method III

The pretreatment procedure was started according to method II but after reoxidation of the catalysts the reaction was started in an air flow (20 ml min^{-1}).

Method IV

For the dehydrogenation of 1.0 g cinnamyl alcohol only 50 mg catalyst (without prereduction) was applied in 20 ml toluene, in the presence of ethylene glycol diacetate as internal standard. Air was replaced by Ar, the reactor was immersed into a preheated oil bath (reaction temperature: 65 °C), and stirring started (1000 min^{-1}).

Method V

One hundred milligrams catalyst (without any pretreatment), 1.0 g 1-phenylethanol, hydrogen acceptor (cyclohexene or vinyl acetate; H acceptor/alcohol molar ratio 2), and 30 ml cyclohexane were given into the reactor. Air was replaced by Ar, the reactor was immersed into a preheated oil bath (reaction temperature: 80 °C), and stirring was started (500 min^{-1}). The reactions were stopped after 1 h.

The reaction mixtures were analyzed by GC (Thermo Quest Trace 2000, equipped with an HP-FFAP capillary column and an FID detector). Products were identified by GC-MS, and by GC analysis of authentic samples. From the reaction mixtures containing nonaqueous solvents (methods I, IV, and V) samples were periodically withdrawn during dehydrogenation and analyzed. In aqueous phase reactions (methods II and III) only the final products were analyzed. To the aqueous slurry containing the catalyst, 3 ml saturated sodium chloride solution and 20 ml toluene were added and

the mixture was stirred for 15 min. After 16 h separation, a sample from the organic layer was analyzed by GC.

2.4. Catalytic hydrogenation

The hydrogenation reactions were carried out in a parallel pressure reactor system Endeavor (Argonaut Technologies) with eight mechanically stirred 15-ml stainless-steel reactors equipped with glass liners and mechanical mixing (750 min^{-1}). Variation of the mixing frequency indicated no external mass-transport limitation in the slow reactions. Intraparticle diffusion effects were unlikely but could not be excluded. Generally, the slurry containing 10 mg catalyst (without prereduction) and 0.5 g acetophenone in 5 ml toluene was stirred at room temperature and 10 bars for 2 h. For hydrogenation in acidic medium, 0.25 ml acetic acid was added to the slurry as well and the reaction was stopped after 1 h. Conversion and product composition were determined by GC analysis as described above.

3. Results

3.1. Catalyst characterization

Some important features of the mono- and bimetallic catalysts and their abbreviations are collected in Table 1. The unpromoted Pd/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ catalysts possessed medium dispersion and monomodal particle size distribution as determined by TEM. The Bi-promoted catalysts were prepared by a method that has been shown to afford dominantly bimetallic particles [12]. The basic idea is that under ambient conditions Bi^{3+} cannot be reduced to Bi^0 by hydrogen on the surface of the support but it is readily reduced on the surface of the Pt or Pd particles to form metal adatoms [26]. Thus, a well-prepared and reduced catalyst contains only small amounts of Bi^{3+} on the support, originating from the incomplete removal (washing) from the high surface area support at the end of catalyst preparation.

Fig. 1 shows the X-ray photoelectron spectra of Bi in the 0.75 Bi–Pd/Al$_2$O$_3$ and 1.0 Bi–Pt/Al$_2$O$_3$ catalysts after reduction by hydrogen at room temperature. In both cases the

Table 1
Characteristics of the mono- and bimetallic catalysts

Catalyst[a]	Abbreviation	Origin	Metal particle size[b] (nm)	Metal dispersion[c]
5 wt% Pd/Al$_2$O$_3$	Pd/Al$_2$O$_3$	Johnson Matthey 324	3.4	0.34
5 wt% Pt/Al$_2$O$_3$	Pt/Al$_2$O$_3$	Engelhard 4759	2.8	0.40
			Surface Bi^0/Bi^{3+} ratio[d]	
0.75 wt% Bi–5 wt% Pd/Al$_2$O$_3$	0.75 Bi–Pd/Al$_2$O$_3$	Synthesized[e]	73/27	
1.0 wt% Bi–5 wt% Pt/Al$_2$O$_3$	1.0 Bi–Pt/Al$_2$O$_3$	Synthesized[e]	63/37	
0.9 wt% Bi–5 wt% Pt/Al$_2$O$_3$	0.9 Bi–Pt/Al$_2$O$_3$	Synthesized[e]	35/65	

[a] Bi contents were calculated from the edge jumps of XANES spectra.
[b] Determined by TEM.
[c] Calculated from the metal particle size.
[d] Determined by XPS analysis.
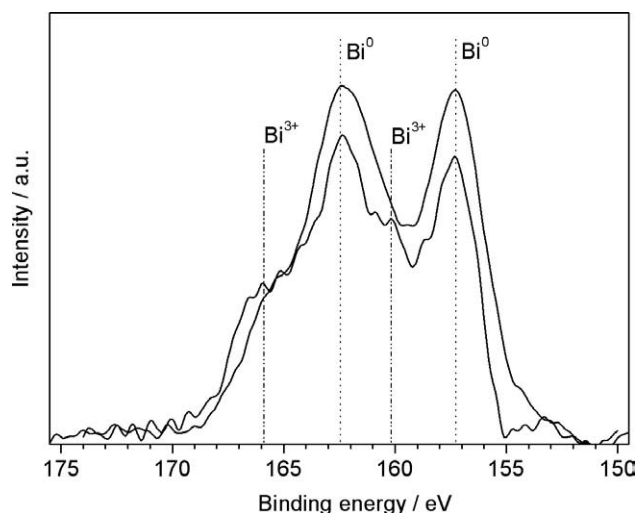[e] By Bi promotion (see Experimental section).

Fig. 1. X-ray photoelectron spectra of Bi in 0.75 Bi–Pd/Al₂O₃ (upper spectrum) and 1.0 Bi–Pt/Al₂O₃ (lower spectrum with larger shoulder at 165.9 eV) catalysts after reduction by hydrogen under ambient conditions.

Table 2
XPS analysis of Bi $4f$-peaks in the bimetallic catalysts after reduction by hydrogen under ambient conditions

		Bi^0		Bi^{3+}	
		Bi $4f_{7/2}$	Bi $4f_{5/2}$	Bi $4f_{7/2}$	Bi $4f_{5/2}$
0.75 Bi–Pd/	Binding energy (eV)	157.2	162.6	160.4	165.8
Al₂O₃	Extent (%)	38.0	35.2	15.2	11.6
	FWHM (eV)	2.95	2.95	2.95	2.95
1.0 Bi–Pt/	Binding energy (eV)	157.4	162.7	160.6	165.9
Al₂O₃	Extent (%)	32.6	30.0	19.2	18.2
	FWHM (eV)	2.7	2.7	2.7	2.7
0.9 Bi–Pt/	Binding energy (eV)	156.4	161.8	158.8	164.4
Al₂O₃	Extent (%)	19.4	15.8	37.8	27.0
	FWHM (eV)	1.96	1.96	1.96	1.96

majority of Bi promoter was in a metallic state at room temperature (Table 1): 63% Bi^0 in 1.0 Bi–Pt/Al₂O₃ and 73% Bi^0 in 0.75 Bi–Pd/Al₂O₃. As discussed above, the reducible fraction of bismuth is located on the Pt or Pd particles. The fraction of unreducible bismuth corresponds to Bi^{3+} species present on alumina; this fraction is assumed to be ineffective in the catalytic dehydrogenation of alcohols. More details of the analysis of Bi $4f$ signals in the bimetallic catalysts can be found in Table 2.

The surface composition of 0.75 Bi–Pd/Al₂O₃ was determined by XPS as well. Compared to the unpromoted Pd/Al₂O₃ the Pd concentration on the surface is lowered from 0.9 to 0.6%. In the case of 0.9 Bi–Pt/Al₂O₃ catalyst the extent of reducible Bi is smaller (35%, Tables 1 and 2); a considerable part of Bi is deposited on the alumina support.

The total Bi content of the bimetallic catalysts was estimated from the edge jumps in the XANES spectra (Table 1). Furthermore, XAS measurements revealed that in the samples exposed to air the Bi constituent was always in an oxidized state (Bi^{3+}), while the noble metal components were mainly in a reduced state. These results are in

Table 3
Hydrogenation of acetophenone (**2**, Scheme 1) to 1-phenylethanol (**1**); for conditions see Experimental section

Catalyst	Conversion (%)	
	Toluene	Toluene + acetic acid
Pd/Al₂O₃	7.6[a]	24[b]
0.75 Bi–Pd/Al₂O₃	3.2[a]	17[b]
Pt/Al₂O₃	–	32[c]
1.0 Bi–Pt/Al₂O₃	–	14[b]

[a] No by-product could be detected by GC.
[b] By-product: α-methylbenzyl acetate.
[c] By-products: α-methylbenzyl acetate, **4** and **5**.

good agreement with the proposed structure of the catalysts: a considerable fraction of surface Pd and Pt atoms is covered by Bi, and upon exposure to air these Bi atoms prevent the oxidation of Pd and Pt atoms below them. The white line at the Pt L_3 edge decreased significantly from Pt/Al₂O₃ toward 0.9 Bi–Pt/Al₂O₃ and 1.0 Bi–Pt/Al₂O₃, the latter thus containing mainly metallic platinum. Also in the case of 0.75 Bi–Pd/Al₂O₃, Pd was dominantly in the metallic state as described previously [40,41].

Additionally, the presence of Bi on the surface of Pd and Pt particles was evidenced by the catalytic hydrogenation of acetophenone (Table 3). Though the product distribution varied with the catalyst and solvent compositions, the conversion was always lower on the Bi-promoted catalysts (by 19–58%) relative to the monometallic reference catalysts. As Bi is inactive in the reaction, the drop in conversion confirms the partial coverage of surface Pt and Pd sites by Bi.

To sum up, characterization of the bimetallic catalysts supports the expectation that Bi has been deposited dominantly on the surface of alumina-supported Pt and Pd particles. This fraction of Bi is expected to influence the rate and selectivity of alcohol dehydrogenation.

### 3.2. Alcohol dehydrogenation: preliminary screening

The dehydrogenation of 1-phenylethanol, 2-octanol, and cinnamyl alcohol has been selected as test reactions. These reactants were commonly used in former studies of the aerobic oxidation [1–3] and transfer dehydrogenation [49–51] of alcohols over platinum-group metal catalysts to represent the transformation of aromatic, aliphatic, and allylic alcohols to the corresponding carbonyl compounds.

The product distribution observed in the dehydrogenation of 1-phenylethanol (**1**) to acetophenone (**2**) in Ar is shown in Scheme 1. Three by-products could be detected on Pt-based catalysts, which formed by hydrogenolysis of the C–O bond (**3**) or saturation of the aromatic ring (**4**, **5**). The latter reactions were absent on Pd-based catalysts that were also more active than the Pt-based catalysts.

The hydrogenation and hydrogenolysis-type side reactions were even more extensive in the dehydrogenation of cinnamyl alcohol (**6**, Scheme 2). Under identical conditions the reactivity of cinnamyl alcohol was lower than that of 1-
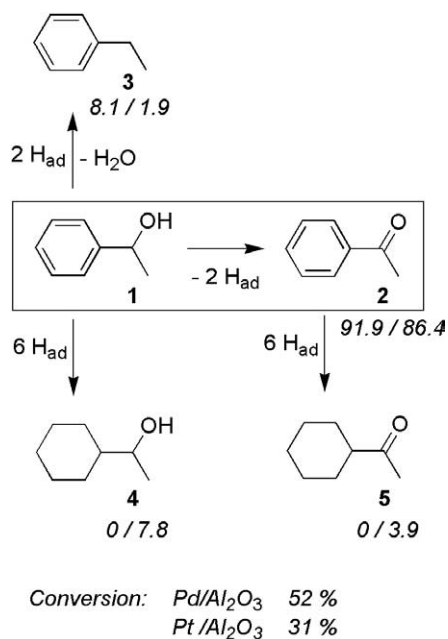
Scheme 1. Dehydrogenation of 1-phenylethanol (**1**) to acetophenone (**2**) and the by-products detected in Ar. Selectivities (in %) achieved by Pd/Al$_2$O$_3$ (first value) and Pt/Al$_2$O$_3$ (second value) are indicated below the formulas (method I, cyclohexane, 3 h).
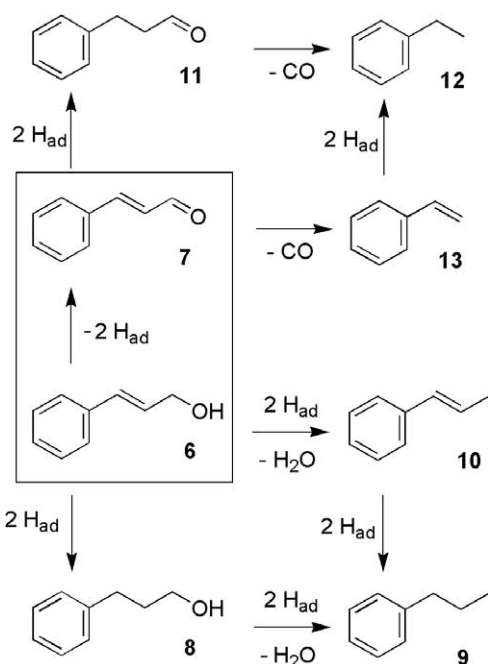
Scheme 2. Reaction network in the dehydrogenation of cinnamyl alcohol (**6**) over Pt- and Pd-based catalysts in Ar.

phenylethanol; the difference is (partly) attributed to decarbonylation of cinnamaldehyde (**7**) and dihydrocinnamaldehyde (**11**) [52]. The extent of these side reactions increased at higher temperature and in apolar solvents (e.g., cyclohexane). In contrast, the presence of oxygen suppressed by-product formation in the dehydrogenation of both alcohols **1** and **6**, and over 99% selectivity to **2** or **7** could be
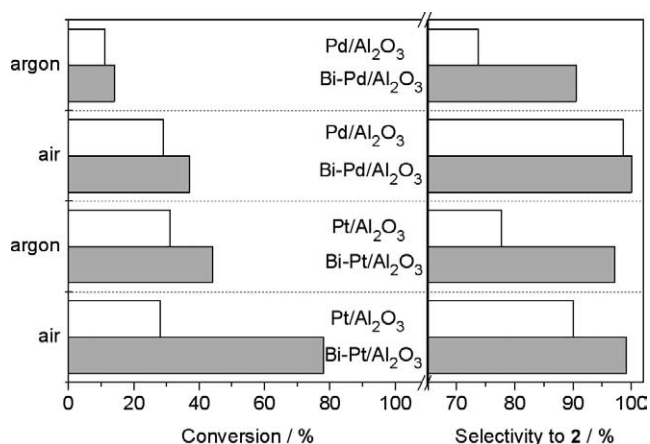

Fig. 2. Dehydrogenation of 1-phenylethanol (**1**) in Ar or in air over 0.75 Bi–Pd/Al$_2$O$_3$, 1.0 Bi–Pt/Al$_2$O$_3$, Pd/Al$_2$O$_3$, and Pt/Al$_2$O$_3$ (aqueous medium, method II in Ar and method III in air; 3 h).

achieved under the best conditions, in agreement with former reports [8,44,53]. Note that the by-products formed by hydrogenation and hydrogenolysis even in the presence of oxygen indicate H coverage of the active sites and thus confirm the dehydrogenation mechanism of alcohol oxidation [52].

In the dehydrogenation of 2-octanol to 2-octanone no by-products could be detected by GC analysis, independent of the catalyst composition but the reaction was very slow on all catalysts tested. This observation is in agreement with the generally poor activity of Pt-group metal catalysts in the dehydrogenation and oxidative dehydrogenation of aliphatic alcohols [54–57]. A specific difficulty of the dehydrogenation of 2-octanol was that the results were irreproducible with the Pt/Al$_2$O$_3$ catalyst in an apolar organic medium. Presumably, the coproduct water remained on the hydrophilic catalyst surface and after a short initial period the catalyst powder adhered to the reactor wall and the reaction stopped. This difficulty could be eliminated by working in a water–surfactant system.

The reaction conditions (solvent, temperature, catalyst pretreatment) of the three test reactions were varied in a broad range to obtain a general overview on the influence of Bi promotion of Pt and Pd and the role of oxygen in the promoter effect. In the following sections some representative examples will be shown that help understanding the influence of oxygen and bismuth promotion.

3.3. Dehydrogenation of 1-phenylethanol

Dehydrogenation of 1-phenylethanol to acetophenone is a good example on the promoting effect of Bi. In this reaction Bi promotion increased the rate and selectivity of both Pt/Al$_2$O$_3$ and Pd/Al$_2$O$_3$ catalysts, independent of the presence or absence of oxygen, and the reaction conditions. A comparative example is shown in Fig. 2, where the reactions were carried out under mild conditions, in a water–surfactant system. Interestingly, the 1.0 Bi–Pt/Al$_2$O$_3$ cata-
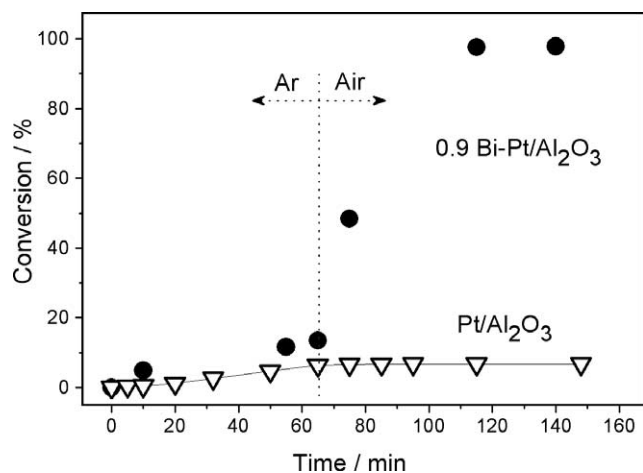
Fig. 3. Dehydrogenation of 1-phenylethanol (**1**) over Pt/Al$_2$O$_3$ and 0.9 Bi–Pt/Al$_2$O$_3$. The argon atmosphere was replaced by air (flow rate: 50 ml min^{-1}) after 65 min (method I, toluene).

Fig. 4. Dehydrogenation of 2-octanol in Ar or in air over 0.75 Bi–Pd/Al$_2$O$_3$, 1.0 Bi–Pd/Al$_2$O$_3$ and unpromoted Pd/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ (aqueous medium, method II in Ar and method III in air; 3 h). The selectivity to 2-octanone was always 100%.

lyst had good selectivity even in Ar where the hydrogen co-product was available in high concentrations for the hydrogenation and hydrogenolysis-type side reactions (Scheme 1).

An important point is that the rate enhancement achieved in air by Bi promotion should be considered only as a qualitative measure of the reaction rate. In the aerobic oxidation of alcohols over Pt-group metal catalysts the reactions are commonly carried out under mass-transport-limited conditions to avoid the rapid "overoxidation" and deactivation of the catalyst [2,4,48,58]. A further difficulty of a comparative study is that applying the same conditions, including the same rate of oxygen supply for all reactions, this rate may be too low for an active catalyst and it performs well below its intrinsic activity while it may be too high for a poorly active catalyst leading to its overoxidation and deactivation. This effect is illustrated by the transient experiments in Fig. 3. Dehydrogenation on Pt/Al$_2$O$_3$ in Ar afforded only 6.4% conversion in 65 min. After replacing Ar by air the catalyst completely lost its activity and the final conversion was still below 7%. In contrast, Bi promotion more than doubled the rate of 1-phenylethanol conversion in Ar (13.5% conversion in 65 min), and after switching to air the reaction was complete within less than 50 min.

3.4. Dehydrogenation of 2-octanol

Bi promotion enhanced the reactivity of both Pd- and Pt-based catalysts in the presence and absence of oxygen, as illustrated in Fig. 4 by reactions carried out in a water–surfactant system. Note that relatively mild conditions had to be chosen to avoid full conversion with the best catalyst, 1.0 Bi–Pt/Al$_2$O$_3$, but under these conditions the unpromoted catalysts afforded only 1% conversion in Ar. The rate acceleration achieved by Bi promotion was more pronounced with Pt/Al$_2$O$_3$ than with Pd/Al$_2$O$_3$ both in Ar and in air.
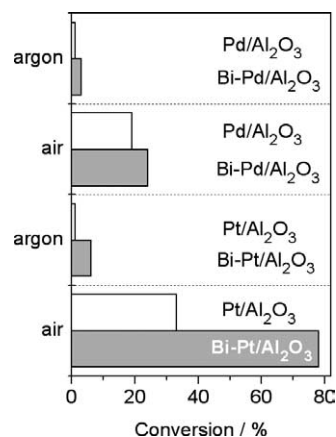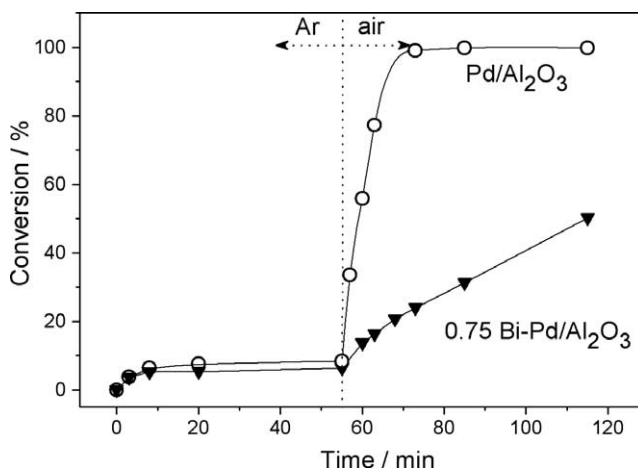

Fig. 5. Oxidation of cinnamyl alcohol (**6**, Scheme 2) over Pd/Al$_2$O$_3$ and 0.75 Bi–Pd/Al$_2$O$_3$ (toluene, method IV). The Ar atmosphere was replaced by air (flow rate: 60 ml min^{-1}) after 55 min. Details of the product distribution are shown in Table 4.

3.5. Dehydrogenation of cinnamyl alcohol

Dehydrogenation of cinnamyl alcohol (**6**, Scheme 2) under Ar represents a case where no rate acceleration could be achieved by Bi promotion. Dehydrogenation of allylic alcohols on Pt and Pd is relatively fast in the presence of a hydrogen acceptor, such as oxygen [52,59] or an olefin [51,54,60]. Here, under Ar (i.e., in the absence of any hydrogen acceptor), the reaction on Pd/Al$_2$O$_3$ slowed down after about 10 min, indicating some catalyst deactivation (Fig. 5). Replacing Ar by air accelerated the dehydrogenation enormously and over 99% conversion was reached within 18 min. The likely reasons for the catalyst deactivation in Ar and reactivation in air are decarbonylation-type side reactions (Scheme 2 and Table 4) and the rapid removal of CO from the Pd surface, respectively [52]. Partial coverage of the Pd surface by Bi decreased the rate in Ar only to a minor extent but in air the negative effect was considerable.

Table 4
Transformation of cinnamyl alcohol in toluene at 65 °C (method IV). For identification of the products **7–13** see Scheme 2

Entry	Catalyst	Atmosphere	Time (min)	Conv. (%)	Yield (%)							Selectivity (%)	
					7	8	9	10	11	12	13	7	8
1	Pd/Al$_2$O$_3$	Argon	55	8.3	4.5	3.4	0	0.2	0	< 0.1	< 0.1	55	40
		Air	+18	99.1	64.3	32.6	< 0.1	0.3	0.7	1.1	< 0.1	65	33
2	0.75 Bi–Pd/Al$_2$O$_3$	Argon	55	6.4	3.7	1.3	< 0.1	1.4	< 0.1	0	< 0.1	58	20
		Air	+60	50.3	35.8	10.6	0.1	2.6	0.3	0.4	0.4	71	21
3	Pt/Al$_2$O$_3$	Argon	55	0.6	0.6	< 0.1	0	0	0	0	0	99[a]	1[a]
		Air	+130	1.5	1.4	0.1	0	0	0	0	0	96	4
4	1.0 Bi–Pt/Al$_2$O$_3$	Argon	55	0.5	0.4	0.1	0	0	0	0	0	87[a]	13[a]
		Air	+60	37.7	37.3	0.4	0	0	0	0	< 0.1	99	1

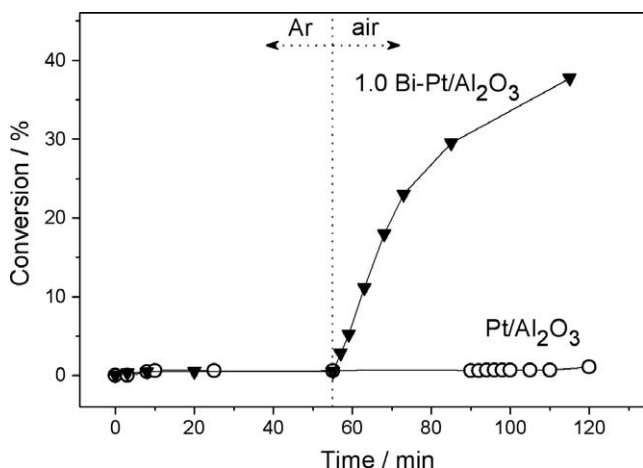[a] Due to the very low conversion (< 1%) determination of selectivity is uncertain.

Fig. 6. Dehydrogenation of cinnamyl alcohol (**6**) over Pt/Al$_2$O$_3$ and 1.0 Bi–Pt/Al$_2$O$_3$ (toluene, method IV). The Ar atmosphere was replaced by air (flow rate: 60 ml min^{-1}) after 55 min. Details of the product distribution are shown in Table 4.

The diminished reactivity is attributed to the lower number of surface Pd sites available for hydrogen adsorption and alcohol dehydrogenation in the Bi-promoted catalyst, as indicated by a drop of the hydrogenation activity (Table 3) and by XPS analysis (Fig. 1, Table 2). Promotion of Pd/Al$_2$O$_3$ by Bi changed the product distribution and resulted in a small enhancement of selectivity to the key product cinnamaldehyde (**7**).

Table 4 and Fig. 6 show that in comparison to Pd/Al$_2$O$_3$, Pt/Al$_2$O$_3$ is much more sensitive to the destructive adsorption of reactant and products: less than 1% conversion was achieved in 55 min in Ar and the reaction was barely accelerated by introducing air. Bi promotion of Pt/Al$_2$O$_3$ had a positive effect only after replacement of Ar by air, leading to higher rate and excellent selectivity. The good performance of Bi-promoted Pt in the aerobic oxidation of cinnamyl alcohol has already been reported [44,59].

We attribute the poor performance of Pt/Al$_2$O$_3$ to poisoning by C$_x$H$_y$-type fragments formed in the decarbonylation type side reactions (Scheme 2) [16]. It is very likely that only a fraction of these species desorbs from the surface as olefins. For example, propenylbenzene (**10**) and styrene (**13**) could be detected in significant amounts by GC analysis of

Table 5
Effect of olefins as hydrogen acceptors on the dehydrogenation of 1-phenylethanol (**1**) over Pd/Al$_2$O$_3$ and Pt/Al$_2$O$_3$ (method V)

H acceptor	Yield (selectivity) to **2** (%)	
	Pd/Al$_2$O$_3$	Pt/Al$_2$O$_3$
No	33 (94)	15 (81)
Cyclohexene	72 (100)	3 (100)
Vinyl acetate	41 (100)	0 (–)[a]

[a] No yield even after 5 h.

the solution. Introduction of air (after 55 min, Figs. 5 and 6) can oxidize CO to CO$_2$ that desorbs from the surface but the oxidative removal of hydrocarbon fragments or dimerized and oligomerized species is not expected. This could be the reason for the poor performance of unpromoted Pt/Al$_2$O$_3$ (1.5% final conversion, Table 4, entry 3; this point is not shown in Fig. 6). Bi promotion had a dramatic effect on the activity but only in the presence of molecular oxygen. Probably, Bi contributes to the oxidative removal of surface impurities or even diminishes their formation due to an ensemble effect (i.e., larger active site ensembles are required for the side reactions).

The assumption that Pt is more sensitive to poisoning by hydrocarbon residues than Pd is supported by additional experiments. For these experiments the dehydrogenation of 1-phenylethanol in cyclohexane under Ar was chosen as this reaction was apparently not affected by catalyst poisoning (Fig. 2). The dehydrogenation reaction in Ar was repeated in the presence of cyclohexene and vinyl acetate as organic hydrogen acceptors (Table 5). Contrary to the expected higher dehydrogenation rate [50,51,54], these olefins poisoned Pt/Al$_2$O$_3$. The reference reactions with Pd/Al$_2$O$_3$ showed the expected behavior: higher rate and selectivity in transfer dehydrogenation with hydrogen acceptors, compared to simple dehydrogenation in Ar.

4. Discussion

Numerous mechanistic models have been suggested for the interpretation of the promoting effect of metal additives (Bi, Pb, Sn, Te, etc.) on the oxidation of alcohols and poly-

ols to the corresponding carbonyl compounds and carboxylic acids. Adopting the dehydrogenation mechanism of alcohol oxidation [2,3,11], two important groups of these models emerge.

(i) The promoter may directly influence the rate and (regio)selectivity of the alcohol dehydrogenation reaction. A plausible example is the oxidative dehydrogenation of polyfunctional alcohols in 2-position, where the high regioselectivity has been attributed to complex formation between a neighboring Pt-group metal–promoter metal bimetallic site and the reactant [1,17,61].

(ii) The second group comprises those models which assume that the promoter does not influence directly the dehydrogenation step but affects the adsorption and transfer of oxygen, including the oxidation of the coproduct hydrogen, the oxidative removal of surface impurities [21,40,62,63], and the improved resistance of the Pt-group metal against "overoxidation" [64] (i.e., the coverage of surface sites by oxygen leading to a slow down of alcohol oxidation [48,65]).

The promoter effect in the dehydrogenation of 1-phenylethanol on 0.75 Bi–Pd/Al$_2$O$_3$ (Fig. 2) can be interpreted by a model belonging to the first group. Addition of Bi to Pd/Al$_2$O$_3$ enhanced the rate of reaction by a factor of 1.3, independent of the presence or absence of oxygen. Clearly, Bi accelerated the dehydrogenation step and its influence cannot be connected to the presence of oxygen. Dehydrogenation of 2-octanol (Fig. 4) provides a further example to this case. Interestingly, in this reaction the rate acceleration by Bi promotion was even higher in Ar (a factor of 3 and 6) than in air (1.3 and 2.4) for Pd/Al$_2$O$_3$ and Pt/Al$_2$O$_3$, respectively. The likely reason is the very low activity of the catalysts in Ar that increases the relative error of the determination of conversions.

Dehydrogenation of cinnamyl alcohol on 1.0 Bi–Pt/Al$_2$O$_3$ is a good example of the second group of models: the promoter effect is clearly connected to the presence of oxygen and Bi has no influence on the alcohol dehydrogenation in Ar (Fig. 6). On the basis of former studies [52] it is probable that Pt/Al$_2$O$_3$ and Bi–Pt/Al$_2$O$_3$ are poisoned by alcohol degradation products in Ar, and Bi deposited on the surface of Pt particles accelerates the oxidative removal of surface impurities when switching from Ar to air.

Dehydrogenation of 1-phenylethanol on Pt-based catalysts reveals a complex effect of Bi. Promotion of Pt/Al$_2$O$_3$ enhanced the reaction rate in Ar by a factor of 1.4 and in air by a factor of 2.8 (Fig. 2). When using another Bi-promoted catalyst under different conditions (Fig. 3), the relative rate acceleration in air was even bigger, compared to the rate acceleration achieved by Bi promotion in Ar. We can conclude that when using these catalysts the role of Bi is not limited to the acceleration of the dehydrogenation of 1-phenylethanol but influences also an additional process that is connected to the transfer of oxygen. This effect may be the enhanced rate of oxidation of the coproduct hydrogen or the oxidative removal of a strongly adsorbed surface impurity.

5. Conclusions

Interpretation of the frequently observed promoter effect in the aerobic oxidation of alcohols is a demanding task. Unambiguous experimental evidence to support a model is rare. A detailed kinetic analysis is troublesome and not always conclusive. In situ techniques are not widely accessible. We propose a simple test to clarify the role of promoter: the comparison of alcohol dehydrogenation in the presence and absence of molecular oxygen. In case there is no promoter effect in inert atmosphere, the role of promoter cannot be attributed to improvement in the dehydrogenation step. On the other hand, a strong rate enhancement or a shift in the product distribution in the absence of oxygen is an evidence of a direct role of promoter in alcohol dehydrogenation and an indication that the role of promoter is not limited to, for example, a better oxygen transfer or improved oxygen tolerance of the noble metal component.

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