Liquid phase oxidation of alcohols with oxygen: *in situ* monitoring of the oxidation state of Bi-promoted Pd/Al₂O₃†

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In situ, time-resolved XAS studies on a Bi–Pd/Al₂O₃ catalyst indicate that Pd, and Bi located on the Pd surface, are in a reduced, metallic state during the oxidation of 1-phenylethanol with molecular oxygen—a key for understanding the role of promoter in the reaction mechanism.

Oxidation of alcohols to carbonyl compounds is an important process in synthetic chemistry. Various solid catalysts are active and selective in this transformation, using molecular oxygen as the sole oxidant.[1–4] Among these materials, supported noble metals seem to be the most versatile and technically attractive catalysts for the oxidation of alcohols, diols and polyols.[5–7] Several papers and patents have been published on the modification of Pt and Pd by metal promoters, in particular by Bi and Pb, that alone are inactive but can dramatically enhance the activity and tune the selectivity.

The assumptions made for the interpretation of the beneficial role of promoters are contradictory and include almost all feasible possibilities. Most of these models are speculative and not supported by measurements on the catalyst in its working state. A plausible model is the geometric blocking of a fraction of active sites by the promoter metal that may accelerate alcohol oxidation as smaller active site ensembles are less active in side reactions leading to the formation of poisoning species.[8] Another model attributes the change in product distribution to complex formation between an α-functionalized alcohol, a surface Pt or Pd atom, and a neighbouring positively charged promoter atom.[6] More recently, the role of promoter was traced to partial leaching of Bi³⁺ and formation of homogeneous complexes.[9] Obviously, determination of the oxidation state of the promoter metal during alcohol oxidation is essential for the scientific evaluation of these proposals.

Here, we report the monitoring of the oxidation state of a bimetallic catalyst during alcohol oxidation using *in situ* X-ray absorption spectroscopy (XAS). XAS in terms of X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) is a powerful technique for *in situ* characterization of solid mono- and bimetallic catalysts used in solid/gas[10–12] and solid/liquid type reactions,[13] including aqueous alcohol oxidation over Pt and Pd.[14–16] These XAS studies offered element-specific determination of the structure of the noble metal (oxidation state, morphology) during alcohol oxidation with molecular oxygen. For *in situ* monitoring of the oxidation state, the XANES region is often valuable.[11,12,16] Thus, we used this technique for characterization of the structure of the promoter metal during dynamic changes of the reaction conditions.
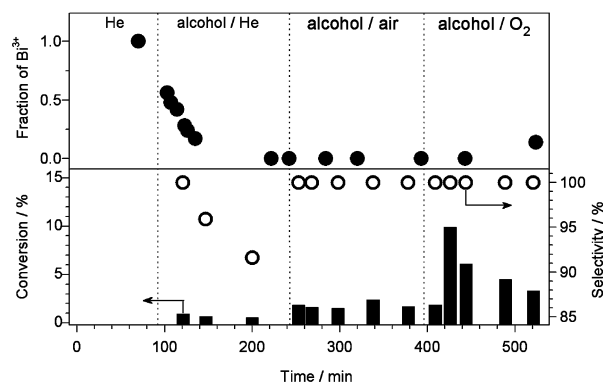
We have chosen a widely studied catalyst system, Bi-promoted Pd, and the oxidation of 1-phenylethanol to acetophenone as a commonly used model reaction. A special technique[17] was applied to deposit mainly Bi adatoms onto the surface of Pd particles in a 5 wt% Pd/Al₂O₃ catalyst to facilitate the interplay between Bi and Pd and thus enhance the promoter effect. XPS analysis revealed that the fraction of Bi, deposited onto Pd and reducible by hydrogen even at room temperature in

the XPS chamber, was 73% (Bi 4f₇/₂ and Bi 4f₅/₂). The rest of the Bi is assumed to be present on the alumina support as Bi³⁺-containing particles (presumably as Bi₂O₃·xH₂O); this fraction was not reducible by hydrogen even at 200 °C.

Preliminary catalytic experiments proved a remarkable promoter effect: the activity of the 0.75 wt% Bi–5 wt% Pd/Al₂O₃ catalyst in the aerobic oxidation of 1-phenylethanol was up to six fold higher than that of the unpromoted catalyst.

Fig. 1 illustrates the (oxidative) dehydrogenation of 1-phenylethanol in toluene in a continuous-flow fixed-bed reactor that served also as the EXAFS cell due to use of X-ray transparent windows. The reactions were carried out at constant temperature (60 °C) and the structural changes in the bimetallic catalyst were induced by variation of the oxygen concentration in the feed. The products were identified by GC analysis (Thermo Quest Trace 2000, HP-FFAP column).

Determination of the structure (oxidation state) of the noble metal constituent was achieved by analysis of the near-edge structure (white-line at 24.36 keV decreases during reduction) and the Fourier transformed EXAFS spectra at the Pd *K*-edge (Pd–Pd scattering is found at 2.5 Å and that for Pd–O at 1.5 Å, Fig. 2).[16] A similar approach was used for the determination of the oxidation state of Bi, where particularly the near-edge structure changed significantly (see ESI†). Assuming that the Bi³⁺ species on the surface of Pd are directly reduced to Bi⁰,[18] linear combination analysis (LCA) of the near-edge spectra of Bi⁰ and Bi³⁺ at the Bi *L₃*-edge was used to determine the oxidation state of Bi on Pd (see ESI†).‡ Interaction of the catalyst with the alcohol reactant in He-saturated toluene afforded the same extent of reduction as observed in hydrogen at 200 °C. Thus, the catalyst exposed to air (only Bi³⁺ is present) and that reduced by 1-phenylethanol (all reducible Bi species are present as Bi⁰) provided suitable reference spectra to

Fig. 1 Oxidation state (●), activity (vertical bars) and selectivity (○) of a Bi–Pd/Al₂O₃ catalyst during (oxidative) dehydrogenation of 1-phenylethanol in a continuous-flow reactor used as EXAFS cell. A similar setup has been described previously.[16] 65 mg powdered catalyst was put in the reactor cell (0.12 ml), which was located in an oven (*T* = 60 °C). The reaction mixture (20.5 mM 1-phenylethanol in toluene) and toluene were stored in three separate tanks, where the liquids could be saturated with He, air or O₂ at 1 bar. The liquid flow rate was 0.68 ml min⁻¹. The extent of Bi³⁺ present on Pd was calculated by linear combination analysis.
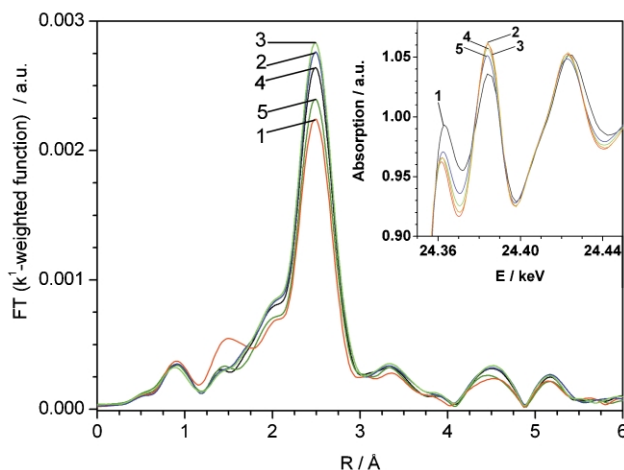
calculate the fraction of reducible Bi^{3+} in the catalyst (see Fig. 1).

Feeding of 1-phenylethanol under He (from 93 min on, Fig. 1) showed that the catalyst was moderately active in dehydrogenation. The drop in selectivity to acetophenone and the formation of up to 8.4% ethylbenzene by C–O bond hydrogenolysis are attributed to reduction of the Pd constituent to Pd^0 and a significant amount of hydrogen present on its surface.[19] This interpretation is supported by the observation that both Pd (spectrum 2 in Fig. 2) and Bi (Fig. 1 and ESI†) were in a reduced state. In the same period the conversion decreased from 0.91% ($t = 121$ min) to 0.53% ($t = 200$ min). This change may be due to establishment of the steady state conditions and to degradation reactions leading to strongly adsorbed by-products[20] (undetectable by GC); two effects that could not be separated from each other.

After 242 min the reaction mixture was changed from He- to air-saturated solution. The conversion increased to about 1.8% and remained at around this value for the next 150 min. The by-product ethylbenzene disappeared indicating that the actual hydrogen concentration on the Pd sites was negligible. During this aerobic oxidation both Bi and Pd remained in a reduced state, despite the presence of oxygen in the feed. Spectra 2 and 3 in Fig. 2 are almost identical and no changes can be observed in the near-edge structure at the Pd K-edge (see inset). In the Fourier transformed EXAFS spectra the same Pd–Pd scattering is present at 2.5 Å. Similarly, linear combination analysis confirms the reduced state of Bi (fraction of reducible Bi^{3+} = 0).

The above conditions are appropriate for the steady state aerobic oxidation of 1-phenylethanol as the reactor was operated in the oxygen transport limited regime. Working in the kinetic region, however, results in a rapid catalyst deactivation due to successive oxidation of the active Pd sites. This phenomenon is commonly termed as "over-oxidation".[5,7] The appropriate conditions for "over-oxidation" are set in the next step by replacing air by oxygen. At first, the higher oxygen concentration enhanced considerably the conversion (9.9% at $t = 426$ min) then the reaction rate decreased monotonously with time. XAS analysis proved that the slow oxidation of Pd (spectrum 4 in Fig. 2) and Bi (increasing fraction of Bi^{3+}, Fig. 1) was not observed before the loss of activity. Oxidation of the Bi promoter occurred in parallel to that of Pd.

Further oxidation of both constituents was observed in oxygen-saturated toluene, in the absence of alcohol. This change is illustrated for the Pd constituent in Fig. 2 (spectrum 5): the Pd–Pd scattering is lower and the white-line at around 24.36 keV in the near-edge region (inset) is slightly higher (for the Bi constituent see ESI†).

The results presented in Figs. 1 and 2 demonstrate that during the aerobic oxidation of 1-phenylethanol both the active metal and the promoter in the Bi–Pd/Al$_2$O$_3$ catalyst are in a reduced state. Their partial oxidation can only be observed when the oxygen concentration is too high in the feed (kinetic regime), which conditions lead to deactivation of the catalyst due to "over-oxidation". Therefore, the positive influence of Bi adatoms on the reaction rate in the presence of oxygen cannot be attributed to (partially) oxidized Bi or to Bi leaching and homogeneous catalysis. A feasible model that is consistent with the reduced state of both metals assumes an ensemble effect of the promoter metal, as mentioned in the introduction.[8] The rate acceleration may also be attributed to bifunctional catalysis assuming that the oxygen-containing species adsorbed on Bi in the neighbourhood of Pd is involved in alcohol oxidation.[21]

Notes and references

‡ XANES experiments at the Pd K- and Bi L_3-edges were recorded at beamline X1 at HASYLAB (DESY in Hamburg) operating at 4.4 GeV in the transmission mode using Si (311) and Si (111) double crystal monochromators. The raw data were energy-calibrated with the respective metal foil, background-corrected, normalized, and Fourier transformed using the WINXAS 2.1 program package.[22] For EXAFS data analysis, Fourier transformation was applied on the k^1-weighted functions in the interval $k = 3.5$–16.4 Å^{-1} for Pd. The LCA fits of Bi L_3-XANES spectra (13.375–13.56 keV) were performed using spectra 1 (oxidized) and 2 (reduced) in the ESI.†

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Fig. 2 Structure of Pd in Bi–Pd/Al$_2$O$_3$ during the reaction series shown in Fig. 1, revealed by Fourier transformed EXAFS data. The inset represents the XANES region of the Pd K-edge. The spectra were taken in He-saturated toluene (1: $t = 44$ min in Fig. 1), in He-saturated solution of 1-phenylethanol (2: $t = 163$ min in Fig. 1), in air-saturated solution of 1-phenylethanol (3: $t = 367$ min in Fig. 1), in O$_2$-saturated solution of 1-phenylethanol (4: $t = 506$ min in Fig. 1) and in O$_2$-saturated toluene (5: $t = 603$ min, not shown in Fig. 1).