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Reactant induced restructuring and corrosion of germanium–palladium catalysts during hydrogenation reactions

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An anomalous rate enhancement with increasing conversion has been observed during the liquid phase hydrogenation of nitrobenzene and crotonaldehyde over Ge/Pd/C catalysts at ambient temperature and atmospheric pressure. Inductive coupled plasma atomic emission spectroscopy and electrochemical measurement of the oxidation state of catalysts during reaction revealed that the bimetallic particles were partially oxidized by the reactants, which resulted in Ge-dissolution and increased exposure of Pd on the surface. It is proposed that the surface and bulk composition of Ge/Pd catalysts are a function of their oxidation state. This behaviour is due to the unusually high mobility of Ge in the Pd lattice and to the good solubility of GeO_2 in polar solvents. The influence of hydrogen transport on the corrosion process and the stability of other X/Pd type bimetallic catalysts during liquid phase hydrogenation are also discussed.

Keywords: restructuring (corrosion) of bimetallic catalysts; germanium–palladium catalysts; hydrogenation of nitrobenzene and crotonaldehyde; catalyst potential

1. Introduction

In recent years there is a growing interest in the structural changes of metal catalysts during reaction. Different types and mechanisms of surface restructuring have been described on the atomic scale and the role of surface geometry, chemisorption and the chemical reaction itself have been thoroughly discussed [1–3]. These considerations deal with gas–solid type reactions with relatively simple adsorbates such as CO or hydrogen.

The situation is more complex in the presence of a liquid phase, where the metallic component can be leached out. This corrosion process has been observed in the hydrogenation of olefinic and acetylenic compounds over Pt/Al_2O_3, $Pb/Pd/CaCO_3$ (Lindlar catalyst) and amorphous Pd–Ge and Pd–Si alloys [4,5]. The phenomenon has been attributed to a "semi-extractive" adsorption of the hydrocarbon and a soluble complex formation with the acetylenic compound.

It has been proved that Pd – in the presence of hydrogen – may undergo considerable structural changes, which are due to some strong metal–reactant interaction [6]. A striking example is the almost 80% decrease of the surface area of a Pd/C catalyst during refluxing in xylene under hydrogen. The restructuring was even more pronounced when quinoline and sulphur were simultaneously present (typical modifiers for the Rosenmund reduction of acid chlorides).

A substantial loss in noble metal content was observed in the aqueous phase oxidation of sugar alcohols to acids with molecular oxygen on Pt/alumina or Pt/C catalysts [7,8]. In these instances the thermodynamic basis of metal dissolution is the partial oxidation of the noble metal in the presence of a good chelating agent. Interestingly, during the oxidation of 1-methoxy-2-propanol to methoxyacetone in an aqueous alkaline medium, only the bulk lead modifier dissolved from the surface of a Pd/C catalyst, whereas the more strongly bound lead adatoms remained unaltered [9]. The phenomenon was explained by the intermediate oxidation state of the catalyst during reaction, which resulted in a differentiation between weakly and strongly bound modifiers.

It is frequently neglected that a metal catalyst can be oxidized even during a hydrogenation reaction. If the reactant is a strong oxidant, such as the aromatic nitro compounds, it can considerably oxidize the metal surface, which may result in corrosion and restructuring under certain conditions. In this paper we report the reactant induced surface restructuring and corrosion of carbon-supported Ge/Pd catalysts and their catalytic performance in the liquid phase hydrogenation of nitrobenzene and crotonaldehyde.

The Ge/Pd catalysts were prepared by reduction of GeO_2 onto carbon-supported Pd by hydrogen. Unique features of the method are that under these conditions (i) Ge can deposit only onto the Pd surface as adatoms and the formation of Ge–Ge bonds (bulk metal deposition on Pd or on the support) is thermodynamically not possible, and (ii) there is a rapid three-dimensional alloy formation due to the high mobility of Ge atoms in the Pd framework [10–12]. Electrochemical and XPS analysis proved the existence of two, energetically different species, Ge^0 and Ge^{n+}. In addition, XRD analysis of unsupported alloys confirmed the formation of ordered PdGe and Pd_5Ge phases [13].

2. Experimental

2.1. CATALYSTS

Distilled water (after ion-exchange) and analytical grade reagents were used. The unsupported Pd was prepared by hydrogenation via the hydroxide [10]. A Pd dispersion of 0.06 was determined from the hydrogen region of an electrochemical polarization curve [14]. A commercial Pd/C catalyst with 10 wt% metal loading was used as received (Dutral, Montedison). The dispersion was 0.19, as determined by TEM and electrochemical polarization [14,15].

The bimetallic catalysts were prepared by selective reduction of Ge^{4+} or Pb^{2+} onto the supported Pd particles. The Ge-promoted Pd/C catalysts were prepared in situ, before nitrobenzene of crotonaldehyde reduction (see below). For the preparation of Pb-promoted Pd/C catalysts, Pd/C was pre-reduced in water by hydrogen, then the proper amount of $Pb(OAc)_2$ in an aqueous $HClO_4$ solution ($pH = 1$–2) was added to the catalyst slurry and the hydrogen treatment was continued. Under these conditions only lead adatoms can deposit onto the surface of carbon-supported Pd particles, since the formation of Pb–Pd bonds (bulk metal) is thermodynamically not possible [13]. The catalyst was filtered off, washed to neutral and dried at 105°C.

2.2. HYDROGENATION PROCEDURE

The hydrogenation reactions were performed in a 200 ml glass reactor, equipped with magnetic stirrer ($n = 1500\ \mathrm{min}^{-1}$) and electrodes. The reactions were carried out under atmospheric hydrogen pressure and at 25°C. 20 mg Pd/C catalyst with the proper amount of GeO_2 in 10 ml water was pre-reduced in situ with hydrogen for 1 h in order to achieve a complete deposition of Ge. 1.20 g nitrobenzene in 15 ml EtOH or 0.70 g crotonaldehyde in 10 ml EtOH was added to the slurry and the hydrogen consumption was measured. The reaction was followed gas-chromatographically. The products were aniline and butyraldehyde ($>95\%$), respectively. The dissolved metal content was determined by inductive coupled plasma atomic emission spectroscopy (ICP-AES) after distilling off the organic compounds from the solution. For the reductions catalyzed by Pb-modified Pd/C, 20 mg catalyst was pre-reduced in 10 ml water and the reaction was performed as described above.

2.3. ELECTROCHEMICAL METHODS

The electrochemical cell, the modified carbon paste electrode and the experimental setup used for cyclic voltammetric measurements have been described previously [9]. 1 mg Pd catalyst powder was placed onto the surface of the flat carbon paste and dispersed on it. Pt rod counter and $Ag/AgCl/KCl_{sat}$ reference electrodes (with double junction to avoid the pollution by Cl^- ions) were used. The polarizations were carried out in 0.5 M aqueous H_2SO_4 electrolyte, in a nitrogen atmosphere at 25°C at a sweep rate of 2 mV s^{-1}. All potentials in the paper are referred to the reversible hydrogen electrode. At first the catalyst was polarized with 12 mV s^{-1} cathodically to 50 mV in 0.5 M aqueous H_2SO_4 electrolyte and then this potential was kept for 5 min. After the addition of some GeO_2-containing electrolyte to the solution (final concentration: 7×10^{-3} M GeO_2, dissolved as

H_2GeO_3) the potential was held at 50 mV for 1 min. The lead deposition onto Pd was made at 50 mV for 1 min in 0.5 M aqueous $HClO_4$ saturated with $PbSO_4$. The anodic polarization was started after replacement of the solution by 0.5 M aqueous H_2SO_4 electrolyte.

The catalyst potential during the hydrogenation reaction was measured with a Pt rod collecting electrode against an Ag/AgCl/KCl_{sat} reference electrode. The reference electrode was separated from the main compartment of the cell by two diaphragms to avoid the pollution of H_2SO_4 electrolyte by Cl^- ions [16,17]. The pH of the reaction mixture was followed with a glass pH electrode and the measured values were corrected accordingly.

3. Results and discussion

3.1. NITROBENZENE HYDROGENATION WITH Ge/Pd/C CATALYSTS

Alloying Pd with Ge suppresses the hydrogen sorption on the bimetallic particles and, accordingly, the higher the surface Ge/Pd atomic ratio, the lower is the activity of these catalysts in the hydrogenation of simple organic reactants, such as olefins, aldehydes, ketones, alcohols or aromatic compounds [10]. The same is true for the reduction of nitro compounds: the initial rate tends towards zero with increasing surface Ge content in the hydrogenation of nitrobenzene (fig. 1). Astonishingly, the catalytic activity increased with time (conversion) and a seven-fold

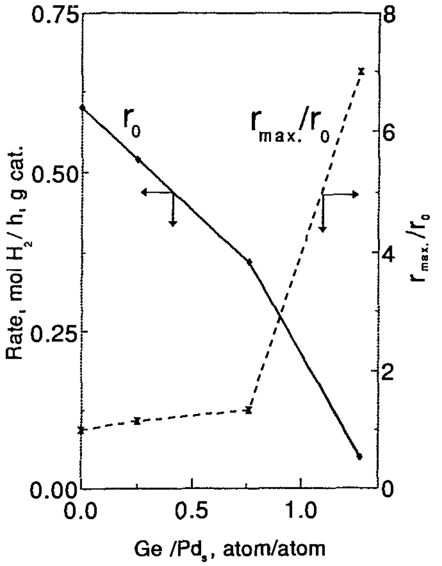

Fig. 1. Rate of nitrobenzene hydrogenation with Ge/Pd/C catalysts as a function of the atomic ratio Ge/Pd_s (r_0: initial rate, r_{max}: maximum rate).

increase in the ratio of maximum rate to initial rate was observed at high (nominal) Ge/Pd_s atomic ratio.

An ICP-AES analysis of the reaction mixture revealed that the increase in the rate of nitrobenzene reduction is accompanied with the partial dissolution of Ge from the bimetallic catalysts (fig. 2). Note that the adsorption of Ge^{4+} on activated carbon is negligible [10]. Thus, the phenomenon may formally be interpreted as a surface enrichment in Pd during reaction, which results in an increase in activity of the bimetallic catalysts.

In order to obtain more information about the processes occurring on a molecular scale, we measured in situ the oxidation state of Ge/Pd/C catalysts. Measurement of the catalyst potential is the only known method to follow the oxidation state during a liquid phase reaction [16,17]. Typically, during catalyst pre-reduction the potential was 0 mV, upon addition of nitrobenzene the potential increased immediately (up to 190 mV) followed by a slow decrease (to 170 mV). At the end of reaction, i.e. above 95% conversion, the potential dropped to about 0 mV.

During pre-reduction with hydrogen the Pd catalyst behaves as a hydrogen electrode: its potential referred to a reversible hydrogen electrode is $E = 0$ mV. During reaction the catalyst potential is a mixed potential [18]. It is determined by two main electrode processes, namely the hydrogen electrode reaction and the nitrobenzene → aniline reaction. The 170–190 mV potential shift is relatively high compared to the 10–60 mV shifts measured under the same conditions in the hydrogenation of various olefinic and carbonyl compounds [10]. The explanation is that nitrobenzene is a strong oxidant (calculated $E_{ox/red} = 826$ mV [19]). Similar

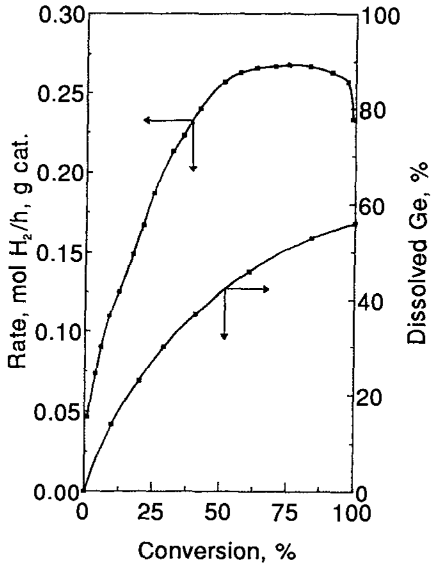

Fig. 2. Rate of nitrobenzene hydrogenation with a Ge/Pd/C catalyst (Ge/Pd_s = 1.3 atom/atom) and the relative amount of dissolved Ge as a function of conversion.

or even higher potential shifts have been reported earlier for the reduction of nitro compounds [19,20].

For the interpretation of the catalyst potential, we measured the cyclic voltammograms of unsupported Pd and Ge/Pd catalysts powders (fig. 3). Note that the voltammograms of carbon-supported and unsupported Ge/Pd catalysts are rather similar, but in the former case the processes taking place on the high surface area carbon partly overlap with those occurring on the metal surface [10–12]. The peaks in the range of 50–350 mV correspond to the oxidation of weakly bonded (mainly dissolved) and strongly bonded (mainly adsorbed) hydrogen [21]. On the Ge/Pd sample the hydrogen ionization peaks are suppressed. The two peaks around 450 and 600 mV are assigned to the oxidation of weakly and strongly bonded Ge adatoms, respectively, but Ge dissolved in the Pd framework is oxidized also in this potential region [11,12]. The broad wave above 700 mV represents the oxidation of surface Pd atoms.

The oxidation of hydrogen and Ge overlap [10–12]. The hatched area under the anodic sweep of the Ge/Pd catalyst represents the estimated oxidation of Ge species. The dotted line indicates the maximum catalyst potential during nitrobenzene reduction. This value is higher than that at the beginning of oxidation of weakly bound Ge, which explains the partial oxidation and dissolution of pre-deposited Ge from the Ge/Pd/C catalysts during reaction.

In order to obtain a more reliable estimation for the potential dependence of the oxidation of surface Ge atoms, we calculated the relative coverage of Pd_s by Ge

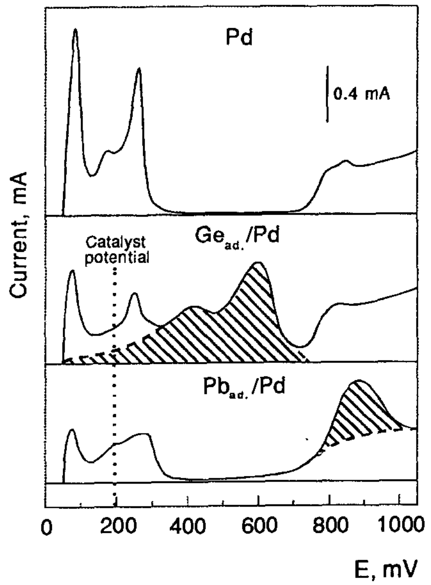

Fig. 3. Positive sweeps of cyclic voltammograms of Pd, Ge/Pd ($\Theta_{Ge} = 0.60$) and Pb/Pd ($\Theta_{Pb} = 0.52$) catalyst powders. The dashed line represents the reaction potential during nitrobenzene reduction.

as a function of the catalyst potential. The calculations are based on a previous study of the Ge/Pd system in a 0.5 M aqueous H_2SO_4 solution, supposing that Ge does not adsorb hydrogen and the H : Pd_s stoichiometry is 1 : 1 [12]. The continuous line in fig. 4 represents the values calculated from the hydrogen sorption on the bimetallic system and the dashed line is an extrapolation to 0 mV. (Between 50 and 0 mV the quantitative determination is ambiguous due to the hydrogen adsorption–desorption equilibrium.) During the preparation of Ge/Pd/C catalysts under atmospheric hydrogen pressure, the potential is 0 mV, which corresponds to 100% relative coverage in fig. 4. The Ge coverage of Pd_s decreases continuously with increasing catalyst potential. At 170–190 mV, which was measured between 5 and 95% conversion of nitrobenzene, the fraction of free surface Pd atoms is quite high which explains the improved activity of restructured catalysts.

It is not seen from fig. 4, but has been proved earlier [10–12], that Ge adsorption on Pd and absorption in Pd are coupled processes. The dissolution of Ge in Pd under a hydrogen atmosphere and the reverse process under oxidative conditions are astonishingly fast and they cannot be separated from Ge adsorption. We propose that the surface and bulk composition of Ge/Pd catalysts are a function of their oxidation state. This unique property is due to the mobility of Ge in the Pd lattice even at room temperature [13] and to the solubility of GeO_2 in many polar solvents.

It was also checked, if there is any effect caused by the aniline product, which can act as a complexing agent, on the corrosion of Ge/Pd/C catalysts. A Ge/Pd/C (Ge/Pd_s = 1.3 atom/atom) catalyst was pre-reduced with hydrogen according to the general hydrogenation procedure, and then stirred further in the presence of

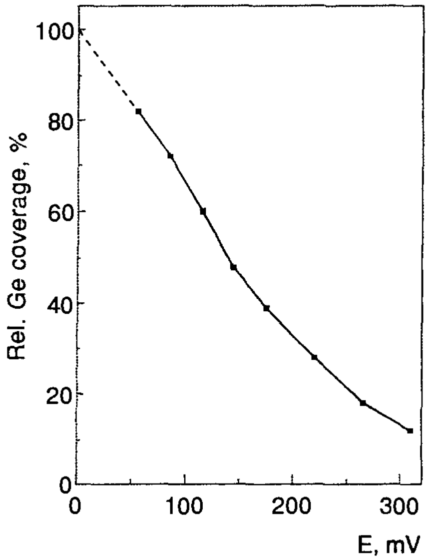

Fig. 4. Relative coverage of Pd by Ge as a function of catalyst potential.

aniline under nitrogen. After 3 h there was no Ge detectable in the reaction mixture. This experiment proved that Ge dissolution during nitrobenzene reduction is unambiguously due to the partial oxidation of the bimetallic particles.

3.2. CROTONALDEHYDE HYDROGENATION WITH Ge/Pd/C CATALYSTS

In general, Ge deposition onto Pd/C decreases the hydrogen sorption and the catalytic activity in the hydrogenation of reducible functional groups. An anomalous increase in reaction rate with increasing Ge/Pd_s atomic ratio was observed in the hydrogenation of some reactants, which possess a C=C double bond conjugated with a hydroxyl, carbon of phenyl group [10]. The average rate of reduction of allyl alcohol (CH_2=CH–CH_2OH) as a function of Ge/Pd_s atomic ratio is shown in fig. 5, as an example. The enhanced rate has been attributed to an ensemble effect of Ge adatoms, resulting in changes in the adsorption of reactant or product.

A similar rate enhancement effect of Ge was observed in the hydrogenation of crotonaldehyde (CH_3–CH=CH–CHO) to butyraldehyde, with the exception that even at very high atomic ratios of Ge/Pd_s the activity of the bimetallic catalysts was higher than that of Pd/C. At such high Ge/Pd_s ratios the hydrogen sorption on the bimetallic particles is very low and the hydrogenation activity is also diminished in many other reactions [10]. The explanation of the anomalous behaviour is again the partial oxidation of the catalysts during reaction. The catalyst potential was 30–35 mV during the reduction of allyl alcohol, while in the hydrogenation of

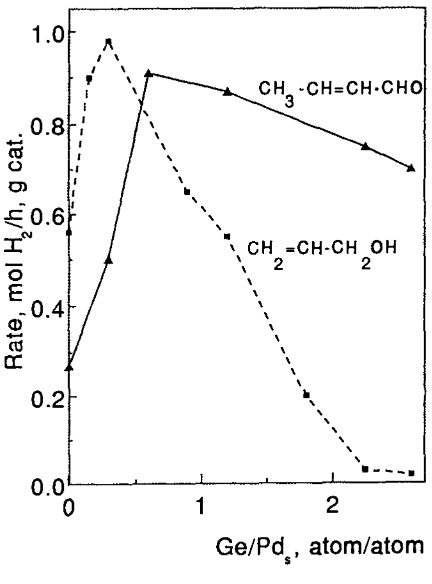

Fig. 5. Relative rate of allyl alcohol and crotonaldehyde hydrogenation with Ge/Pd/C catalysts as a function of the atomic ratio Ge/Pd_s.

crotonaldehyde the potential of the catalyst slurry was around 90 mV. According to fig. 4, the latter potential shift may cause a considerable Ge corrosion, which was confirmed by ICP-AES analysis of the reaction mixture. It seems that the corrosion process results in a surface Ge/Pd_s ratio, which is close to the optimum for this reaction.

The 30–35 mV potential shift, measured in the hydrogenation of allyl alcohol, is not enough for a detectable restructuring (corrosion) of the Ge/Pd/C catalysts. This indicates that the potential of the catalyst slurry plays a crucial role in the restructuring process.

3.3. GENERAL CONSIDERATIONS ON THE STABILITY OF BIMETALLIC CATALYSTS DURING HYDROGENATION REACTIONS

The corrosion stability of metals is a function of several parameters. Here we discuss only two of them: (i) the nature of the alloying component (X) in the X/Pd system and (ii) the role of transport processes.

The stability of Pd-based bimetallic catalysts is usually much better than that of the Ge/Pd system. An example is the frequently used Pb/Pd (Lindlar-type) catalysts. The curve in the bottom of fig. 3 represents the anodic sweep of the cyclic voltammogram of a Pb/Pd catalyst powder. The oxidation of lead adatoms occurs above 700 mV (hatched area), i.e. in this respect lead adatoms behave similarly to surface Pd atoms. Note that the oxidation of a surface lead atom bound to another lead atom (Pb–Pb, "bulk" deposition) occurs usually at much lower potential than that of a Pb_{ad}–Pd_s structure and the difference is a function of solvent and pH [22,23].

During the hydrogenation of nitrobenzene with Pb/Pd/C catalysts of various Pb : Pd ratio, the potential shift was less than 200 mV in the whole conversion range and no metal dissolution could be detected, as expected from fig. 3. Similar oxidation stability of several other bimetallic catalysts, such as Bi/Pd, Tl/Pd or Sn/Pd, may be expected on the basis of electrocatalytic studies of these systems [22,23].

Our reactor worked in a kinetic regime, which is important in order to minimize the oxidative corrosion of the catalyst. If the rate of hydrogen supply is lower than that of the surface chemical reaction, the potential shift during nitrobenzene reduction can reach higher values by several hundreds mV. This shift may be large enough for the oxidation and corrosion of the noble metal component. An example is the hydrogenation of 2,4-dinitrotoluene on Pd/C [5]. Dissolution of Pd could be suppressed only when the reactor was operated in a kinetic regime.

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