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Calculation of Reaction Rate and Selectivity of Dehydrolinalool Hydrogenation over Pd–Ru Alloy Membrane Catalysts

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The calculation of the electron work function and the filling number of the d-band in the bulk and in the first layer, considering the segregation of components in Pd–Ru alloys to be the same as membrane catalysts, has enabled us to explain and calculate the changes in catalyst activity and selectivity in dehydrolinalool hydrogenation with varying Ru content in the alloys.

Pd alloy membrane catalysts[1] appear to be convenient models for kinetic, spectral and theoretical investigations of the hydrogenation mechanism because of their uniform composition, the absence of diffusion limitations,[2] and the lack of influence of catalyst support. The hydrogenation of dehydrolinalool, DHL (3,7-dimethyloct-6-en-1-yn-3-ol) into linalool (3,7-dimethyloct-2,6-en-3-ol) over membrane catalysts from Pd-alloys with 2, 6, 8 and 10% Ru has been chosen for a theoretical consideration of the hydrogenation mechanism because Pd–Ru membrane catalysts exceed catalysts derived from other alloys in activity and selectivity.[3]

The electronic structure of the Pd–Ru-alloys was calculated from the Bethe–Pierls coherent potential approximation.[4] The electronic properties of the layers of the alloy parallel to the surface were described with Green's functions,

$$G_{\lambda i} = (E - \epsilon_{\lambda i} - \Delta_\lambda)^{-1} \qquad (1)$$

where $\lambda = 1, 2, \ldots i$ is the number of the layer, Δ_λ is the self energy of the λth layer and $\epsilon_{\lambda i}$ is the energy of the d electrons of the ith metal. Eqn. (2) is obtained,

$$\epsilon_{\lambda i} = \epsilon_i + U_i N_{\lambda i} \qquad (2)$$

where ϵ_i is the mean energy of the d-level of pure metal atoms, $N_{\lambda i}$ is the number of d-electrons of the ith metal in the λ layer and U_i is the intra-atomic Coulomb integral.

The d-bandwidths of Pd and Ru and the difference between the mean energies ϵ_i of the Pd and Ru d-bands were taken from ref. 5. The fine structure of the densities of the alloy d-states was calculated by introducing the initial model density of states ρ_0 for the FCC lattice.[6] In our model of the surface interacting with rapidly adsorbing molecules we assumed that charge transfer takes place and that surface concentrations of the components differ from the bulk concentrations only in the first three layers. This is confirmed by experimental data on surface

Table 1 Calculated Ru concentrations in the first layer of the catalyst surface (X_1), the filling numbers of the d-band in the first layer (N_1) and in the bulk (N_b) and the work function of the electrons for Pd–Ru alloys

	Pd	Pd–Ru(2)	Pd–Ru(6)	Pd–Ru(8)	Pd–Ru(10)
X_1 (atom %)	0	7	18	16	11
N_1 (electron per atom)	9.20	9.18	8.74	8.86	9.18
N_b (electron per atom)	9.32	9.32	9.24	9.11	8.98
W (eV)	4.80	4.65	4.35	4.35	4.35

segregation in Pt–Ni, Pd–Ni and Pt–Rh alloys.[7]

After calculating the densities of states in the layers $[\rho_{\lambda i} = (\mathrm{Im}/\pi) G_{\lambda i}]$ and the filling numbers of the d-band, $N_{\lambda i}$, and assuming an electron transfer of *ca.* 1 electron per atom into the common band, the Fermi energy E_F and the d-electron contribution to the free energy E of the system were determined, eqn. (3).

$$E = \sum_{\lambda} \left[\int^{E_F} (X_\lambda \rho_{\lambda A} + (1 - X_\lambda) \rho_{\lambda B}) \mathrm{d}E - U_i [X_\lambda N^2_{\lambda A} + (1 - X_\lambda) N^2_{\lambda B}] \right] \quad (3)$$

The surface concentrations of the elements X_λ were estimated by minimizing the free energy of the system $F = E - TS$ with respect to the number of atoms in the alloy and the number of electrons in the layer being fixed.

The calculated Ru concentrations in the first layer of the catalyst surface (X_1), the filling numbers of the d-band in the first layer (N_1) and in the bulk (N_b) and the work function of the electrons in the alloys are shown in Table 1. The segregation of Ru on the surface of the Pd–Ru alloys under the action of hydrogenation catalysis has been determined by ESCA.[8]

As a result of our investigation into the kinetics of hydrogenation and deuteriation of DHL on Pd–Ru membrane catalysts,[2,3,9] it has been shown that the rate-determining stage of the process is the addition of the H-atom dissolved in the alloy to the molecule of acetylenic alcohol adsorbed on the surface of the catalyst.

According to quantum-chemical calculations[10] of the reactivity indices of acetylenic and ethylenic alcohols in hydrogenation reactions, activation of the substrate occurs through electron transfer from a metal to an anti-bonding π-orbital. The decrease of work function with increasing Ru concentration in the alloy (Table 1) thus favours growth in activating ability of the alloy. The activation of the hydrogen atoms results from interaction of its s-electron with the d-electrons of the alloy.[11–13] The decrease of d-band filling in the bulk of the alloy (Table 1) results in a lowering of its hydrogen activation ability, thus compensating for the growth in activating ability with respect to the substrate.

Considering the hydrogenation mechanism over various alloys to be similar, we may rearrange the Arrhenius equations for hydrogenation reactions over Pd and its alloys, eqn. (4) into eqn. (5).

$$\begin{cases} k_{\mathrm{Pd}} = k_{0_{(\mathrm{Pd})}} e^{-E_{\mathrm{Pd}}/RT} \\ k_i = k_{0_i} e^{-E_i/RT} \end{cases} \quad (4)$$

$$\ln \frac{k_i}{k_{\mathrm{Pd}}} = \ln \frac{k_{0_i}}{k_{0_{(\mathrm{Pd})}}} + \frac{(E_{\mathrm{Pd}} - E_i)}{RT} \quad (5)$$

As the pre-exponential terms for the Pd–Ru alloys are similar (within experimental error[3]), so $\ln(k_{0_i}/k_{0_{(\mathrm{Pd})}}) \cong 0$, and at constant temperature eqn. (6) results.

$$\ln k_i = \ln k_{\mathrm{Pd}} + A(E_{\mathrm{Pd}} - E_i) \quad (6)$$

Considering that the changes in activity of the alloys investigated depend mainly upon alterations in their electronic structure, in electron-donating ability and in filling of the d-band, we may represent eqn. (6) in the form eqn. (7).

$$\ln k_i = \ln k_{\mathrm{Pd}} + \alpha(W_{\mathrm{Pd}} - W_i) + \beta(N_{b_{(\mathrm{Pd})}} - N_{b_i}) \quad (7)$$

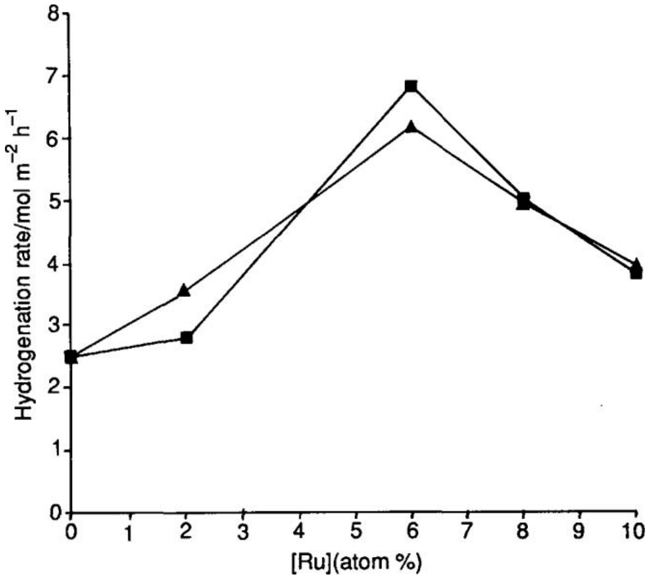

Fig. 1 Hydrogenation rates of dehydrolinalool at 403 K on Pd–Ru membrane catalysts; ■, experimental; ▲, calculated

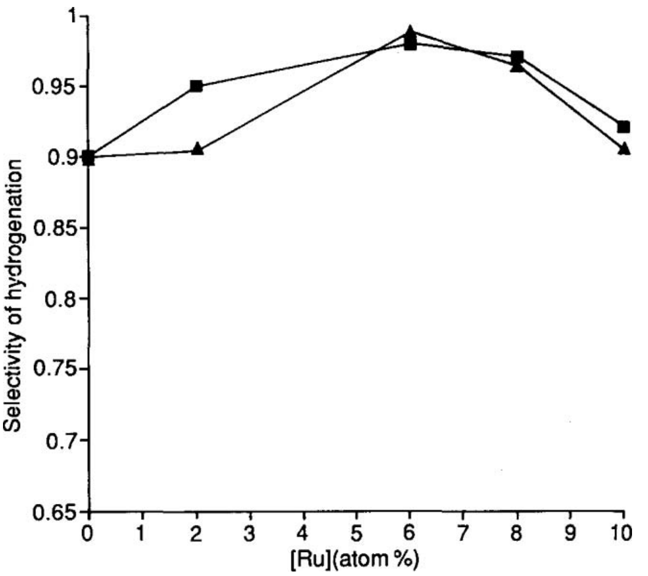

Fig. 2 Selectivities of dehydrolinalool hydrogenation into linalool on Pd–Ru membrane catalysts; ■, experimental; ▲, calculated

Coefficients α and β display the significance of changes in work function and of d-band filling of the alloys in their activating action upon the substrate and hydrogen. As the reaction is zero-order with respect to substrate, it enables us to represent at constant hydrogen pressure eqn. (7) in the form eqn. (8) for reaction rates.

$$\ln r_i = \ln r_{\mathrm{Pd}} + \alpha(W_{\mathrm{Pd}} - W_i) + \beta(N_{b_{(\mathrm{Pd})}} - N_{b_i}) \quad (8)$$

Using experimental values[3] of DHL hydrogenation rates over Pd and Pd–Ru alloys at 363 K and at atmospheric hydrogen pressure, we have determined α and β values which provide the best coincidence of experimental and calculated reaction according to regression analysis: $\alpha = 2.3$, $\beta = -1.75$, correlation coefficient 0.95. The α and β values obtained are a measure of the influence of the work function and d-band filling decrease upon the catalytic activity of the alloys with increasing Ru concentration. Work function decrease favours reaction acceleration, but a d-band filling decrease does not.

In fact, the ability of the alloy surface to adsorb molecules of acetylenic alcohol rather than ethylenic ones should favour an increase in its selectivity. As was shown[14] by work function measurement for Pt, the adsorption of acetylenic and ethylenic compounds proceeds with a shift of electron density from adsorbate to metal. Moreover, acetylenic compounds are better donors of electrons than ethylenic ones. Thus, a lowering of filling numbers in the first layer of the alloy (Table 1) should favour its ability to preferentially adsorb molecules of acetylenic compounds. Determining the reaction selectivity as the ratio of hydrogenation rate into linalool to the sum of hydrogenation rates into linalool and dihydrolinalool, we may write eqn. (9) for the selectivity, analogous to eqn. (8).

$$\ln s_i = \ln s_{\mathrm{Pd}} + \gamma(N_{1_{(\mathrm{Pd})}} - N_{1_i}) \qquad (9)$$

Regression analysis of eqn. (9) gives $\gamma = 0.20$ (correlation coefficient 0.66), *i.e.* the decrease of electron work function in the alloy with respect to Pd favours an increase in selectivity.

The results of the calculations of hydrogenation rates and selectivities according to eqns. (8) and (9) and the corresponding experimental values are shown in Figs. 1 and 2.

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