



Kinetics and mechanism of butene isomerization/hydrogenation and of 1,3-butadiene hydrogenation on palladium



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ABSTRACT

Combined studies of adsorption and hydrogenation have been carried out using Pd black electrochemically deposited in a loose packed thin layer in order to avoid co-adsorption on a support. Pd black covered with a monomolecular layer of strongly adsorbed hydrogen and exposed to butadiene shows a very low hydrogenation rate, more than two orders of magnitude lower than the rate of hydrogenation of a mixture of butadiene and hydrogen. This result reveals that the second step of hydrogenation according to the reaction scheme of Horiuti and Polanyi via a semi-hydrogenated intermediate needs subsurface hydrogen loading. While the first step towards a surface alkyl requires a negatively charged surface hydride for nucleophilic attack the subsequent electrophilic attack proceeds with a positively charged hydrogen from the subsurface region. Strong support for this view is given by the kinetics of isomerization/hydrogenation of *cis*-2-butene which shows at low hydrogen pressure fast isomerization and slow hydrogenation rate. The access of hydrogen to the catalyst surface is regarded as rate determining step of butene respectively butadiene hydrogenation. The consequence of increased hydrogen access to the Pd surface is an enhanced diffusion of hydrogen from surface to subsurface positions thus leading to an increased hydrogenation rate.

Furthermore in the state of selective hydrogenation of 1,3-butadiene towards butenes the surface is densely covered by butadiene.

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1. Introduction

For hydrogenation and isomerization of unsaturated hydrocarbons Horiuti and Polanyi [1] proposed a reaction scheme assuming that the hydrogenation of alkenes occurs in two steps. The half-hydrogenated intermediate is regarded as an adsorbed alkyl radical.

At atmospheric pressure and 300 K SFG spectra acquired during C₂H₄ hydrogenation did not give evidence of any resonances which could be attributed to the half-hydrogenated intermediate. Furthermore, π -bonded ethene which is regarded as the most likely reactive species produces only a very small SFG signal in the C–H stretching frequency range, as a consequence of its nearly parallel geometry on the Pd(1 1 1) surface [2,3].

As spectroscopic studies which till now have been applied do not promise any further penetration into the mechanism of hydrogenation of unsaturated hydrocarbons the aim of our study was to use various kinetic experiments in particular those combined with

simultaneous adsorption measurements for mechanistic investigations.

The selective hydrogenations of dienes, e.g. 1,3-butadiene, 1,5-cyclo-octadiene and 1,5,9-cyclo-dodecatriene towards the monoenes are of industrial interest. In these cases the competitive adsorption of diene and monoene plays a crucial role for selectivity towards the monoene. In a former study of adsorption [4–7] using Pd black deposited as a thin layer on Pd foil it could be shown that saturation of 1,3-butadiene is reached at an adsorption stoichiometry of about one butadiene molecule to four Pd surface atoms, but for 1-butene already at about one butene molecule to five Pd surface atoms. If the surface at maximum butadiene coverage is exposed to 1-butene no additional adsorption of butene is observed. In the opposite experiment with complete coverage by 1-butene a rather slow but finally complete displacement of butenes by butadiene occurs. The TOF of this displacement is smaller than 10^{−2} s^{−1} while the selective butadiene hydrogenation including butene desorption at low *p*_{H₂} shows a TOF of about 1 s^{−1} [7]. These results reveal that a simple displacement in the case of butadiene hydrogenation must be excluded and thus also the concept of the “thermodynamic factor”. Formed butene is immediately desorbed due to the rather high enthalpy of reaction which in the moment of completed hydrogenation is concentrated on the butene molecule just formed. The

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resultant vacant site is not large enough for butene readsorption. Unfortunately at present there is no chance to calculate such complicated adsorption/desorption processes or even to visualize them [8].

Our study using various kinetic experiments in particular those combined with simultaneous adsorption measurements concerns the isomerization and hydrogenation of butenes and the hydrogenation of 1,3-butadiene.

2. Experimental

Selective hydrogenations of dienes respectively of alkynes to alkenes are usually carried out on Pd supported on silica or alumina in gas phase or liquid phase procedure. In all these cases combined studies of adsorption and hydrogenation cannot be carried out because in most cases adsorption on the support is predominant. Therefore we used Pd black electrochemically deposited on a Pd foil in a loose packed thin layer in order to avoid mass transfer limitations.

2.1. Preparation of the catalyst

Pd is deposited on a Pd foil as cathode from aqueous solution of PdSO_4 and H_2SO_4 at a current density of $10^{-2} \text{ A cm}^{-2}$. The loaded foil is thoroughly washed with distilled water and dried. The thickness of the foil is $35 \mu\text{m}$. The Pd deposit corresponds to $0.8 \mu\text{m}$ Pd on both side of the foil. Adsorption of N_2 , H_2 , butene and butadiene and also the kinetics of hydrogenation of the latter two have been studied using this catalyst. However, the small Pd crystallites (diameter of about 25 nm) show reasonable stability only at temperatures below 323 K so that desorption of adsorbed gases could only be carried out for N_2 . For adsorption measurements of hydrogen, butadiene, and butene a special procedure as described in Section 3 has been applied to circumvent the problem of cleaning the surface.

Scanning electron micrographs of the Pd black catalyst at low magnification reveal that the electrochemical deposition leads to a dendritic morphology as shown in Fig. 1. Micrographs of higher magnification show that the dendritic microstructure consists of crystallites with an average size of about 25 nm. No changes of morphology have been observed after treatment of this catalyst with hydrogen at 333 K. The Pd 3d XP spectrum of the untreated Pd catalyst (after washing, drying and evacuating) indicates Pd metal and the presence of a PdO overlayer. After mild reduction with 3000 Pa H_2 at 333 K for 2 h PdO is no longer present demonstrating complete reduction.

2.2. Sorption studies

Sorption experiments were carried out by the static method at temperatures not higher than 323 K. Fig. 2 shows the experimental unit, which contains a GC/MS unit for the analysis of the gas in the adsorption cell. A low volume chamber allows the removal of very small samples so that the pressure and composition of the content of the adsorption cell is only marginally changed. This small sample is diluted with helium and conducted to the GC/MS unit for quantitative analysis. The construction of the gas sampling system avoids stagnant volumes, so that the whole amount of the gas sample is available for the analysis. For all studies the fraction of butene includes all isomers. The amounts of substance of adsorbed and desorbed gases were evaluated by mass balances.

This experimental unit is suited for the study of multicomponent adsorption but also for the study of chemical reactions in the adsorption cell.

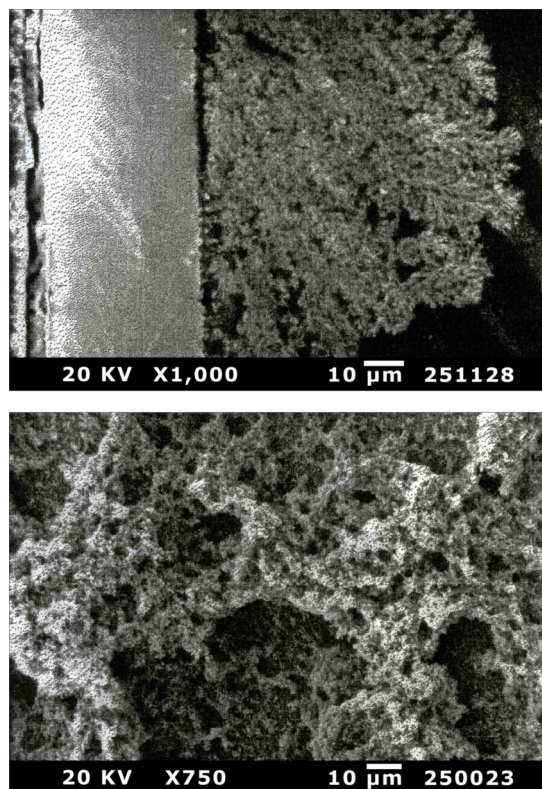


Fig. 1. Scanning electron micrographs of Pd black on Pd foil.

2.3. Kinetic studies

The vapor phase hydrogenation of 1,3-butadiene on Pd black/Pd foil was studied using a continuously operated recycle reactor (CST-reactor), realized by a jet stream through a nozzle at the reactor inlet. With this CST-reactor reaction rates could be directly measured, Fig. 3. A more detailed description of this type of recycle reactor is given in Ref. [9].

In contrast to the butene hydrogenation the rate of isomerization is extremely high so that the highly active Pd black layer of about $10 \mu\text{m}$ on Pd foil was not suitable to study the kinetics of isomerization. Therefore, we used an egg-shell catalyst with 0.1% Pd on Al_2O_3 , cylindrical type: diameter 1.2 mm, length about 5 mm, length of active layer (40–80 μm). Even for this catalyst with highly dilute Pd the isomerization of butenes is strongly influenced by

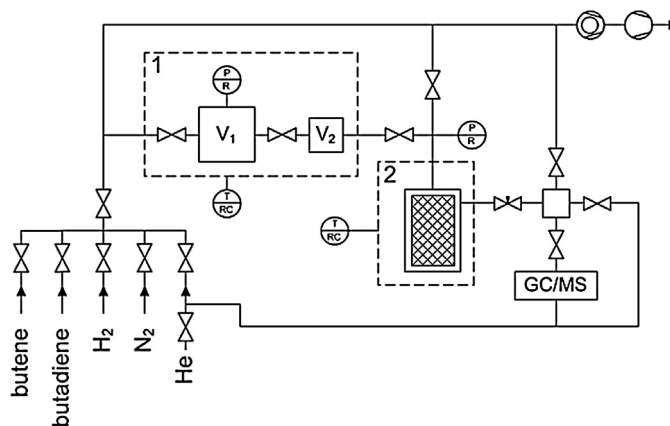


Fig. 2. Experimental unit for combined adsorption and reaction rate studies.

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