INVESTIGATION OF HETEROGENEOUS CATALYSTS AND OF CATALYTIC HYDROGENATION IN GAS PHASE BY ELECTROCHEMICAL METHODS

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Abstract

A special electrochemical measuring cell was developed for the investigation of processes taking place on the surface of supported industrial metal catalysts above 100 °C in the presence of hydrogen. The dependence of cell voltage on the partial pressure of hydrogen, the activation of catalysts, the hydrogenation of benzene and selective hydrogenation of phenol was investigated with this special measuring method.

Introduction

The great majority of electrochemical catalytic studies is carried out in liquid phase, around room temperature. However, a significant proportion of heterogeneous catalytic hydrogenations takes place at sufficient rate only above 100 °C, and the reactants are in gas or vapour phase. The classical electrochemical cells can, of course, not be applied under such conditions.

A special measuring cell was developed in our laboratory [1] which enables the processes taking place on the surface of supported industrial metal catalysts in the presence of hydrogen to be investigated. Measurements can be carried out both independently of the catalytic reaction and during hydrogenation reactions.

Discussion

The measuring cell

The scheme of the special galvanic cell can be seen in Fig. 1 in sectional view. The lower part of a glass tube (1) made of sodium glass is closed by a membrane (2) made of Dole type glass. This glass membrane acts as the solid electrolyte of the cell, and at the same time it separates of reference and the measuring electrodes. On the inner surface of the glass tube a silver film (3) is

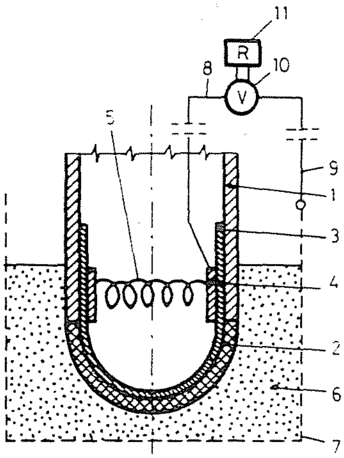

Fig. 1. Cross section of the electrochemical cell for measurement of the catalyst's potential in gas phase

deposited. Against this silver layer a platinum ring (4) is pressed by spring (5), thereby ensuring electric contact. The electric cable (8) of the inner electrode is attached to the platinum ring. Air is fed into to inner space of the glass tube, i.e. the reference electrode of the cell is an $Ag/Ag_{2}0/0_{2}$ (air)-electrode. This reference half-cell is in contract with the supported metal catalyst (6), placed into a basket (7) made of nickel or silver net providing electric contact with the catalyst. The catalyst, contacted with hydrogen, is the measuring electrode of the cell, the terminal (9) of which is connected to an oscillating capacitor electrometer (10) of high input impedance.

On the basis of the electrode processes the voltage (E) of the galvanic cell can be written as

$$E = E_{S,T} + \frac{RT}{F} \ln \frac{a_H}{(K_H)^{1/2}} \qquad (1)$$

where a_H is the activity of adsorbed hydrogen atoms, K_H is the equilibrium constant of the adsorption of atomic hydrogen and $E_{S,T}$ is the sum of all factors which are invariant at constant temperature. This equation correlates the change of cell voltage with the change of the activity or surface concentration of adsorbed hydrogen.

Measurements in the presence of hydrogen

The measuring cell shown in Fig. 1 was placed in a tubular reactor the temperature of which and the feed rates of the reactants could be controlled precisely. The temperature dependence of the cell voltage was studied with a great number of widely different catalysts, and a linear relationship was obtained in all cases (this corresponds to eq. (1)). As examples of different types of catalyst 55 wt% nickel supported on SiO_2, 0.5 wt% Pd on clinoptliolite and 0.35 wt% Pt on SiO_2 may be mentioned.

The dependence of the cell voltage on the partial pressure of hydrogen was also investigated and a linear dependence of cell voltage on the logarithm of the reciprocal of partial hydrogen pressure (corresponding to eq. (1)) was found.

The variation of cell voltage as a function of time of activation with hydrogen of supported nickel, palladium and platinum catalysts can be seen in Fig. 2. The three curves are similar in character: the cell voltage reaches a constant value after an initially fast change.

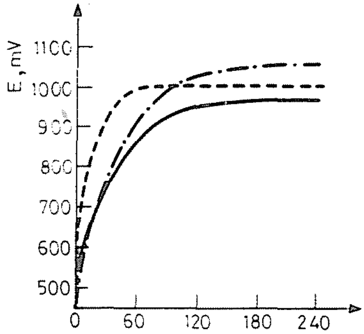

Fig. 2. Cell voltage (E) as a function of time (min) during activation of catalysts

In the case of a Ni/SiO_2 catalyst, nickel oxide was found to be present on the catalyst at the beginning of measurements, and this was reduced to the active metal upon the effect of hydrogen, and the surface concentration of adsorbed hydrogen atoms increased. The progress and then the termination of this process were shown by the change and subsequent stabilization of the cell voltage. By this time the catalyst, according to our investigations, has reached its maximum activity in the hydrogenation of benzene.

The Pd/Klinosorb catalyst (Fig. 2. dashed line) was prepared by the reduction of palladium hydroxide. This catalyst was used to investigate the selective hydrogenation of phenol to cyclohexanone. With catalyst impregnated with palladium chloride (i.e. not converted to the hydroxide), the cell voltage reaches the maximum value much more slowly. This maximum is lower by more than 150 mV than the value obtained with the catalyst prepared from palladium hydroxide, and the catalyst is less active and less selective.

In addition to following the progress of reduction, this experimental method may promote the development of catalyst with optimum properties for given purposes and the control of the reproducibility of catalyst preparation.

Measurements during hydrogenation reactions

In these experiments the voltage of a special galvanic cell formed in the catalyst bed was recorded continuously during the operation of an integral tubular reactor. A characteristic recording obtained in the hydrogenation of benzene can be seen in Fig. 3. According to gas chromatographic measurements, a stable cell voltage corresponds to constant conversion value, i.e. the reactor works in steady state. Upon feeding benzene with 2.29 mol% thiophene content (Fig. 3 dashed line), the conversion gradually decreased, and no constant cell voltage could be measured. The stabilized cell voltage values are plotted in Fig. 4 as a function of contact time (the reciprocal space velocity).

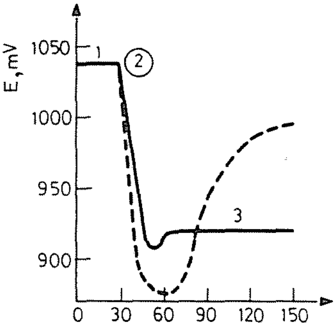

Fig. 3. Changes of the cell voltage during hydrogenation of benzene on Ni/Si0$_2$ catalyst. The straight line, *1*, indicates the *E* stabilized in hydrogen; benzene feed began at the time shown by *2*, the stabilized section, *2*, of E$^{(\pm 1\text{mV})}$ indicates the steady state of the reactor

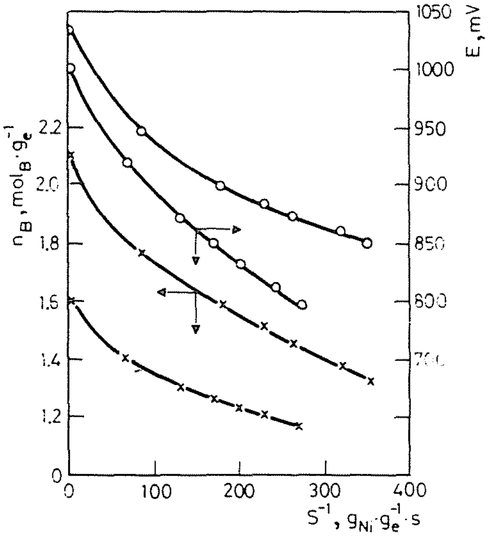

Fig. 4. Cell voltage in steady state during hydrogenation of benzene. Temperature, 165°C; catalyst, Ni/SiO$_2$; hydrogen-benzene mole ratio, $n^0_{H_2}/n^0_B = 6{:}1$(x——x) and 10:1 (0——0)

This steady value is also influenced by the hydrogen to benzene mole ratio.

The relationship between the partial pressures of the reactants and cell voltage was also investigated under conditions where the extent of hydrogenation reaction was negligible. It can be established from these measurements that the adsorption processes of benzene and hydrogen are to a certain extent concurrent processes on the surface of the nickel catalyst, but the adsorption of cyclohexane is negligible.

The selective hydrogenation of phenol to cyclohexanone was studied on Pd/Klinosorb catalyst [2]. This reaction can be characterized by the following kinetic equation:

$$W = k \frac{K_H \cdot p_F \cdot p_H}{[1+(K_H \cdot p_H)^{1/2}]^2} \tag{2}$$

In the case of the two mechanisms corresponding to this kinetic equation, selective hydrogenation takes place on a palladium surface almost completely covered with hydrogen (3). This statement is supported by the cell voltages measured during selective hydrogenation (Fig. 5). Moreover, the relationship between the partial pressure of phenol and cell voltage proves that there is a concurrent adsorption of hydrogen and phenol (Fig. 6). With increasing partial pressure of hydrogen, the partial pressure of phenol influences the cell voltage, i.e. the surface concentration of adsorbed hydrogen, to a decreasing extent. Extrapolating these data to the higher partial pressure of hydrogen used during hydrogenation reactions it can be seen that in this case the adsorption of phenol is negligible.

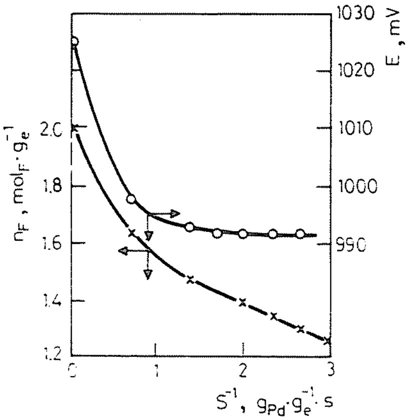

Fig. 5. Cell voltage in steady state during selective hydrogenation of phenol to cyclohexanone. Catalyst, Pd/Klinosorb; temperature, 165°C; mole ratio of hydrogen to phenol, 6:1

The results described in this section illustrate, at the same time, that the electrochemical method can be applied to support reaction mechanisms assumed on the basis of kinetic data.

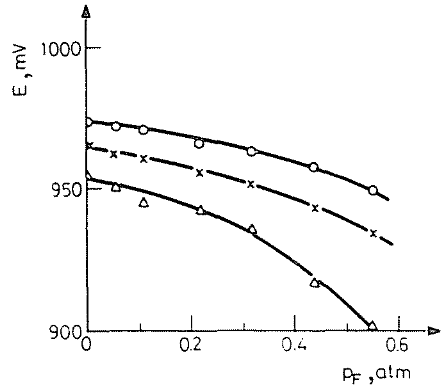

Fig. 6. Dependence of the cell voltage on partial pressure of phenol. Catalyst, Pd/Klinosorb; temperature, 165°C; partial pressure of hydrogen, 0.015 (0); 0.01 (x); 0.005 (Δ)

Conclusions

A very significant advantage of this special electrochemical method is that measurements can be carried out under the conditions of catalytic reactions using the acting catalysts as measuring electrode. Hence, it is not necessary to extrapolate experimental data obtained eventually under very different conditions to the actual conditions of the catalytic reaction. By eliminating the great uncertainties arising from the extrapolation, electrochemical methods enable one to draw conclusions which have to a certain extent stronger experimental foundations.

According to our investigations [4, 5], this method may also have industrial relevance, since it can be used to check the operation of the catalyst and the reactor.

References

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