JOURNAL OF CATALYSIS 42, 425–434 (1976)

# An Electrochemical Measuring Method for Studies of Metal Catalysts in Gas-Phase Heterogeneous Catalytic Reactions

J. PETRÓ, T. MÁTHÉ, AND A. TUNGLER

*Research Group for Organic Chemical Technology, Hungarian Academy of Sciences,*
*Müegyetem rkp. 3, 1111-Budapest XI, Hungary*

Received June 16, 1975

An electrochemical measuring system has been developed for studying metal catalysts in contact with hydrogen and vapor-phase reactants at temperatures above 100°C. The measuring system is a special galvanic cell in which the catalyst itself functions as measuring electrode. The electromotive force (emf) of this cell is continuously recorded in the course of catalyst activation and catalytic reactions. The system has been used for studying supported nickel, palladium, and platinum catalysts in tube reactors. Based on the presumed electrode processes taking place in the measuring cell, emf values measured with different catalysts and changes in the emf values taking place under the effect of various factors acting on the surface concentration of hydrogen (partial pressure of hydrogen, temperature, concentrations of reactants, catalyst poison, catalyst deactivation) have been interpreted.

## INTRODUCTION

Continuous efforts are being made in heterogeneous catalysis to increase available information concerning the surface state of catalysts and the changes occurring on the surface. Electrochemistry deals typically with surface phenomena and is therefore particularly valuable for studying metals. Especially relevant is the applicability of electrochemistry to studying the amount and nature of hydrogen sorbed on metal surface.

The applicability of electrochemical methods is limited to the metal–solution interface. Many heterogeneous catalytic processes reach appropriate rates only at temperatures significantly higher than 100°C and the reactants are in the vapor phase. Under such conditions classical electrochemical methods cannot be applied. If, however, a measuring cell (measuring electrode–electrolyte–reference electrode) could be developed that would be stable in operation at temperatures above 100°C, liquid-phase electrochemical studies could be extended to the vapor phase.

Druz and co-workers (1–3) were the first to attempt the extension of electrochemical methods on studies of gas-phase catalytic hydrogenation. The measuring cell was a glass tube sealed at one end. Its external surface was coated with a porous platinum layer. The tube was filled with a potassium nitrate–sodium nitrate mixture into which a platinum wire was inserted. Subsequently the tube was sealed. In this arrangement, platinum acts as the oxygen electrode, and glass is the solid electrolyte. Later the reference electrode was modified: The internal surface of the glass tube was also coated with a porous platinum layer in contact with air. The external platinum layer (i.e., the measuring electrode) was saturated with hydrogen; benzene and cyclohexane, respectively, were then led to it in a stream of hydrogen. Simultaneously the electromotive force of the galvanic cell was measured by compensation. The results, measured in the temperature range of 180 to 300°C, demonstrated that hydrogen displaces benzene from the surface and that benzene hydrogenation does not take place on platinum completely saturated with hydrogen; the adsorption of hydrogen and cyclohexane is not concurrent.

The simply-constructed galvanic cell used by Druz and co-workers corresponded with regard to the overall electrode reaction to a hydrogen–oxygen cell. They established an electromotive force of 1240 mV, only slightly dependent on temperature. Haber (*4*) calculated the electromotive force of the hydrogen-oxygen cell from thermodynamic data (free energy change in the hydrogen–oxygen reaction) and experimentally determined it, using molten salt for electrolyte. His results indicated that the electromotive force decreases with temperature. Bockris and Huq (*5*), working with carefully purified electrodes and electrolyte, measured 1225 mV at 25°C, a value close to the theoretical 1228–1232 mV. Reversible operation of the platinum/oxygen electrode can only be ensured under very pure conditions, because the exchange current of the electrode is small (*6*).

Our objective was to develop a measuring system allowing continuous control of changes taking place on the surface of nonsupported and supported catalysts, independent of the catalytic reaction and in the course of hydrogenation reactions (*7*, *8*).

## EXPERIMENTAL

### *The Measuring System*

A sectional diagram of our special galvanic cell is shown in Fig. 1. The lower end of the glass tube, *1*, made of sodium glass is sealed with the membrane, *2*, made of Dole glass; this membrane is the solid electrolyte. The internal surface of the tube is coated with the silver or platinum film, *3*, this being the internal electrode of the measuring system, its reference half-cell. The platinum ring, *4*, is pressed against the metal film with the spring, *5*, to ensure contact. The terminal, *8*, of the reference half-cell is connected with the platinum ring. The reference half-cell is in contact with the granular metal catalyst, *6*, enclosed in the basket, *7*, made of nickel or silver mesh which serves as terminal. This is the measuring electrode whose terminal, *9*, is connected to the high input-resistance oscillation capacitor electrometer, *10*. The resistance of the measuring system is mainly determined by the resistance of the Dole glass membrane separating the reference half-cell from the measuring electrode. The composition of the membrane is 22 wt% $Na_2O$, 6 wt% CaO, and 72 wt% $SiO_2$. Its conductivity at 25°C is $1.10^{-12}$ ohm$^{-1}$ cm$^{-1}$. Glass is a unipolar conductor, with only $Na^+$ ions moving. The mobility of the cations, i.e., the conductivity of the glass, is low at ambient temperature but increases exponentially with temperature. The temperature range where glass conductivity is high enough to

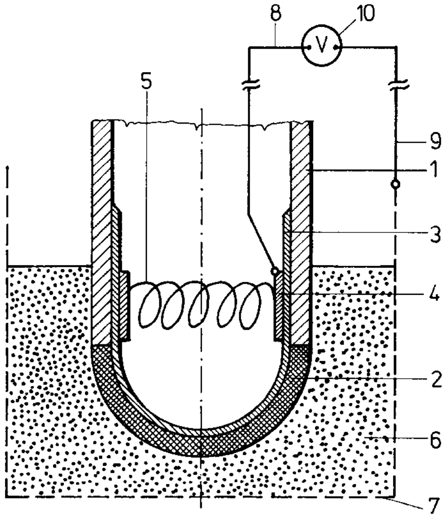

FIG. 1. Cross section of the measuring cell.

allow measurements depends on its $Na^+$ content. Dole glass conductivity, for example, allows measurement at ambient temperature. Consequently, it is expedient to use "soft" glass at lower temperatures and "hard" glass (poor in $Na^+$) at higher temperatures. Owing to its good conductivity, relatively thick membranes (1–2 mm) of Dole glass can be used, so that electrodes which are less sensitive to breakage can be made without too high resistances of the reference half-cell. Our measurements indicated that the total internal resistance of the electrode chain does not exceed $10^9$ ohms and in the majority of cases is $10^6$–$10^8$ ohms. This value depends on the thickness of the membrane and on temperature. However, in the case of supported catalysts, if the metal content is below 1 wt%, the internal resistance of the total electrode chain may also be affected by the contact resistance between the reference half-cell and the catalyst and by the thickness of the catalyst layer between the glass membrane and the metal mesh. Therefore we measured the electromotive force of the galvanic cell with an oscillation capacitor electrometer with an input resistance greater than $10^{15}$ ohms. In this manner, practically no current passed through the electrodes during measurement and no polarization occurred. Stability of measurements was ensured (in addition to the difference between the input resistance of the electrometer and the internal resistance of the cell being more than seven orders of magnitude) by connecting the electrode terminals with screened cables, *8* and *9* in Fig. 1, to the electrometer. In this manner, the usual interfering effects occurring at measurements of small dc voltages in systems with large internal resistances could be eliminated.

As mentioned in the Introduction, it is difficult to ensure reversible operation of the platinum/oxygen electrode. We therefore studied the stability of the reference electrodes in detail, since their stability is the precondition that the measured change in the electromotive force will indicate only the change in the potential of the measuring electrode, i.e., of the catalyst. For this purpose, we used three different cells: (i) platinum/hydrogen – platinum/hydrogen/hydrogen concentration cell; (ii) platinum/platinum oxide/air – platinum/hydrogen; (iii) silver/silver oxide/air – platinum/hydrogen. The cells were similar to the system shown in Fig. 1, except that the external surface of the glass membrane was coated with a platinum film in contact with hydrogen. Hydrogen was led to the platinum film in the interior of cell (i) and air to the platinum film in cell (ii) and to the silver film in the interior of cell (iii). The stability of the electromotive force was continuously recorded within the temperature range of 120 to 300°C. Experiments demonstrated that the electromotive force of the hydrogen concentration cell (i) and of the hydrogen–oxygen cell containing the silver/silver oxide/air electrode (iii), apart from an initial formation period of 10–20 hr, was stable within ±1 mV. Electromotive forces pertaining to different temperatures were well reproducible.

Stability tests at constant temperature for periods of more than 500 hr gave results constant within ±1 mV. The stability of the electromotive force of the cells was also confirmed by polarization of the cells with a 1 mA current for some minutes: After cutting off the polarizing voltage, the electromotive force returned to its original value. The electromotive force of the hydrogen–oxygen cell (ii) containing the platinum/platinum oxide/air electrode was found to be unstable, and particularly large changes were observed after polarization. We therefore decided to use the silver/silver oxide reference electrode in measurements. In addition to stability, this electrode has the further advantage that it is simpler to prepare than the platinum/platinum oxide electrode.

### *Experimental Apparatus*

The measuring system presented in Fig. 1 is built into the catalyst bed of a conventional tube reactor. The reactor is placed in an electric tubular furnace whose heating voltage and temperature are controlled. The temperature of the catalyst bed is measured with an iron–constantan thermocouple located close to the reference half-cell, and it is recorded with a compensograph. The flow of hydrogen to the reactor and the flow of argon (used as diluting gas) were stabilized by pneumatic supply units. The flow rate was measured with differential manometers. For deoxygenation, the gases were led over a copper catalyst on a silica gel support and dried by passing through a column filled with a molecular sieve. Uniform feed of the reactants was ensured by a metering device fitted with a synchronous motor.

## RESULTS

### *1. Temperature Dependence of the Electromotive Force*

$Ni/SiO_2$ catalyst containing 55 wt% nickel, particle size 1–1.4 mm, was filled into the metal mesh catalyst holder of the apparatus. After activation of the catalyst (discussed later) the emf was measured in a hydrogen flow, at various temperatures, with the silver/silver oxide/air reference electrode. At each temperature, the emf was continuously recorded for more than 2 hr with a compensograph. After an initial period of some minutes, the emf values became stabilized within ±2 mV. Repeated temperature dependence experiments yielded reproducible results within this accuracy range even when fresh catalyst was filled into the apparatus. Similar experiments were carried out with palladium catalyst on a molecular sieve support (0.5 wt% Pd). The values obtained with these two catalysts were stable within ±2 mV and are presented in Fig. 2. Temperature dependence is linear with both catalysts, but the slopes differ.

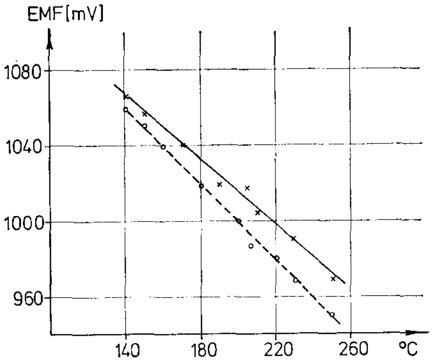

FIG. 2. Temperature dependence of the electromotive force. Pressure of hydrogen: 1 atm; catalysts: $Ni/SiO_2$ (X——X) and Pd (O- - -O).

### *2. Dependence of emf on Partial Pressure of Hydrogen*

The partial pressure of hydrogen was varied by dilution with 99.9%-purity argon. Measurements were carried out with decreasing and increasing partial pressures of hydrogen. Identical values were obtained in the two series of experiments, demonstrating that the catalyst functioned reversibly as a measuring electrode. Results obtained with 55 wt% $Ni/SiO_2$ and 0.5 wt% Pd on a molecular sieve support and 0.35 wt% $Pt/Al_2O_3$ catalyst are shown in Fig. 3. The electromotive force is plotted against the logarithm of the reciprocal partial pressure of hydrogen ($\ln(1/p_{H_2})$). The linear relationship corresponds to the Nernst equation. The results shown in this figure also demonstrate that the measuring method is not only suited for catalysts containing high percentages of metal but also for supported catalysts with less than 1% of metal.

### *3. Studies of Catalyst Activation*

In those cases where activation of the catalyst consists in reduction of a metal salt (usually oxide or hydroxide) to metal, our measuring system allows us to follow

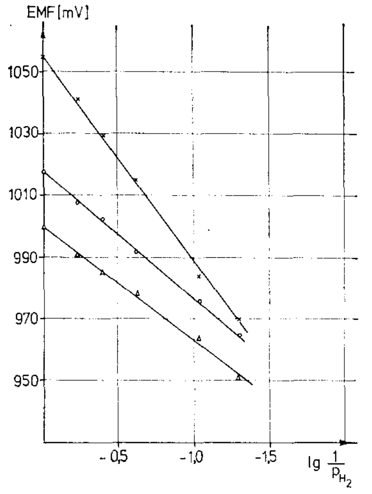

FIG. 3. Dependence of the electromotive force on partial pressure of hydrogen. Catalysts: $Ni/SiO_2$ (○), 0.5 wt% Pd (△), and 0.35 wt% $Pt/Al_2O_3$ (×).

the progress of the process and to state when the catalytically active surface layer is completed.

Figure 4 presents emf vs time for a catalyst prepared from nickel oxide in a hydrogen flow at 250°C. At the beginning of the experiment, we heated the catalyst in argon to 250°C and subsequently gradually changed the gas stream to hydrogen. It may be seen that after the introduction of hydrogen, the emf changes rapidly and becomes stable after about 3 hr. Control measurements showed that at this moment maximum activity of the catalyst had been reached.

A similar activation curve was obtained with the 0.5 wt% palladium catalyst on a molecular sieve support (reduction of palladium hydroxide to metal). The activation of this catalyst was complete in 1 hr (Fig. 4). This catalyst was used for phenol hydrogenation to cyclohexanone (*9*), and had a selectivity exceeding 95%. We found that the emf value stabilized in the course of activation depends on the mode of catalyst preparation. Values of the emf measured with catalysts that were optimum for selective hydrogenation were found within a rather narrow range of 980 to 1020 mV. This suggests the use of the method in developing optimum catalysts for a given reaction.

The third curve in Fig. 4 was obtained in the course of activating a reforming catalyst containing 0.35 wt% platinum on alumina. Here almost 3 hr were required to reach stable emf values. The highest emf values were measured with this catalyst, although this was the one activated at the highest temperature (360°C). The results obtained with supported platinum and palladium catalysts demonstrate the applicability of the method to follow the activation of catalysts with relatively low metal contents below 1%.

### *4. Changes in emf under the Influence of Oxygen*

Figure 5 shows emf changes under the influence of small amounts of oxygen introduced into the hydrogen stream. The emf was first measured in pure hydrogen at 170°C with the above-mentioned $Ni/SiO_2$ catalyst (55 wt% Ni). At *1*, 2 vol% oxygen was introduced into the hydrogen stream. Under its effect, the emf rapidly decreased. At *2*, we shut off the oxygen, and the emf

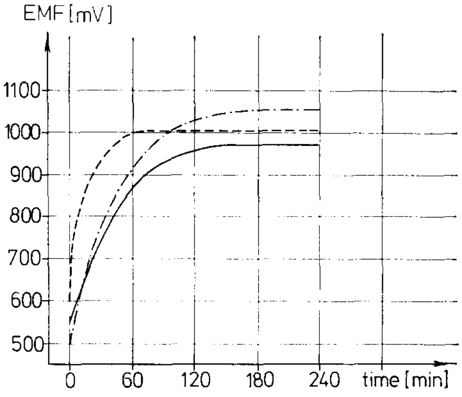

FIG. 4. Changes of the electromotive force during catalyst activation. Catalysts: $Ni/SiO_2$ (——) at 250°C, 0.5 wt% Pd on molecular sieve support (- - - -) at 200°C, and 0.35 wt% Pt on alumina support (—·—·) at 360°C.

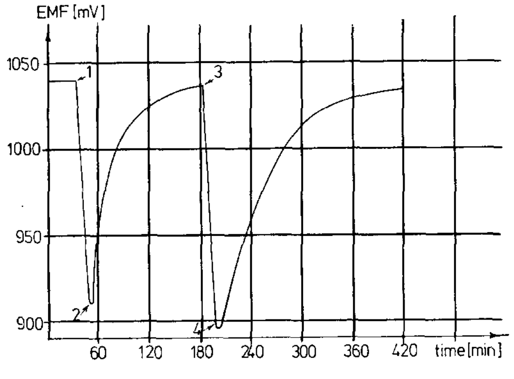

FIG. 5. Changes of the electromotive force under the effect of oxygen. At *1* and *3* a 2 vol% oxygen inlet is made into the pure hydrogen stream, and at *2* and *4* oxygen is shut off, leaving pure hydrogen. Ni/SiO$_2$ catalyst.

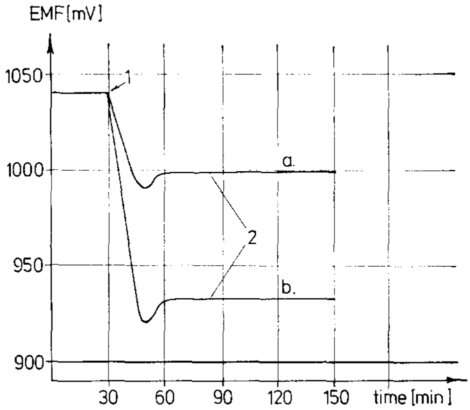

FIG. 6. Changes in the electromotive force during hydrogenation of benzene over Ni/SiO$_2$. Benzene feed in began at *1*, and the straight lines, *2*, indicate the steady state.

gradually approached the initial value in pure hydrogen. Repeated introduction of oxygen at *3* and shut-off at *4* caused a similar effect. This figure demonstrates that small amounts of oxygen in hydrogen significantly reduce the emf and shift the potential of the hydrogen electrode (measuring electrode) towards that of the oxygen reference electrode.

### *5. Changes in emf during Hydrogenation Reactions*

Benzene was hydrogenated at 170°C with the Ni/SiO$_2$ catalyst, and emf values were continuously recorded during the reaction. Figure 6 shows two such records. Benzene feed began at *1*. The straight section denoted by *2* indicates a value stabilized within ±1 mV. In this section, the temperature of the catalyst bed was constant and so was conversion of benzene, as found by gas chromatography of reactor outlet samples taken at intervals of 5 min. Thus, stabilization of the emf indicated steady-state operation of the reactor.

We studied the effect of the mole ratio of hydrogen to benzene on the emf values stabilized in the course of hydrogenation. The curves in Fig. 6 represent experiments with a higher (Curve a) and a lower (Curve b) mole ratio of hydrogen to benzene. The total flow rate of the stream entering the reactor was kept constant in all experiments by suitably diluting the mixture with argon. It can be seen from the figure that the stabilized emf value is smaller at smaller mole ratios of hydrogen to benzene. Conversion and emf values belonging to the stabilized sections denoted by *2* in Fig. 6 are listed in Table 1.

Figure 7 represents emf vs mole ratio of hydrogen to benzene for two different feed

TABLE 1

The Electromotive Force Measured under Steady-State Conditions during Hydrogenation of Benzene[a]

| $n_{H_2}/n_B$ | Benzene feed (mol/hr) | | | |
|---|---|---|---|---|
| | 0.1115 | | 0.223 | |
| | emf (mV) | Conversion (%) | emf (mV) | Conversion (%) |
| 1:1 | 1015 | 21.3 | 1005 | 29.2 |
| 2:1 | 1007 | 34.8 | 980 | 40.3 |
| 3:1 | 998 | 47.3 | 932 | 49.9 |
| 6:1 | 978 | 90.5 | 850 | 92.2 |
| 10:1 | 945 | 100 | — | — |

[a] Temperature, 170°C; catalyst, Ni/SiO$_2$.

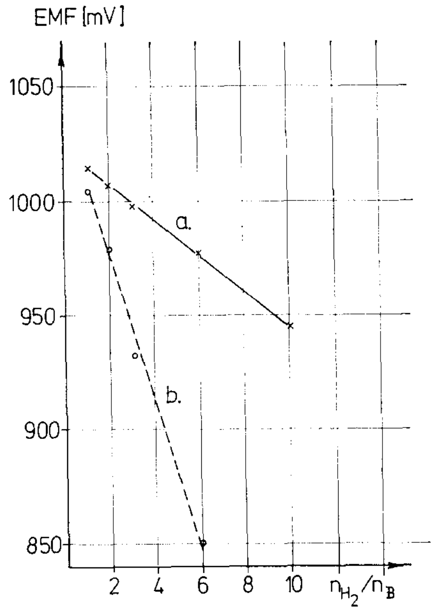

FIG. 7. Electromotive force measured in steady state during hydrogenation of benzene vs mole ratio of hydrogen to benzene (cf. data in Table 1). Temperature, 170°C; benzene feed in, 0.1115 mol/hr (×——×) and 0.223 mol/hr (○- - -○); catalyst, $Ni/SiO_2$.

rates of benzene. The results give two straight lines differing in slope, that is, emf is also dependent on feed rate: the emf is higher for the lower feed rate at identical mole ratios of hydrogen to benzene (Curve a).

### 6. *Effect of Catalyst Poison*

The effect of catalyst poison on the emf is shown in Fig. 8. Portion *1* of the curve represents the emf value stabilized in hydrogen; benzene (or benzene containing the catalyst poison) was introduced at *2*; portion *3* of the curve represents the emf value stabilized in the course of the catalytic reaction. The dotted line corresponds to hydrogenation of benzene containing 2.29 mol% thiophene at 170°C, while the continuous line represents hydrogenation of pure benzene under identical conditions. In the latter case, similar to the results reported in Section 5, conversion is constant (91.2%) for the portion of the curve where the emf is stabilized. With thiophene-containing benzene, conversion decreases gradually from the initial 91.2% to 62%, and no constant emf value is established.

This experiment and the results discussed in the earlier sections demonstrate that continuous information obtained by the electrode system in the course of the reaction allows us to control the state of the catalyst and hence the steady-state operation of the catalytic reactor.

### 7. *Deactivation of the Catalyst*

Figure 9 shows emf and conversion vs operation period (in hours) of the catalyst, for the selective hydrogenation of phenol to cyclohexanone on a molecular sieve-supported palladium catalyst (0.5 wt% Pd). Phenol feed rate (0.066 mol/hr), hydrogen to phenol mole ratio (6:1), and catalyst temperature (165°C) were kept at constant values in the course of the experiment. The figure demonstrates that the electrode system is suited for following the process of catalyst deactivation, since emf

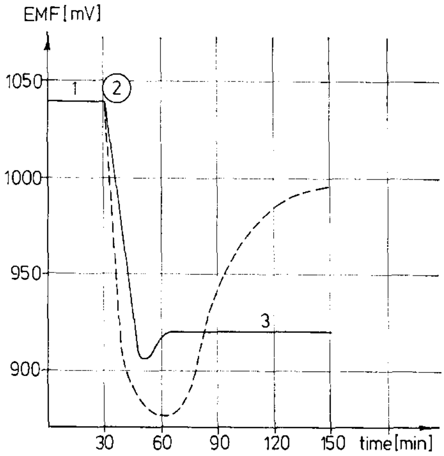

FIG. 8. Effect of catalyst poison during hydrogenation of benzene. The straight line, *1*, indicates the emf stabilized in hydrogen; benzene feed began at the time shown by *2*; dotted line corresponds to hydrogenation of benzene containing 2.29 mol% thiophene; catalyst, $Ni/SiO_2$.

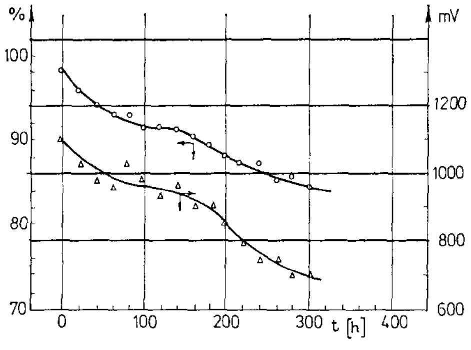

FIG. 9. Change of the electromotive force (△) and the conversion (○) during selective hydrogenation of phenol to cyclohexanone. Temperature, 165°C; catalyst, 0.5 wt% Pd on molecular sieve support; feed rate of phenol, 0.066 mol/hr; mole ratio of hydrogen to phenol, 6:1.

and conversion curves are almost parallel to one another.

## DISCUSSION

The essential reactions taking place on the hydrogen electrode in the aqueous phase are as follows: Gaseous hydrogen is dissolved in the electrolyte and dissociatively adsorbed on the surface of the metal electrode:

$$H_{2(g)} \rightleftarrows H_{2(aq)} \rightleftarrows 2H_{(ads)}; \qquad (1)$$

then the protons pass through the metal–solution interface:

$$2H_{(ads)} \rightleftarrows 2H^+ + 2e^-. \qquad (2)$$

From the above reactions, the potential of the hydrogen electrode is

$$E = E_0 + \frac{RT}{2F} \ln \frac{(a_{H^+})^2}{p_{H_2}}, \qquad (3)$$

where the value of $E_0$, by convention, is zero at all temperatures, $a_{H^+}$ is the proton activity, and $p_{H_2}$ is the partial pressure of hydrogen.

The processes taking place on the metal catalyst, i.e., the measuring electrode, in contact with the glass electrolyte and gas-phase hydrogen presumably differ to a certain extent from the above equations. As a working hypothesis, we assume the processes controlling the emf value to be as follows.

Gas-phase hydrogen is adsorbed molecularly and subsequently atomically on the surface of the catalyst:

$$H_{2(g)} \rightleftarrows H_{2(ads)} \rightleftarrows 2H_{(ads)}. \qquad (4)$$

Protons are formed and pass through the catalyst–glass interface, leaving electrons behind on the catalyst:

$$2H_{(ads)} \rightleftarrows 2H^+ + 2e^-. \qquad (5)$$

The protons entering the surface layer of the glass will become attached to nonbridging oxygen ions, i.e., oxygen atoms in a terminal position:

$$2H^+ + 2[-\overset{|}{\underset{|}{Si}}-O^-] \rightleftarrows 2[-\overset{|}{\underset{|}{Si}}-OH], \qquad (6)$$

and simultaneously current flow across the glass starts.

The overall electrode process at the measuring electrode is consequently

$$H_{2(g)} + 2[-\overset{|}{\underset{|}{Si}}-O^-] \rightleftarrows 2[-\overset{|}{\underset{|}{Si}}-OH] + 2e^-, \qquad (7)$$

and the potential of the catalyst relative to the surface layer of the glass (the phase-boundary potential) is

$$E_C = E_C{}^0 + \frac{RT}{2F} \ln \frac{a_{pr}{}^2}{a_{sa}{}^2 \cdot p_{H_2}} \qquad (8)$$

or

$$E_C = E_C{}^0 + \frac{RT}{F} \ln \frac{a_{pr}}{a_{sa} \cdot (p_{H_2})^{\frac{1}{2}}}, \qquad (9)$$

where $E_C{}^0$ is a constant independent of temperature, $a_{pr}$ the activity of the protonized group, and $a_{sa}$ the activity of the silicate anion.

Equations (3) and (9) are identical with respect to the dependence of the electrode potential on the partial pressure of hydrogen but differ insofar as, in Eq. (9), the activity of the silicate anion (present in very low concentrations) and the activity of the protonized silicate anions appear instead of proton activity in the aqueous phase figuring in Eq. (3).

Equation (9) implies that at constant temperature the electrode potential and, hence, the emf measured in the system (no change taking place in the reference electrode) depend solely on the partial pressure of hydrogen, since presumably the activities of the silicate anion and of the protonized groups will not change.

The slopes of the straight lines in Fig. 3, representing the dependence on hydrogen partial pressure, and the slopes calculated by means of Eq. (9) for the given temperatures are the following (in millivolts/ln $pH_2$): Ni 41 and 47.4 at 205°C; Pd 38 and 46.9 at 200°C; Pt 65 and 69 at 360°C. A comparison of the measured and calculated values demonstrates that the measured slopes are lower than the calculated ones, and the closest approach is obtained with the platinum catalyst. Since the same reference half-cell was used with all three catalysts, it may be assumed that the differences are due to Eq. (4) or (5) being not fully reversible. Experiments are under way that will embrace a broader temperature range and may help to elucidate the electrode processes.

More exact information could be obtained by kinetic studies of the electrode processes. However, our experience is that measurements similar to the various polarization methods used in the liquid phase are complicated by the fact that in the unipolarly conducting glass the charge-carrier sodium ions accumulate in the surface layer under the effect of the polarizing current.

Interpretation of emf values measured under different conditions is facilitated by a transformation of Eq. (9). Let us express the equilibrium constant $K_{\mathrm{H}}$ for the atomic adsorption of hydrogen according to Eq. (4):

$$K_{\mathrm{H}} = a_{\mathrm{H}}^2/p_{\mathrm{H}_2}, \qquad (10)$$

where $a_{\mathrm{H}}$ is the activity of the adsorbed hydrogen atoms and is in conceptual relationship with the surface concentration. Let us substitute Eq. (10) into Eq. (9):

$$E_{\mathrm{C}} = E_{\mathrm{C}}{}^0 + \frac{RT}{F} \ln \frac{a_{\mathrm{pr}}(K_{\mathrm{H}})^{\frac{1}{2}}}{a_{\mathrm{sa}} \cdot a_{\mathrm{H}}}. \qquad (11)$$

The equilibrium constant $K_{\mathrm{H}}$ presumably depends on the nature of the adsorbing metals (adsorption isotherm), i.e., its value differs from metal to metal. Since it can be related to the nature of the active sites of the surface, different values of $K_{\mathrm{H}}$ are conceivable even on the surface of one and the same metal catalyst. Also, all processes affecting the nature of the active sites of the catalyst may also affect the value of $K_{\mathrm{H}}$.

The results of measurements obtained when applying the system to catalytic reactions can be brought into relationship with Eq. (11).

The dependence of $K_{\mathrm{H}}$ on the adsorbing metal may serve as an explanation for the finding that emf values measured in hydrogen on different types of catalyst deviate (e.g., the value measured on Pt is higher than that measured on Ni).

In the initial stage of activation, the surface concentration of adsorbed hydrogen atoms is substantially lower than in the later stages. It will gradually increase with the metal being catalytically activated, and the completion of the activation process is indicated by the establishment of a constant value.

In the course of benzene hydrogenation, $a_{\mathrm{H}}$ will reach a constant value on the surface of the catalyst in the steady-state reactor. The constant values measured in the course of the reaction will, however, decrease close to linearly with increasing mole ratios of hydrogen to benzene (cf. Fig. 7). This can be explained by the decrease of $a_{\mathrm{H}}$ with increasing conversion (cf. Table 1). The extent of the decrease is also affected by the partial pressure of benzene, and this is the reason for the steeper slope of the results obtained with higher partial pressure of benzene. (No quantitative relationships can be derived from our experiments carried out in an integral reactor.)

The decrease of the electromotive force in the course of catalyst deactivation (cf. Fig. 9) can also be interpreted by the decrease of the surface concentration of adsorbed hydrogen atoms, since our kinetic studies (*10*) demonstrated that the rate of the selective hydrogenation of phenol depends on the surface coverage of hydrogen atoms.

On the basis of our figures demonstrating the factors that affect the value of the electromotive force, and of the assumed electrode processes, it can be stated that the measuring system in which the catalyst in operation is directly applied as measuring electrode can successfully be utilized for following the activation process of the catalysts and the steady-state operation of the catalytic reactor and the catalyst itself. Changes occurring in the stable emf value corresponding to the steady state may be caused by changes in temperature, partial pressure of hydrogen, and mole ratio of the reactants, by the presence of catalyst poison, and by deactivation of the catalyst.

## CONCLUSION

Our electrochemical measuring system, applicable in the vapor phase and consisting of special oxygen and hydrogen electrodes with a solid electrolyte (glass) was found to operate reversibly and reproducibly. The reference half-cell can be directly placed into the catalyst bed of a vapor-phase reactor. Establishing contact between the glass membrane of reference half-cell and the metal catalyst, the latter is the hydrogen electrode controlling the electromotive force of the cell. It follows from the Nernst equation of the measuring electrode that all factors having an effect on the surface concentration of hydrogen (activity of the adsorbed hydrogen), such as partial pressure of hydrogen, concentrations of reactants, flow rate, poisoning and deactivation, will bring about a change in the emf value which can be continuously recorded. The interpretation of emf changes is facilitated by the facts that it is usual in catalytic reactors to record temperature and total pressure and that the input concentration of the reactants is known.

Our method yields valuable, instantaneous, and continuous indirect information concerning the catalyst surface, both independently of catalytic reactions and in the course of such reactions. This information is useful in basic research and also helpful in solving practical problems.

## REFERENCES

1. Druz, V. A., and Sokolskii, D. V., *Tr. Inst. Khim. Nauk Izd. Akad. Nauk Kazah. SSR* (Alma-Ata) **8**, 45 (1962).
2. Druz, V. A., Utegulov, D. V., and Sokolskii, D. V., *Dokl. Akad. Nauk SSSR* **162**, 373 (1965).
3. Druz, V. A., Utegulov, D. V., and Sokolskii, D. V., *Zh. Fiz. Khim.* **40**, 1483 (1966).
4. Haber, F., *Z. Anorg. Chem.* **51**, 245 (1906).
5. Bockris, J. O'M., and Huq, A. K. M. S., *Proc. Roy. Soc.* **A237**, 277 (1956).
6. Ives, D. J. G., "Reference Electrodes," p. 367. Academic Press, New York and London, 1961.
7. Csürös, Z., Petró, J., Máthé, T., and Tungler, A., U. S. Patent No. 3,654,111 (1972).
8. Csürös, Z., Petró, J., Máthé, T., and Tungler, A., Ger. Patent No. 2,024,026 (1974).
9. Csürös, Z., Petró, J., Máthé, T., Tungler, A., and Bakos, M., Hung. Pat. No. 159,608 (1969).
10. Máthé, T., Petró, J., and Tungler, A., to be published.