Physical Chemistry

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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Potentiometric Study of Catalytic Hydrogenation in Dielectric Media

Catalytic hydrogenation of unsaturated compounds is often carried out in nonpolar organic solvents with high specific resistance. In this connection, the possibility of extending the method for measuring the potential of a dispersed catalyst to media with dielectric properties is of considerable scientific and practical interest (1). The usual procedure (2) makes it possible to study hydrogenation in solutions with an electrical conductivity of $10^{-8}\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$ and higher. In some cases the conductivity of the solution can be increased by adding salts, acids, and alkalis, but this may affect the course of the reaction. Changing the design of the reference electrode (3) likewise does not lead to a noticeable expansion of the range of potentiometric measurements. Using an electrometric amplifier with an input resistance of $10^{13}\ \Omega$, it proved possible to measure the potential of a catalyst in alcohol-heptane mixtures (4). The potential values were close to theoretical ones at specific resistances below $5\cdot10^{9}\ \Omega\cdot\mathrm{cm}$. In solutions containing less than 9% ethanol, triboelectricity arose during stirring and affected the instrument readings.

Fig. 1. Electrode for measuring the potential of a powdered catalyst in dielectric media.
1 —contact wire; 2 —calomel half-cell; 3 —electrolytic key; 4 —metallized Schott filter.

In the present work, the possibility has been investigated of measuring the potential of a powdered catalyst suspended in a liquid dielectric by means of two varieties of a new measuring electrode (Fig. 1), which is insensitive to the effect of the space charge of static electricity. This was achieved by introducing a conducting shield that unites, as an equipotential surface, the contact wire and the electrolytic key. The shield is formed by soldering the contact wire into the Schott filter of the calomel half-cell. Small grains of platinum are fused into the outer part of the filter of one of the electrodes studied; the filter of the second electrode was not subjected to metallization.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Figure 2 presents the most probable mechanism of operation of the electrode. When the reaction vessel is shaken, catalyst particles, on the surface of which ionized hydrogen atoms are located, penetrate into the film of KCl solution enveloping the metallic parts of the electrode. Electrons from the catalyst are transferred to the electrode. As a result, the potentials of the electrode and the catalyst are equalized. At the same time, hydrogen ions, which balanced the negative charge communicated to the electrode, leave the outer sheath of the electric double layer of the catalyst particle. The specific feature of the new measuring electrode

consists in the fact that ion exchange takes place not in the dielectric, but in the electrolyte film.

It is not difficult to show that in the experiments it was indeed the potential of the catalyst that was measured, and not that of the contact wire. For example, when the wire is saturated with hydrogen in the absence of catalyst, the potential, as a rule, does not reach a reversible value even with prolonged shaking. The character of the potential shift in the presence and in the absence of catalyst is also different. Thus, 0.8 ml of piperylene shifts the electrode potential within 5 min by +8 mV from the reversible value, whereas in an experiment with 1.5 g of skeletal nickel catalyst it shifts it by +30 mV. The experiments were carried out in the apparatus described earlier (^{5}). The catalyst potential was measured by a Poggendorf compensation circuit with a high-resistance potentiometer of the PPTV-1 type.

Fig. 2. Scheme for imposing a potential on the catalyst particle by the measuring electrode.
1 –contact wire; 2 –catalyst particle; 3 –liquid dielectric; 4 –electrolyte film.

Skeletal nickel, washed successively with water, 96% ethanol, absolute ethanol, and benzene, was used as the catalyst. Benzene and *n*-heptane served as solvents; the objects of study were transpiperylene, allyl alcohol, and *n*-benzoquinone. Before hydrogenation, the catalyst was presaturated with hydrogen while being shaken for one hour. The kinetic curves for the hydrogenation of allyl alcohol have a complex form and consist of several sections inclined at different angles to the abscissa axis. The reversible hydrogen potential of the metallized electrode fluctuates within 660-675 mV, and that of the nonmetallized electrode within 620-650 mV. The abscissae of the inflection points on the potential and kinetic curves coincide.

Fig. 3. Hydrogenation of allyl alcohol (nickel 0.2; 0.8; 2.0 g, allyl alcohol 1.0 ml; solvent benzene, stirring intensity 400 strokes/min, temperature 40°).

Immediately after the introduction of piperylene, the catalyst potential shifts to the cathodic side by 20-30 mV, then to the anodic side to +10–+30 mV, and at the end of the reaction again returns to the initial value. Piperylene mixes with benzene in all ratios and, as a result, is only weakly adsorbed on the catalyst. Since the potential shift is small, the active surface under these conditions is almost entirely occupied by hydrogen (see Table 1).

Similar regularities were observed in the hydrogenation of allyl alcohol (Fig. 3, Table 1). In the upper part of Fig. 3, as well as in Fig. 4, the kinetic curve is shown, and in the lower part the potential curve. An increase in the amount of the unsaturated compound from 0.5 to 1.5 ml leads to an increas-

Table 1

Effect of experimental conditions on the hydrogenation rate and catalyst potential

Hydrogenated compound	Solvent	Experiment temperature, °C	Amount of hydrogenated compound, ml	Catalyst charge, g	Stirring intensity, strokes/min	Average hydrogenation rate, ml/min	Reversible hydrogen potential, mV	Maximum potential shift during the reaction, mV, to the cathodic side	Maximum potential shift during the reaction, mV, to the anodic side
Trans-piperylene	Benzene	7.0	0.2	0.8	310	27.2	675.7	20	7
Trans-piperylene	Benzene	7.0	1.0	0.8	310	34.9	668.0	37	14
Trans-piperylene	Benzene	7.0	1.0	0.8	400	28.8	661.0	23	20
Trans-piperylene	Benzene	7.0	2.0	0.8	310	37.1	675.0	29	32

Hydrogenated compound	Solvent	Experiment temperature, °C	Amount of hydrogenated compound, ml	Catalyst charge, g	Stirring intensity, strokes/min	Average hydrogenation rate, ml/min	Reversible hydrogen potential, mV	Maximum potential shift during the reaction, mV, to the cathodic side	Maximum potential shift during the reaction, mV, to the anodic side
Allyl alcohol	Benzene	7.0	0.5	0.8	310	14.4	656.0	54	37
Allyl alcohol	Benzene	7.0	0.5	0.8	600	80.8	674.0	21	41
Allyl alcohol	Benzene	7.0	1.5	0.8	310	48.8	682.0	10	100
Allyl alcohol	Benzene	7.0	1.5	0.8	600	103.0	690.0	–	85
Allyl alcohol	Benzene	7.0	2.5	0.8	400	77.3	654.0	8	118
Allyl alcohol	Benzene	7.0	2.5	0.8	600	100.2	679.0	–	88
Allyl alcohol	Benzene	7.0	1.0	0.2	400	23.6	679.0	2	76

Hydrogenated compound	Solvent	Experiment temperature, °C	Amount of hydrogenated compound, ml	Catalyst charge, g	Stirring intensity, strokes/min	Average hydrogenation rate, ml/min	Reversible hydrogen potential, mV	Maximum potential shift during the reaction, mV, to the cathodic side	Maximum potential shift during the reaction, mV, to the anodic side
Allyl alcohol	Benzene	20.0	1.0	0.2	400	31.8	673.0	–	87
Allyl alcohol	Benzene	40.0	1.0	0.2	400	19.2	683.0	–	95
Allyl alcohol	Benzene	7.0	1.0	2.0	400	20.1	668.0	10	49
Allyl alcohol	Benzene	40.0	1.0	2.0	400	25.9	689.0	–	59
Allyl alcohol	Abs. ethanol	20.0	1.0	0.8	400	82.1	673.0	–	373
Allyl alcohol	50% ethanol	20.0	1.0	0.8	400	16.2	585.0	–	129
Allyl alcohol	Water	20.0	1.0	0.8	400	19.6	590.0	–	64

Fig. 4. Hydrogenation of *p*-benzoquinone (nickel 2.0 g, benzoquinone 0.5 g; solvent benzene; stirring intensity 400 strokes/min, temperature 20°)

Figure 4: Fig. 4. Hydrogenation of *p*-benzoquinone (nickel 2.0 g, benzoquinone 0.5 g; solvent benzene; stirring intensity 400 strokes/min, temperature 20°)

Hydrogenated compound	Solvent	Experiment temperature, °C	Amount of hydrogenated compound, ml	Catalyst charge, g	Stirring intensity, strokes/min	Average hydrogenation rate, ml/min	Reversible hydrogen potential, mV	Maximum potential shift during the reaction, mV, to the cathodic side	Maximum potential shift during the reaction, mV, to the anodic side
Allyl alcohol	Benzene	20.0	1.0	0.8	400	74.6	676.0	–	66
Quinone	Benzene	20.0	0.5 g	0.8	400	1.6	664.0	–	528
Quinone	Benzene	20.0	0.5 g	2.0	400	10.1	685.0	–	136
Quinone	Benzene	40.0	0.5 g	0.8	400	5.5	698.0	–	379

···the hydrogenation rate from 14.4 to 48.8 ml/min (at 310 strokes/min and 0.8 g Ni) and the shift of the catalyst potential from 37 to 100 mV. A further increase in the concentration of allyl alcohol has almost no effect on the reaction rate or on the magnitude of the potential shift. The average potential shift on the metallized electrode is higher by 15 mV. The reaction order decreases from 1.2 at 0.5 ml alcohol to 0 at 2.5 ml. With an increase in stirring to 400 and 600 strokes/min, the form of the kinetic and potential curves remains unchanged, while the reversible hydrogen potential becomes more cathodic. In benzene and water the potential shift is the same, but in water the potential shifts rapidly, and in benzene slowly, reaching its minimum value in the first case after absorption of 1.5%, and in the second after 64% of hydrogen.

Fig. 4. Hydrogenation of *p*-benzoquinone (nickel 2.0 g, benzoquinone 0.5 g; solvent benzene; stirring intensity 400 strokes/min, temperature 20°)

In the hydrogenation of benzoquinone (Fig. 4), the catalyst potential instantaneously shifts to the anodic side, then remains constant for some time and, at the end of the experiment, rapidly reaches the reversible value. Being a strong oxidizing agent, quinone is adsorbed on the catalyst as an active electron acceptor.

The results obtained make it possible to assert that the new electrode described can be used both in dielectric and in conducting media. With its aid, data have for the first time been obtained on the change in po-

surface concentrations of the reacting substances during catalytic hydrogenation in hydrocarbon media. In water and aqueous-alcohol mixtures the sensitivity of the measuring circuit is somewhat reduced, apparently because of removal of the conducting film from the electrode surface. At the same time it has been established that metallization of the filter creates conditions that facilitate electron exchange between the catalyst particles and the measuring electrode.

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