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CHEMICAL KINETICS AND CATALYSIS

Deactivation of Supported Nickel-Based Hydrogenation Catalysts with Sulfide Ions

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Abstract—Kinetics of the liquid-phase hydrogenation of a multiple carbon bond is studied in an aqueous medium on supported nickel catalysts at different hydrogen pressures in the system under conditions of partly controlled deactivation of the active surface sites with sulfide ions. The pattern of deactivation of the active surface sites of Ni/SiO₂ catalysts containing different amounts of the active metal on the surface with sulfide ions in water is determined. The resistance of the studied catalysts to deactivation during the reduction of diethyl maleate (DM) and propen-2-ol-1 is determined experimentally. It is shown that the catalyst is more resistant to deactivation during the hydrogenation of propen-2-ol-1; this finding is attributed to the steric factor. It is found that the hydrogen pressure in the system does not affect the deactivation pattern. Excessive pressure slightly alters the deactivation resistance of the catalyst during the hydrogenation of propen-2-ol-1. It is shown experimentally that the catalytic properties of nickel in liquid-phase hydrogenation reactions can be controlled by introducing small amounts of a catalytic poison into the system at high hydrogen pressures.

Keywords: liquid-phase hydrogenation, adsorption complex, catalyst activity, catalytic poison **DOI:** 10.1134/S0036024419110220

INTRODUCTION

In the last 30 years, catalytic processes of the hydrogenation of organic compounds of different classes with gaseous hydrogen have almost supplanted all other industrial reduction techniques. The most commonly used catalysts are systems that contain nickel, palladium, platinum (less frequently), and other transition metals as the main active metal that can be promoted with different compounds. According to well-known theoretical principles [1, 2], the laws governing the adsorption of reactants determine the activity and selectivity of heterogeneous catalysts. An understanding of these laws is necessary for the development of scientifically grounded methods for the selection of optimum catalyst systems and the prediction of the catalytic effect. It is not by chance that the expansion of the areas of application of the theory of adsorption in studies of the kinetics and mechanisms of heterogeneous catalytic processes is considered to be a priority direction of the development of the theory of catalysis formulated by the European Federation of Catalytic Societies (EFCATS).

It has been shown experimentally that during adsorption on the surfaces of metals and catalysts based on them, hydrogen is adsorbed in different adsorption states that differ in type and the energy of bonding to the catalyst surface [3-5]. The adsorption states of hydrogen are in turn directly related to the energy of intermediate interactions. We may therefore assume it is the nature and energy characteristics of adsorbed hydrogen that determine the rate and selectivity of hydrogenation reactions. Concepts of different reactivities of individual adsorbed hydrogen forms are frequently used to interpret the kinetic laws of hydrogenation of different classes of compounds [6, 7]. However, the published approaches to estimating the reactivity of adsorbed hydrogen are extremely limited. The authors of [2, 8] proposed an approach to experimentally determining the reactivity parameters and thermodynamic characteristics of adsorbed hydrogen that was based on the partly controlled deactivation of active surface sites of metals due to introducing small amounts of catalytic poisons into a catalyst system without changing the composition and structure of the reaction system in general. The cited authors showed that this approach allows us to estimate the reactivity of individual adsorbed hydrogen forms in liquid-phase hydrogenation reactions according to the regional rate [8]; in addition, we can select optimal catalyst systems with predetermined activity and selectivity.

No.	[NiO], wt %	$S_{\rm sp},{\rm m^2/g}$	С, %	<i>R</i> , µm	<i>d</i> , nm	<i>l</i> , nm
1	23.2	264 ± 0.7	11	5	0.297	17.7
2	16.4	296.3 ± 0.9	9	5	0.287	15.5
3	15.8	317.6 ± 0.5	7	5	0.293	10.0
4	8	338.4 ± 0.5	5	5	0.288	9.8
5	6.9	362 ± 0.9	4	5	0.275	9.5
6	4.7	364 ± 0.8	0.6	5	0.255	9.1

 Table 1. Main physicochemical properties of the studied nickel catalysts

[NiO] is the amount of supported NiO, C is the active metal content, r is the particle radius, d is the interplanar spacing, and l is the crystallite size.

The aim of this work was to study the pattern of deactivation of silica gel-supported nickel catalysts for the liquid-phase hydrogenation of multiple carbon bonds by introducing measured amounts of sulfide ions into the system at atmospheric and high hydrogen pressures in the system.

EXPERIMENTAL

A number of silica-supported nickel catalysts (Ni/SiO_2) with different concentrations of the active metal were used in this work. The catalysts were synthesized as described in [9]. Silica gel L 5/40 was used for the synthesis. The average particle radius was 5 μ m, and the specific surface area was 390 \pm 5 m²/g. The structural and mechanical properties of the catalysts are presented in Table 1.

Our kinetic studies of the liquid-phase hydrogenation reaction were conducted by static means under unsteady conditions in a pressurized liquid reactor with vigorous stirring at a hydrogen pressure in the system of 0.1-0.9 MPa. Catalyst activity was estimated from the rates of hydrogenation of a model compound at conversion of less than 0.1.

The deactivation selectivity was estimated according to Bartholomew [10], based on an analysis of the kinetic parameters of the studied process and specially modified for liquid-phase hydrogenation reactions. This required determination of the preferential adsorption of the deactivating agent particles on certain atomic ensembles of the surface.

This approach is based on analyzing a plot constructed in the A = f(C) coordinates, where catalyst activity A and specific amount of the catalytic poison in the system C are normalized to the equations

$$A = r_{0,C} / r_{0,C=0}, \tag{1}$$

$$C = n_i / n_{\rm max}, \tag{2}$$

where $r_{0,C}$ and $r_{0,C=0}$ are the initial hydrogenation reaction rates in a given solvent (activity) for deactivated and nondeactivated catalysts, respectively; n_i is the amount of the catalytic poison introduced per gram of catalyst; and n_{max} is the amount of the catalytic poison

introduced per gram of catalyst, at which the catalyst completely loses activity.

In this case, selective etching is understood as the preferential adsorption of the poison at low poison concentrations on the most active surface sites. The preferred blocking of regions with lower activity leads to antiselective deactivation. If the drop in activity is linearly dependent on the concentration of the adsorbed poison, the poisoning is nonselective.

Diethyl maleate (DM) and propen-2-ol-1 were selected as model hydrogenated compounds containing multiple carbon bonds. These compounds interact with hydrogen in a 1:1 stoichiometry to form negligible amounts of byproducts and intermediates. The controlled deactivation of the active catalyst sites was achieved as described in [2] by adding strictly defined amounts of a 0.05 M sodium sulfide solution with a pH value corresponding to the pH of the reaction medium to the bulk phase. The catalyst was etched in the titration mode in a hydrogen atmosphere with vigorous stirring of the liquid phase. According to preliminary studies, the maximum drop in catalyst activity at a certain amount of the etching agent is achieved within 15 min; a further increase in the deactivation time at a test temperature of 303 K does not result in an appreciable drop in the activity of the nickel catalyst; most commonly, it is within the experimental error. Water was used as the solvent.

Direct potentiometry was used to determine the S^{2-} ion concentrations. Measurements of the residual sulfide ion concentrations after catalyst deactivation suggest the amount of sulfide remaining in the solution was below the detection limit.

The effect hydrogenation has on the structural and mechanical properties was determined on a TESCAN VEGA 3 SBHSEM scanning electron microscope combined with an energy dispersive spectrometer with an Oxford Instruments NanoAnalysis x-ACT detector. Elemental mapping of the catalyst surface was conducted before the kinetic testing and immediately after the testing. An example of elemental mapping of catalyst 2 (see Table 1) after DM hydrogenation at a hydrogen pressure of 0.9 MPa and a temperature of 30°C is shown in Fig. 1.



Fig. 1. Scanning microscope-synchronized electronic map of elemental distribution over the surface for catalyst 2 (see Table 1) after DM hydrogenation in water at a hydrogen pressure of 0.9 MPa, a temperature of 30° C, and an amount of sodium sulfide introduced per gram of catalyst of 0.840 mmol(Na₂S)/g(Ni).

RESULTS AND DISCUSSION

To determine the effect deactivation processes have on the activity of supported nickel in the studied liquid-phase hydrogenation reactions, apparent rates r_{app} and rate constants k_{app} of the processes were first calculated with the equations

$$r_{\rm app} = \frac{\Delta V}{\Delta t},\tag{3}$$

$$k_{\rm app} = \frac{r_{\rm app} \rho \times 760}{\alpha P_{\rm H_2} \times 60},\tag{4}$$

where ΔV is the amount of hydrogen (mL) that reacts within time Δt (s), α is the Bunsen coefficient for hydrogen at 303 K (cm³(H₂)/cm³(l. ph.)), ρ is the



Fig. 2. Rate of hydrogen absorption during DM hydrogenation in water at different amounts of introduced sodium sulfide: (1) 0, (2) 0.050, (3) 0.100, and (4) 0.500 mmol(Na₂S)/g(Ni). Conditions of hydrogenation: $T = 30^{\circ}$ C; $m_{cat} = 2.5$ g; amount of reduced metal (Ni), 11%; pressure, 0.1 MPa.

apparent density of the catalyst (4.5 g/cm³ for the selected catalyst), and $P_{\rm H_2}$ is the hydrogen pressure in the test.

The kinetic laws of the reduction of the model compounds in the presence of the supported nickel catalyst at a hydrogen pressure in the system of 0.1 and 0.9 MPa and different amounts of the catalytic poison introduced into the system are shown in Figs. 2-5.

According to the data shown in Figs. 2–5, deactivation of the catalyst's surface does not alter the kinetic laws; it only reduces the catalyst's activity; the reaction rate constant calculated with formula (4) remains virtually unchanged at different hydrogen pressures in the system. The results from the mathematical processing of the kinetic laws according to



Fig. 3. Rate of hydrogen absorption during propen-2-ol-1 hydrogenation in water at different amounts of introduced sodium sulfide: (1) 0, (2) 0.050, (3) 0.100, and (4) 0.500 mmol(Na₂S)/g(Ni). Conditions of hydrogenation: $T = 30^{\circ}$ C; $m_{cat} = 2.5$ g; amount of reduced metal (Ni), 11%; pressure, 0.1 MPa.



Fig. 4. Rate of hydrogen absorption during DM hydrogenation in water at different amounts of introduced sodium sulfide: (1) 0, (2) 0.210, (3) 0.420, (4) 0.630, and (5) 0.840 mmol(Na₂S)/g(Ni). Conditions of hydrogenation: $T = 30^{\circ}$ C; $m_{cat} = 2.177$ g; amount of reduced metal (Ni), 11%; pressure, 0.9 MPa.

Bartholomew [10] suggest the catalyst's surface undergoes deactivation selectively; the deactivation becomes nonselective only at substantial sulfide ion concentrations in the system. In addition, catalyst deactivation with respect to the reduction of DM and propen-2-ol-1 proceeds at different rates, as is shown in Table 2.

The data in Table 2 suggest that in the case of DM reduction, introducing a catalytic poison into the system leads to a more rapid loss of catalyst activity than with propen-2-ol-1 hydrogenation. The catalyst was more resistant to deactivation at atmospheric hydrogen pressure; upon an increase in pressure to 0.9 MPa, the dependence of the degree of deactivation on the catalytic poison concentration becomes more complex. We believe this finding can be attributed to the heat of hydrogenation of propen-2-ol-1 (-(127-130) kJ/mol) being lower than that of DM (-(141-158) kJ/mol). This ensures smaller adsorption- and catalysis-

 $r, cm^{3}(H_{2})(sg(Ni))^{-1}$



Fig. 5. Rate of hydrogen absorption during propen-2-ol-1 hydrogenation in water at different amounts of introduced sodium sulfide: (1) 0, (2) 0.210, (3) 0.420, (4) 0.630, and (5) 0.840 mmol(Na₂S)/g(Ni). Conditions of hydrogenation: $T = 30^{\circ}$ C; $m_{cat} = 2.176$ g; amount of reduced metal (Ni), 11%; pressure, 0.9 MPa.

induced deformations of the active metal surface and thus a smaller loss of activity. The data can also be attributed to the steric factor: a propen-2-ol-1 molecule is smaller than a DM molecule, so it has more opportunities to approach the surface of a catalyst that is partly blocked by sulfide ions.

According to [5, 11], the distribution of hydrogen over the surfaces of bulk and supported nickel-based catalysts with respect to individual forms remains approximately constant in different solvents; the greatest contribution to the shift of the adsorption equilibrium of hydrogen comes from the catalyst deactivation [12, 13]. However, though the kinetic laws of the hydrogenation of compounds containing carbon carbon double bonds are of the same type at hydrogen pressures in the system of 1-9 atm, they differ in activity at low conversions of the hydrogenated compound and in the susceptibility to deactivation caused by the

 Table 2. Deactivation coefficients calculated by the Bartholomew method for the supported nickel catalyst at different hydrogen pressures in the system

Compound	1	2	3	4	5	6	K			
	$K_{\rm d}$, g(Ni)(mmol(Na ₂ S)) ⁻¹									
0.1 MPa										
DM	4.4	4.7	6.3	6.5	5.8	6.0	5.6			
Propen-2-ol-1	1.3	1.6	2.0	1.5	1.6	1.8	1.6			
0.9 MPa										
DM	4.4	6.8	5.7	5.2	12.2	15.9	8.4			
Propen-2-ol-1	2.3	1.8	1.2	1.0	1.4	2.8	1.8			

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targeted introduction of catalytic poisons into the system. This can be attributed to the different reactivities of not only individual adsorbed hydrogen forms but also the hydrogen acceptor.

The authors of [8] demonstrated the possibility of calculating the rate constants using individual active sites of the nickel surface using a complex of kinetic and adsorption calorimetric experimental data and calculated the rate constants for the reduction of multiple carbon bonds involving three adsorbed hydrogen forms at atmospheric pressure. The authors used a model of a surface with discrete heterogeneity [14, 15] to calculate the relative amounts of molecular and atomic hydrogen on the surface of a bulk nickel catalyst: the adequacy of this model was later confirmed in a direct experiment [16]. We may assume that an increase in the hydrogen pressure in the system does not lead to the formation of fundamentally different adsorbed hydrogen forms: this factor only alters the ratio of the forms without changing their reactivity. In the future, regional rates can be used to recalculate the number of individual hydrogen forms on the surfaces of catalysts and their contribution to the reduction of DM and propen-2-ol-1 at a hydrogen pressure of 0.9 MPa.

CONCLUSIONS

Introducing a sulfide ion into a reaction system allows us to modify the surfaces of supported nickel catalysts in order to ensure not only a differentiation of rates, which is of fundamental importance in determining the reactivity of hydrogen characterized by different adsorption energies, but also variation in catalyst susceptibility, depending on the steric factor. The proposed approach allows us to increase and (of primary importance) predict a catalyst's selectivity in the reduction of certain functional groups.

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