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The Tian–Calvet calorimetry as a method for investigating heterogeneous hydrogenation catalysts based on IMC disperse powders

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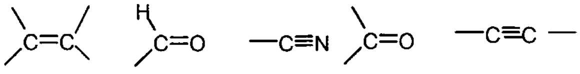
Abstract

The interaction of hydrogen with $LaNi_{3,5}Cu_{1,5}$ — a catalyst for hydrogenation of organic compounds — was studied in a wide temperature range (308–373 K) by the Tian–Calvet differential heat-conduction calorimetry. The *P–C–T-*, *Q–C–T-* diagrams and the results of mathematical treatment of the calorimertic data are presented. The formation mechanism of active hydrogen solved in metal matrix is proposed.

Keywords: Intermetallic compounds; Calorimetry; Catalytic activity; Hydrogen in metals

1. Introduction

The intermetallic compounds (IMC) of the $CaCu_5$ type, containing rare-earth metals and transition metals (Ni, Co), are well known as hydrogen storage materials. They absorb approximately 500–600 volumes of molecular hydrogen per one volume of the solid (metal) phase at 300–350 K and pressures below 5–10 atm. This absorption is accompanied by activation of molecular hydrogen with formation of H_2^* molecules and solid solution of active "atomic" hydrogen, that is placed in the R_2T_2 (R: rare-earth metal, T: Ni or Co) holes of IMC crystal structure. The heats of formation of the hydride phase containing ca. 50 at.% hydrogen, do not exceed 30–40 kJ/mol H_2. So, IMC hydride phases can be considered as original "chemical accumulators" of atomic hydrogen weakly bound with metal matrix. Its high mobility and enhanced migration from the bulk to the surface of the sample attract much interest in applying such systems for the catalytic processes involving hydrogen. For instance, disperse powders of these IMC have great catalytic activity in the reactions of low temperature hydrogenation of multiple C–C bonds and functional groups like



For more complex organic molecules, the selective hydrogenation of different functional groups is possible, yielding products with desired structure and properties.

For the first time, this phenomenon was reported in [1–5]. IMC hydrides, containing Ni and Cu together — $LaNi_4CuH_{4.3}$, $LaNi_4CuH_{6.3}$ and especially $LaNi_3Cu_2H_{3.7}$ — were shown to be active catalysts of propylene and ethylacetoacetate (EAA) hydrogenation. Being modified by (+)-tartaric acid, these

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compounds can promote enantioselective hydrogenation of EAA [3,4].

The great catalytic activity of the IMC based on the $LaNi_5$ with 40–60% Ni substituted by Cu was connected with the optimal value of the bond energy of hydrogen with such IMC matrix. The importance of the structure of surface active center (“cluster”), which involve both transition metals Ni and Cu, was pointed out in this connection.

The principle of catalytic action the hydrides is based on their ability to activate and transfer molecular hydrogen according to the scheme proposed in [2]:

$$AB_n + H_2 \rightarrow AB_nH_x$$

$$AB_nH_x + R \rightarrow AB_nH_{x-2} + RH_2$$

$$AB_nH_{x-2} + H_2 \rightarrow AB_nH_x$$

$$R + H_2 \xrightarrow{AB_nH_x} RH_2$$

Evidently, when developing new effective hydrogenation catalysts based on IMC hydrides, the crucial aspect is the mechanism how “atomic” hydrogen is formed on active centers of surface. The form in which hydrogen exists in the hydrides upon varied concentration and IMC-matrix structure is also very important. To determine both the mechanism of hydrogen atomization on the surface and its chemical form in the bulk, new, non-classical methods of investigation are necessary, which stretch beyond the classical area of physical chemical analysis. The novel methods require novel concepts of approach to interpretation of experimental data.

To investigate the formation mechanism of “active” hydrogen solved in metal matrix of the $LaNi_{3,5}Cu_{1,5}$ — one of the active catalysts for the hydrogenation of organic compounds molecules multiple bonds — the Tian–Calvet differential heat-conduction calorimetry was applied in the present work. The method is based on studying hydrogen absorption dynamics by the registration of heat effects of interaction in IMC–H_2 system at hydrogen “titration” of metal phase. The hydrogen absorption occurs without an induction period and that is why this technique can be used in studying catalytic hydrogenation reactions in the presence of IMC as hydrogen activator.

2. Experimental

The IMC $LaNi_{3,5}Cu_{1,5}$ was obtained by arc-melting the high purity metals (La = 99.8%, Ni = 99.96%, Cu = 99.5%) under purified argon flow, subsequent homogenization during 300 h at 870 K, and quenching in cold water. The X-ray phase analysis showed that the sample $LaNi_{3,5}Cu_{1,5}$ contained an only phase with hexagonal structure ($a = 5.060$ Å, $c = 4.020$ Å). The chemical analysis has confirmed that the sample composition corresponded to the formula $LaNi_{3,5}Cu_{1,5}$ ($Ni = 3.47 \pm 0.16$, $Cu = 1.51 \pm 0.09$).

The hydrogen used was the purest available ($<10^{-5}$ vol.% impurities) and was obtained by the desorption from the hydride phase based on $LaNi_5$.

The calorimetric apparatus included the calorimeter (differential automatic microcalorimeter DAC-1-1A) and a gas titration device. The temperature in the thermostat was maintained constant within ±0.2 K.

At every temperature, three to five independent measurements were carried out using samples of different mass in the range 1–1.5 g.

The technique applied was previously described in detail [6,7]. The calorimetric titration by small hydrogen portions allowed us to study the interaction in $LaNi_{3,5}Cu_{1,5}$–H_2 system at almost equilibrium conditions and to obtain a complex information about different aspects of such interaction.

The registration of heat effect of absorption or desorption of definite amounts of hydrogen as time function opens the possibility not only to construct *P–C–T* diagrams but also to obtain differential molar enthalpies of hydrogenation in different phase regions. The experimental calorimetric data were successfully applied for the study of hydrogenation reaction mechanism at various hydrogen concentrations in the solid phase [6]. For this purpose the well-known Erofeev–Avrami’s equation $[-\ln(1-\theta)]^{1/n} = kt$ was used. The conversion extent $\theta_k = \left(\sum_{i=1,\dots,k} W_i/W_\Sigma\right)$ 100% was determined using the values of the thermal emission upon absorption of each hydrogen portion W_i and value W_Σ corresponding to the complete sample hydrogenation. Next, the dependence of the sample hydrogenation or dehydrogenation extent θ versus time of the equilibrium achievement t was represented in logarithmic coordinates, $\ln[-\ln(1-\theta)]$ versus $\ln t$. The n parameter, that is calculated as tangent of the angle between graph slope and "time" axis, allows to evaluate the mechanism of the reaction [8].

3. Results

The hydrogen absorption in the system $LaNi_{3.5}Cu_{1.5}$–H_2 was studied at 308, 328, 353 and 373 K. To stabilize the process characteristics, the sample was subjected by 3–5 times cycling in hydrogen atmosphere at every temperature before collecting data for *P–C* diagram construction. The corresponding isotherms are presented in Fig. 1. The type of "pressure–composition" curves is considerably dependent on the temperature.

At $T < 353$ K, the diagrams of the $LaNi_{3.5}Cu_{1.5}$–H_2 system have "classic" shape. The isotherms have three phase regions — α-phase region or hydrogen solid solution in the initial crystal matrix, plateau region or α- and β-phases coexistence and β-hydride region.

At $T > 353$ K, the region of α- and β-phases coexistence is not observed. Finally, solid solution of hydrogen in the metal IMC lattice was obtained.

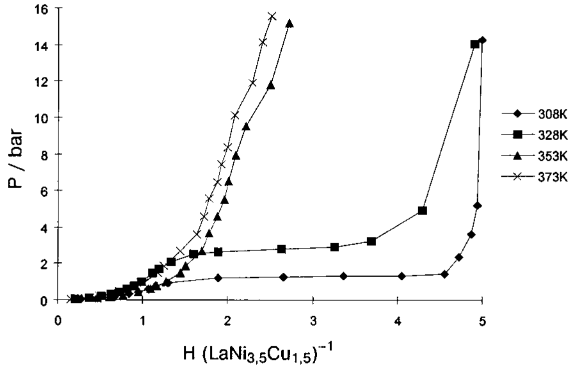


Fig. 1. Isotherms of hydrogen absorption in the $LaNi_{3.5}Cu_{1.5}$–H_2 system.

The type of heat-emission (heat-absorption) graph, which allows to determine the reaction rate, is fundamentally different in the regions of α-solution and α + β-equilibrium. The very fast hydrogen absorption process in α-region changes to relatively slow and more exothermic chemical reaction of β-hydride formation and then, in the region of hydrogen solution in β-phase, the process is again fast.

The calorimetric titration technique was used for experimental determination of the differential enthalpies and entropies of $LaNi_{3.5}Cu_{1.5}$ hydrogenation at 308 and 328 K. The dependence of $|\Delta H_{dif}|$ values versus absorbed hydrogen amount at 308 K is depicted in Fig. 2. At 328 K, the dependence is of the same

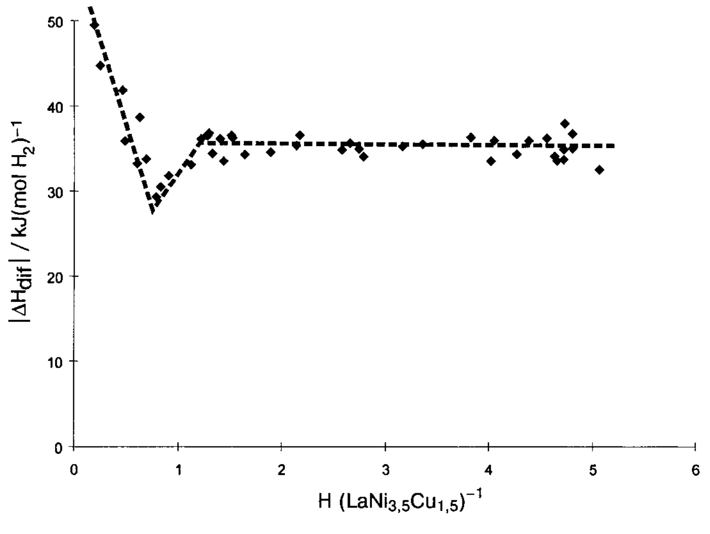


Fig. 2. Dependence of differential molar enthalpy of hydrogen absorption vs. its content in $LaNi_{3.5}Cu_{1.5}$–H_2 system at 308 K.

Table 1
Thermodynamic parameters of the $LaNi_{3.5}Cu_{1.5}$ hydrogenation

T (K)	ΔH_{dif} (kJ/mol H_2)	ΔS_{dif} (J/mol H_2^* K)
308	−35.3 ± 1.4	−116.6 ± 4.5
328	−36.1 ± 1.4	−118.6 ± 4.2

type. Such behaviour was similar to that observed in the system $LaNi_5$–H_2 [9]. It was noted that using the calorimetry method allows to monitor processes at low hydrogen concentrations in the solid phase and to obtain the information about the nature of the bound hydrogen. The initial, most exothermic, effect corresponding to chemisorption is followed by less exothermic one, which is connected with hydrogen trapping or an active "atomic" hydrogen formation. The subsequent increase of $|\Delta H_{dif}|$ value up to the phase boundary indicates the essentially normal α-solid solution behaviour.

In the $\alpha + \beta$-region, there is linear dependence of the emitted or absorbed heat versus mass of the substance just reacted. Thus, the differential molar enthalpy value in the plateau region is constant within the experimental error and independent of the sample hydrogenation extent.

The corresponding results are presented in Table 1. At temperatures exceeded 353 K, the absence of plateau region on the *P–C–T* diagram does not allow to define the differential enthalpies values of hydrogen absorption process in $LaNi_{3.5}Cu_{1.5}$–H_2 system with appropriate authenticity.

Fig. 3 presents a comparison of absorption isotherm in the $LaNi_{3.5}Cu_{1.5}$–H_2 system at 308 K with the corresponding "kinetic" curve, which is constructed in logarithmic coordinates $\ln[-\ln(1-\theta)]$ versus $\ln t$. The curve reflecting dependence of conversion extent θ versus time t consists of two linear segments with different slopes.

The first segment corresponds to formation of solid solution of hydrogen in the initial IMC lattice. The value of n, which is lower than 1, points towards diffusive nature of the process.

The second segment with $n > 2.5$ is associated with the chemical reaction of the β-hydride phase formation. The mechanism of such reactions is the nucleation and nucleus growth of the new phase, β-hydride in our case.

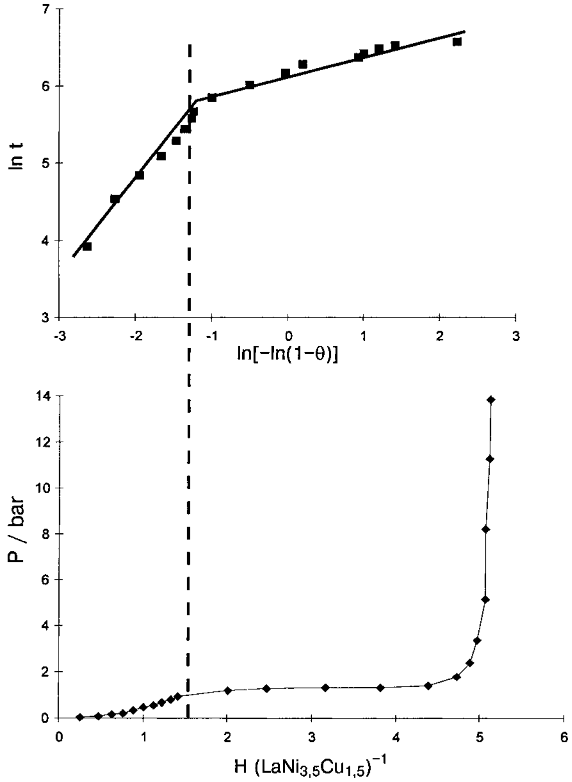


Fig. 3. Comparison of isotherm with the dependence of conversion extent θ on time t for system $LaNi_{3.5}Cu_{1.5}$–H_2 at 308 K.

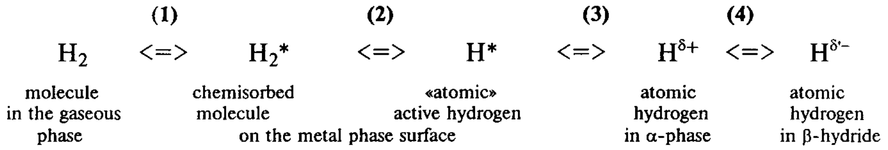
The change of the hydrogen absorption mechanism occurs in the moment when β-phase nuclei first appear in the IMC–H_2 system, i.e. during transition from the hydrogen solid solution phase to a $\alpha + \beta + H_2$-equilibrium.

4. Discussion

Analysis of the data, which have obtained not only by means of the described here technique of the IMC calorimetric titration by small hydrogen portions, demonstrates that in the $LaNi_{3.5}Cu_{1.5}$–H_2 system, similar to $LaNi_5$–H_2 [10], the dependence of different parameters of hydrogenation process on concentration of hydrogen in the solid phase is pronounced. There is a critical value of hydrogen concentration which corresponds to the transition from the α-solution to a two-phase $(\alpha + \beta)$-equilibrium. In this special point, both types of the *P–C–T*- and *Q–C–T*-diagrams and the interaction mechanism of hydrogen with IMC are radically changed. Besides, the volume of the solid phase increases spontaneously by 14% [11].

Such simultaneous change of the hydride phase properties can be explained, as suggested in [10], by the different nature of interaction of hydrogen with IMC in α-solid solution and in β-hydride. The experimental crystallographic data [12,13], investigations of the chemisorption process — one of the first stages of the hydrogen interaction with IMC matrix — and high mobility of hydrogen atoms in α-phase, characteristic for the diffusive mechanism of H-atoms penetration into the solid phase, all together allow us to suppose that hydrogen atoms in the α-solution are positively charged. The reason of this positive charge of hydrogen chemisorbed at the active centers of surface ($\delta+$), lies in partial donation of their s-electrons to the conduction band of the metal. During further hydrogenation process, the concentration of $H^{\delta+}$ atoms dissolved in the solid phase becomes sufficient to oxidize the very IMC matrix. At the moment, the lattice volume increases sharply. This increase is associated with the change in the effective volume of H-atoms whose charge in the β-phases turns into nearly zero or slightly negative $\delta'-$. The coexistence of the hydrogen atoms with positive and negative charges in the same hydride phase in the "$LaNi_{3.5}Cu_{1.5}$–H_2" system (and "IMC–H_2" also) essentially enlarges the set of hydrogenation reactions where such catalysts can be applied.

The following scheme of the hydrogen activation process, crucial for the catalytic activity, is proposed:



The scheme presented can be modified dependent on IMC nature, structure and chemical composition, as well as external hydrogen pressure.

The (1), (2) and (3) stages proceed with very small activation energies. It can be concluded from the profile of the calorimeter signal during hydrogen titration of the IMC in the α-phase region. The splitting of the overall signal into those corresponding to stages (1), (2) and (3) is observed on hydrogen desorption thermograms under definite conditions, which are, however, of more complicated and multi-step nature.

It is likely, that $H^{\delta+}$-hydrogen in the α-phase, particularly if the α-region on the *P–C–T*-diagram is narrow, must have chemical activity and structural properties very close to chemisorbed hydrogen on the IMC surface. From this viewpoint, α-phase can be considered as a "transition state" between chemisorbed molecular hydrogen and stoichiometric β-hydride.

The study of mechanism how hydrogen interact with the IMC proves to be useful for search for novel materials perspective as hydrogenation catalysts. So, the rate of hydrogen absorption allows to judge the compound catalytic activity. For instance, the absorption process in the region of "dilute" α-solid solution of hydrogen in the metal phase proceeds by the diffusive mechanism and the absorption rate is much greater then in the $\alpha + \beta$-equilibrium region, where the rate is limited by a rather slow chemical transformation $\alpha \rightarrow \beta$. Since the area of α-phase on the *P–C–T*-diagrams of different "IMC–H_2" systems can vary (for instance, for $LaNi_{3.5}Cu_{1.5}$ studied here this area is one of the broadest) it becomes possible to carry out directed search for catalysts suitable for different hydrogenation reactions.

5. Conclusions

The Tian–Calvet differential heat-conducting calorimetry appears to be very useful for investigating catalytic hydrogenation reactions in the presence of $LaNi_{3.5}Cu_{1.5}$ ($LaNi_5$-type IMC in more general case) as a hydrogen activator. The most important advantage of this technique is the possibility to avoid the superimposition of the different hydrogenation stages on to each other, and to monitor processes at low hydrogen concentrations in the solid phase. Such studies allow to propose the mechanism of formation of active hydrogen dissolved in metal matrix, this process being important for the compound catalytic activity, and to obtain the information about the chemical behaviour of hydrogen in α- and β-phases.

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