ENERGETIC ANALYSIS OF THE PROTON TRANSFER IN Pt/Al_2O_3 CATALYST

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Se propune o secvență de procese implicate în »hydrogen spillover» pe un catalizator Pt/Al_2O_3, compatibil cu modul de evoluție al conductivității electrice. Analiza energetică a acestei secvențe dovedeşte că mecanismul propus este corect.

A sequence of processes involved in the hydrogen spillover of on a Pt/Al_2O_3 catalyst was proposed, compatible with the observed behavior of the electrical conductivity. The energetic analysis of this sequence proves that the proposed mechanism is correct.

Keywords: hydrogen spillover, conductivity, energetic analysis, Pt/Al_2O_3 catalyst

1. Introduction

Hydrogen spillover refers to the diffusion of surface hydrogen species from metal sites where they are produced by the dissociation of hydrogen molecules to an oxide or carbon based support that has no activity for dissociative hydrogen adsorption. There are hypotheses that spillover hydrogen can be either a solvated proton or a proton-electron pair. Over metal oxides, hydrogen spillover seems to occur by moving over –OH surface groups with hydrogen exchange (proved by D_2 experiment). However, hydrogen spillover over a carbon surface is accompanied by simultaneous electron and ion conductivity.[1]

Hydrogen spillover has an extremely important contribution to catalytic hydrogenation reactions [2], but it can be involved also in synthesis, partial oxidation, cracking and isomerization reactions.[3-5]

Hydrogen spillover has emerged as a possible technique for achieving high-density hydrogen storage at near-ambient conditions in lightweight, solid-state materials. This is why an increasing number of studies was devoted to this subject during the last decade.[6-10] In many cases the absorbent material is a nanostructured one.[11-15] Increased storage effectiveness by catalysed spillover was also in view.[16]

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The mechanism of the spillover process was investigated, as well.[17-19] Theoretical models were proposed by several researchers.[20-22]

2. Energetic analysis

The behavior of the conductivity of a Pt/Al_2O_3 catalyst, during the adsorption of hydrogen was investigated in previous papers.[23] It was observed that if the catalyst's surface contains water or oxygen traces, the variation of conductivity during the hydrogen flow is of the "overshoot" type. A few competing processes are responsible for this behavior, including the hydrogen oxidation with adsorbed oxygen, which favors further dissociation of hydrogen molecules. The transformation of hydrogen atoms into hydrated protons is another important process. The spill over of hydrated protons from platinum to alumina involves the adsorbed water molecules.

The aim of this study is to analyze, from the thermodynamic point of view, the reaction sequence suggested in order to explain the answer of the electrical conductivity, to the hydrogen flow, by means of the protonic conduction of the supported catalyst.

The following reactions were taken into account as proceeding during the hydrogen adsorption on incompletely superficially cleaned Pt/Al_2O_3 catalyst (the index "s" is for species at the catalyst's surface):

$$Pt_s + ½\ H_2 \longrightarrow Pt_s\text{–}H \quad (1)$$

$$Pt_s\text{–}O + 3/2\ H_2 \longrightarrow Pt_s\text{–}H + H_2O_s \quad (2)$$

$$Pt_s\text{–}H + H_2O_s \longrightarrow Pt_s + H_3O^+_s + e^- \quad (3)$$

$$e^- + Pt_s \longrightarrow e^-(Pt_s) \quad (4)$$

(the electron is captured in the conduction band of the metal).[24]

$$2\ OH^- \longrightarrow H_2O(g) + O^{2-}_s + V_{O^{2-}} \quad (5)$$

$$V_{O^{2-}} \longrightarrow V^{+}_{O^{2-}} + e^- \quad (6)$$

$$Pt_s\text{–}H + O^{2-}_s \longrightarrow Pt_s + OH^-_s + e^- \quad (7)$$

($V_{O^{2-}}$ stands for anionic oxygen vacancies in the alumina lattice).

The platinum surface is partially oxidized, Pt_s–O bonds are present. A value of –105 kJ/mol was reported for the enthalpy of formation of one mole of oxygen atoms chemisorbed on platinum.[25]

Reaction (1) was investigated by many authors [26,27], including thermodynamic studies.[28,29] The calorimetric determination of the enthalpy of this reaction yielded a value of –21 kJ/mol, while the value obtained from adsorption isotherms at different temperatures was –25 kJ/mol.

The values reported for the heat of reaction (2), named titration reaction are in strong disagreement. The value given by Sen and Vanice [25] was –103 kJ/mol H_2, while Spencer et al. [30] reported -225 kJ/mol H_2. With the second value one obtain a value of the heat of adsorption of water of –126 kJ/mol. The first value yields a value of the heat of formation of adsorbed water of about –186 kJ/mol, lower than the enthalpy of formation of water vapor (–241.9 kJ/mol) which is not reasonable. Basset et al. [29] and Fubini et al. [31] reported values of the heat of adsorption of water on alumina of –75 and –105 kJ/mol H_2, respectively.

We consider that a part of the energy delivered by reaction (2) is used in the formation of hydrated protons. The thermal balance of the process :

$$Pt_s{-}O + 3/2\ H_2 \longrightarrow H_3O^+{}_s + Pt_s + e^- \qquad (8)$$

representing the sum of reactions (2) and (3) was performed, using the absolute value of the heat of formation of gas phase oxonium ion, evaluated with data recommended by Bartmess et al. [32], i.e. $\Delta H^0_f(H_3O^+) = 597$ kJ/mol.* It is easily seen that the thermal effect of reaction (8) is highly positive if the non-adsorbed oxonium ion is considered (650 kJ/mol). If the heat of formation of the hydrated proton (406 kJ/mol) is used instead of that of the gas phase oxonium ion, one obtain only about 175 kJ/mol, for the heat of reaction (8). This endothermic effect can be compensated by the negative heat of chemisorption of the oxonium ion on alumina (which should be much larger in absolute value than that of water) and by the energy associated to the electron capture in the conduction band of platinum (reaction 4).[24] The above energy values show that water should be present on the surface of alumina in order that the formation of hydrogen ions (hydrated) could be possible. The strong bonding of the oxonium ions on the surface of alumina pleads for a reorientation mechanism of conduction and not for a diffusion one.

By using the above mentioned data, one obtain for the thermal effect of reaction (3) a very high positive value i.e. > 940 kJ/mol, which cannot be compensated by the heat of adsorption. If the hydrated proton is considered instead of the oxonium ion the heat of reaction (3) would be at least 460 kJ/mol, without consideration of the ion adsorption. Levy and Boudart [33] considered that reaction (3) should be exothermic (without giving any explanation for that). This means that the heat of adsorption of the hydrogen ion should be large

* This value is obtained from $\Delta H^0_f(H^+) = 1533.8$ kJ/mol, $\Delta H^0_{hydr}(H^+) = -1124.5$ kJ/mol, $\Delta H^0_{hydr}(H_3O^+) = -477$ kJ/mol and $\Delta H^0_f(H_2O,l) = -285.8$ kJ/mol

enough, as to turn, together with the capture of the electrons resulting from the reaction, in the conduction band, this thermal effect to negative.

The increase in conductivity due to the formation of chemisorbed oxonium ions and to the presence of water molecules on the surface of alumina is partially compensated by dehydroxylation of alumina's surface. Herrmann [34,35] has thoroughly analyzed the formation of anionic vacancies. This is a result of the dehydroxylation reaction (5), which proceeds in alumina at temperatures exceeding 400°C. Such temperatures can be reached locally, as a consequence of the titration reaction (2).

The anionic vacancies do not remain neutral at high temperatures, reached on some sites, due to the titration reaction. The thermal energy is sufficient to ionize their first electron (reaction 6) [34] The dehydroxylation process (5) is compensated by the regeneration of hydroxyl groups by means of spill-over hydrogen (reaction 7). The sum of bond energies Al–O + O–H largely exceeds the sum of bond energies Al=O + Pt–H, so that this process is exothermic.

Fang and co-workers [36] have determined the thermodynamic parameters for the dissociative adsorption of hydrogen on a Rh/Al_2O_3 catalyst. They found for the reaction :

$$Rh_s + ½\ H_2 \longrightarrow Rh_s\text{–}H \qquad (9)$$

similar to reaction (1), a slightly higher thermal effect of –32.2 kJ/mol H_2.

They reported also the heat of the reaction :

$$Rh_s\text{–}H + OH/Al_2O_3 \longrightarrow Rh + H_2O/Al_2O_3 \qquad (10)$$

which was found to be nearly thermoneutral (-4800 J/mol). We consider that not OH radicals are involved, but OH^- ions, so that reaction (10) would be similar to reaction (3), followed by :

$$H_3O^+_s + OH^-/Al_2O_3 \longrightarrow H_2O_s \qquad (11)$$

The sequence of reactions (3), (4), (11) is therefore likely to be energetically favorable, but less than the sequence (8), (4), (11). This pleads for the involvement of chemisorbed oxygen in the formation of hydrogen ions, responsible for the electrical conductivity of the catalyst.

3. Conclusion

It was demonstrated that the proposed spillover mechanism involving adsorbed water and oxygen molecules, compatible with the behavior of the electrical conductivity of the Pt/Al_2O_3 catalyst is energetically favorable and consequently highly probable. The increase in conductivity, taking place during the hydrogen flow is related to the formation of water molecules and hydroxyl groups, with the implication of hydrogen spillover. Water molecules play the role of additional source and transporter of protons in the conduction process. The

formation of hydrated protons becomes thermodyninamically possible due to the reaction of hydrogen with adsorbed oxygen.

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