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VIII INTERNATIONAL CONFERENCE
ON MECHANISMS OF CATALYTIC REACTIONS

On Quantitative Description of Metal Particles Size Effect in Catalytic Kinetics[1]

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Abstract—Quantitative description for turnover frequency dependence on the metal cluster size for a two-step catalytic cycle was performed based on a thermodynamic approach, which accounts for changes of the chemical potential upon adsorption depending on the metal cluster size. Such analysis revealed a possibility for turnover frequency to exhibit a maximum. A very good correspondence between calculated and experimental data in hydrogenation and decarboxylation reactions over palladium was achieved.

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Structure sensitivity, i.e. dependence of the reaction rate on particle size, is currently under intensive investigation [1– 5]. Such dependences are observed typically in the cluster domain of 2–20 nm. Although size depended rates are often reported in the literature on a qualitative level, quantitative kinetics is very rarely described.

A quantitative thermodynamic approach was considered in [6, 7] with the aim to describe the size depended Langmuir–Hinshelwood mechanism in the two-step catalytic cycle. The general treatment takes into account surface energy excess due to an intrinsic increase in chemical potential with size decrease as discussed by Parmon [8] as well as the changes in chemical potential upon adsorption.

It was previously demonstrated [6] that for catalytic reactions over nanoparticles not only the rates but also reaction orders can differ from those obtained for large nanoclusters. Comparison with experimental data for Fischer–Tropsch synthesis on cobalt supported on carbon nanofibers, as well as for croton aldehyde hydrogenation over gold supported on TiO_2 was utilized for illustrating applicability of the thermodynamic analysis for the explanation of nanoparticle size effect on kinetics.

In the current work we would like to extent the treatment developed in [6, 7] to hydrogenation of ethene on supported Pd catalyst [9] and decarboxylation of fatty acids [10].

[1] The article is published in the original.

KINETIC MODEL

The change in the Gibbs energy (ΔG) upon adsorption is given by equation

$$\Delta G_{ads,\infty} = \Delta G_{ads}(r) + \delta_{int}, \quad (1)$$

where $\Delta G_{ads,\infty}$ is the Gibbs energy of adsorption on infinite clusters, $\Delta G_{ads,\infty}$ is the Gibbs energy of adsorption on nanoclusters and δ_{int} is the intrinsic chemical potential increment due to excessive surface energy. Equation (1) is based on an assumption that the excess of surface energy present in nanoparticles is relaxed upon adsorption. In the simplest treatment the chemical potential increment is inversely proportional to the particle radius r:

$$\delta_{int}(r) = \delta'_{int}/r, \quad (2)$$

where δ'_{int} is the size-independent term in intrinsic chemical potential increment, which value is twice as high as σV_m (here σ is the surface tension and V_m is the partial molar volume of the substance forming the condensed phase). Note that the surface tension of metals is within a range of 1–2 J/m^2, while the molar volume of catalytically active metals is within a range of 6–10 cm^3/mol. For this case lower adsorption rate is observed for larger particles explaining the decrease of turnover frequency (TOF) with particle size, if the rate is determined by adsorption.

Alternatively, when there is stress imposed by adsorbed species, the corresponding change in the Gibbs energy is expressed by

$$\Delta G_{ads,\infty} = \Delta G_{ads}(r) - \delta_{ext}(r), \quad (3)$$

where δ_{ext} is the external (induced) chemical potential increment for nanoclusters with adsorbed species in relation to clusters of infinite size. This assumption

leads to larger adsorption constant and higher adsorption rate for larger particles.

In the two-step mechanism with two kinetically significant steps [11], one of the several surface intermediates is the most abundant, while all the others are present on the surface at much inferior concentration levels:

$$(1)\ Z + A_1 \rightleftharpoons ZI + B_1,$$
$$(2)\ ZI + A_2 \rightleftharpoons Z + B_2,$$
$$A_1 + A_2 \rightleftharpoons B_1 + B_2,$$

where A_1 and A_2 are reactants, B_1 and B_2 are products, Z is the surface site and I is an adsorbed intermediate.

The rate of the reaction v in the case of ideal surfaces under steady-state conditions is given by [11]

$$v = \frac{k_1 P_{A_1} k_2 P_{A_2} - k_{-1} P_{B_1} k_{-2} P_{B_2}}{k_1 P_{A_1} + k_2 P_{A_2} + k_{-1} P_{B_1} + k_{-2} P_{B_2}} = \frac{\omega_1\omega_2 - \omega_{-1}\omega_{-2}}{\omega_1 + \omega_2 + \omega_{-1} + \omega_{-2}}, \quad (4)$$

where P_{A_1}, P_{A_2}, P_{B_1}, P_{B_2} are partial pressures (for gas-phase reactions) or concentrations (for liquid-phase reactions), k_i is kinetic constants, and ω_i is frequencies of steps (i.e., $\omega_1 = k_1 P_{A_1}$, etc.).

If use of the relationship between thermodynamics and kinetics expressed by Brønsted equation $k = gK^\alpha$ [12], where k is the rate constant, K is the equilibrium constant, g and α (Polanyi parameter, typically equal to 0.5) are constants, the rate constants for the steps are given as

$$k_1(r) = k_1 e^{\alpha_1 \Delta\delta'/r}, k_{-1}(r) = k_{-1} e^{(\alpha_1 - 1)\Delta\delta'/r},$$
$$k_2(r) = k_2 e^{(\alpha_2 - 1)\Delta\delta'/r}, k_{-2}(r) = k_{-2} e^{-\alpha_2 \Delta\delta'/r}, \quad (5)$$

where $\Delta\delta' = \delta_{int}(r) - \delta_{ext}(r)$. Note that the values of $\Delta\delta(r)$ could be either positive or negative depending on which type of surface energy excess is dominating, internal or external. Assuming for the sake of clarity that $\alpha_1 = \alpha_2 = \alpha$ and that the overall reaction is irreversible the following rate expression can be obtained:

$$v(r) = \frac{k_1 k_2 P_{A_1} P_{A_2} e^{(2\alpha - 1)\Delta\delta'/r}}{k_1 P_{A_1} e^{\alpha\Delta\delta'/r} + (k_2 P_{A_2} + k_{-1} P_{B_1}) e^{(\alpha - 1)\Delta\delta'/r}} = \frac{\omega_2 e^{(\alpha - 1)\Delta\delta'/r}}{1 + \frac{\omega_2 + \omega_{-1}}{\omega_1} e^{-\Delta\delta'/r}} = \frac{p_1 e^{(\alpha - 1)\Delta\delta'/r}}{1 + p_2 e^{-\Delta\delta'/r}}, \quad (6)$$

where $p_1 = \omega_2$ and $p_2 = (\omega_2 + \omega_{-1})/\omega_1$. Equation (6) can account for a maximum of the rate (TOF) as a function of the particle size.

To find the position of the maximum let us analyze a reciprocal dependence of the rate and search for the minimum of the reciprocal function:

$$\left[\frac{1}{r}\right]' = \left[\frac{1}{p_1} e^{(1-\alpha)\Delta\delta'/r} + \frac{p_2}{p_1} e^{-\alpha\Delta\delta'/r}\right]' = 0. \quad (7)$$

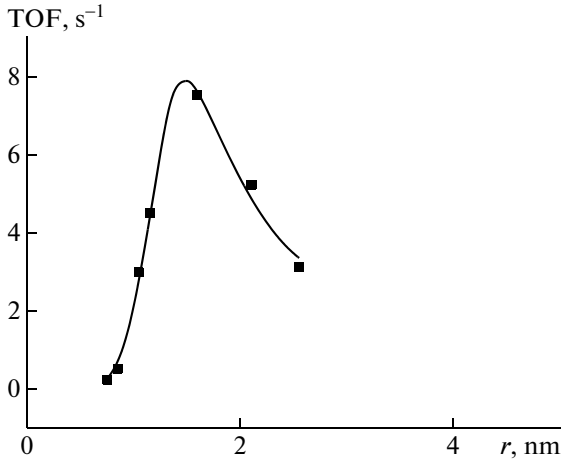

Fig. 1. TOF versus Pd particle radius for Pd/TiO_2 at $H_2 : C_2H_4 = 1 : 1$ in ethene hydrogenation at 293 K and ethene concentration 8.6×10^{-4} mol/l. Points are experimental data, curve—calculation according to Eq. (6).

Straightforward analysis shows that at rate maximum the value of the cluster radius for $\Delta\delta'$ is given by equation

$$(r)_{at\,max} = \frac{\Delta\delta'}{\ln\frac{\alpha p_2}{1 - \alpha}}. \quad (8)$$

If external surface energy excess is dominating, e.g., there are differences in the changes in the chemical potential upon adsorption depending on the cluster size, $\Delta\delta' < 0$ and

$$(r)_{at\,max} = \frac{|\Delta\delta|}{\ln\frac{1 - \alpha}{\alpha p_2}}. \quad (9)$$

COMPARISON WITH EXPERIMENTAL DATA: HYDROGENATION

In [9] hydrogenation of ethene on nanoscale catalyst particles at atmospheric conditions was reported with special emphasis on the influence of the Pd particle size on the reactivity at industrially relevant process conditions varying the support and the hydrogen to ethene ratio. The structural sensitivity of the hydrogenation of ethene is under debate as outlined in [9]. The apparent discrepancies could be attributed to the variation in experimental conditions and materials.

The authors [9] presented TOF values as a function of Pd particle size for Pd/TiO_2 catalyst at $H_2 : C_2H_4$ ratios 1 : 1 and 5 : 1. Hydrogenation of ethene was carried out at atmospheric pressure at reaction temperature of 293 K and ethene concentration of 8.6×10^{-4} mol/l.

Experimental data from [9] are redrawn in Fig. 1 demonstrating a very clear maximum at the stoichiometric ratio between hydrogen and ethene. Several explanations for the maximum were advanced in [9]

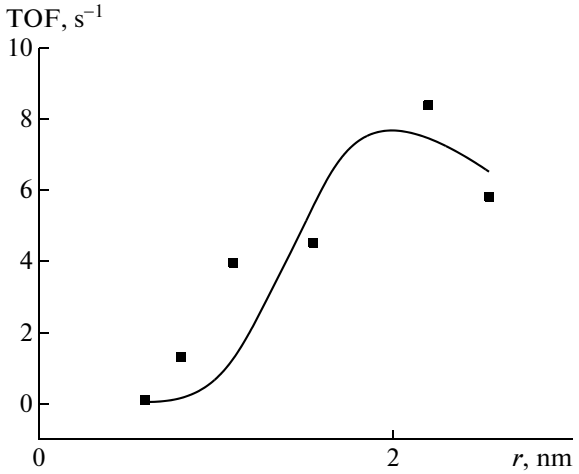

Fig. 2. TOF versus Pd particle radius for Pd/TiO_2 at $H_2 : C_2H_4 = 5 : 1$ in ethene hydrogenation at 293 K and ethene concentration 8.6×10^{-4} mol/l. Points are experimental data, curve—calculations according to Eq. (6) with parameters $\Delta\delta'$ and α as in Fig. 1.

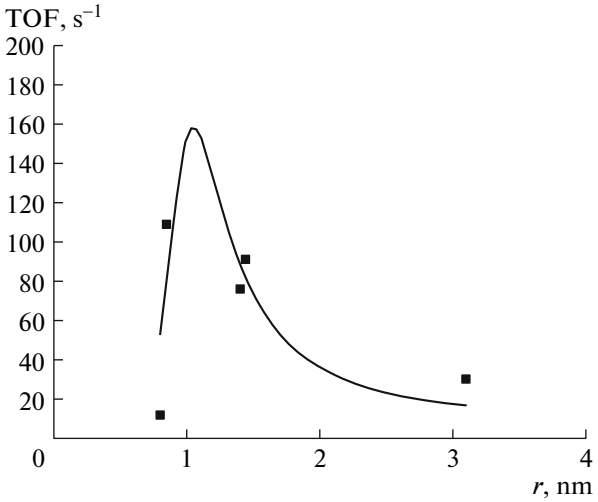

Fig. 3. TOF versus Pd particle radius for Pd/C in decarboxylation of palmitic and stearic acids mixture [10]. Points are experimental data, curve—calculations according to Eq. (6) with parameters $\Delta\delta'$ and α as in Fig. 1.

taking into account either a requirement of a unique configuration of several metal sites or involvement of subsurface hydrogen. In the present contribution chemical potential changes depending on the size of the metal cluster serve merely as a thermodynamic descriptor of these more mechanistic explanations.

The calculations done using Origin 7.5 software demonstrate a good correspondence between experiments data [9] and calculations according to Eq. (6). The value of Polanyi parameter is close to 0.5 often observed in heterogeneous catalytic reactions [11], while the value of $\Delta\delta'$ is also in very good correspondence with the surface tension of palladium (1.7 J/m^2 [13]) and its molar volume (8.56 cm^3/mol).

Theoretical analysis in accordance with Eq. (8) clearly shows that the position of the maximum in turnover frequency as a function of cluster size depends on the frequencies of steps (e.g. on the ratio of $\frac{\omega_2 + \omega_{-1}}{\omega_1}$), and thus on the partial pressures of the reactants. According to experimental data [9] the maximum activity for Pd/TiO_2 shifts from a Pd particle size of 3 nm (i.e. radius 1.5 nm) for stoichiometric conditions to larger particles sizes of about 4.2 nm (i.e., radius 2.1. nm) for excess of H_2.

Calculated values for TOF in ethene hydrogenation on Pd/TiO_2 as a function of the Pd particle radius in H_2 excess ($H_2 : C_2H_4 = 5 : 1$) are given along with experimental data [9] in Fig. 2. Since at these conditions there is only one data point after maximum and moreover $\Delta\delta'$ and α should not depend on the partial pressures, the same values of these parameters as for the stoichiometric conditions were used in numerical data fitting. Figure 2 demonstrates applicability of Eq. (6) for description of TOF experimental dependences on palladium cluster size (radius).

COMPARISON WITH EXPERIMENTAL DATA: DECARBOXYLATION

In the catalytic deoxygenation of fatty acids the effect of metal particle size on activity has been previously investigated by the present authors in [10], where the main aim was to systematical study of metal particle size and dispersion effects on catalytic deoxygenation of a mixture of palmitic and stearic acids. Four different 1 wt % Pd/C catalysts supported on a synthetic mesoporous carbon Sibunit were prepared by deposition of palladium hydroxide yielded by hydrolysis of palladium chloride at pH 8–10. The different metal dispersions were achieved by changing the pH of the palladium hydroxide solution. The metal cluster size was determined using high resolution TEM. More details of the experimental set-up, catalytic experiments and catalyst characterization are given in [10].

The catalysts were tested in palmitic and stearic acid deoxygenation at 300°C under 17.5 bar pressure of H_2–Ar mixture (Fig. 3). As can be seen from Fig. 3 a sharp maximum was obtained for the catalyst with dispersion of 65%. Since no quantitative analysis of the data was performed in [10] it was interesting to evaluate applicability of the thermodynamic approach, proposed by Parmon [8] and further developed in [6, 7] to describe structure sensitivity in decarboxylation. The results of calculations are presented in Fig. 3 as well fixing once again $\Delta\delta'$ and α to the same values as determined for palladium catalysts in ethene hydrogenation. This procedure was utilized since otherwise due to an insufficient number of experimental points the system is overparametrized. As clearly visi-

ble from Fig. 3 the thermodynamic approach advocated in the present work is capable to explain a very sharp dependence of the reaction rate on the radius of palladium particles.

Thus, quantitative description for turnover frequency dependence on the metal cluster size resulting in optimum metal dispersions in hydrogenation and decarboxylation reactions over palladium was performed. A thermodynamic approach, based on the differences in the changes of chemical potential upon adsorption depending on the metal cluster size, was utilized, showing a very good correspondence between experimental and calculated data.

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REFERENCES

1. Schlögl, R. and Abd Hamid, S.B., *Angew. Chem., Int. Ed. Engl.*, 2004, vol. 43, p. 1628.
2. Narayanan, R. and El-Sayed, M.A., *Top. Catal.*, 2008, vol. 47, p. 15.
3. Henry, C.R., *Appl. Surf. Sci.*, 2000, vol. 164, p. 252.
4. Klasovsky, F and Claus, P, in *Metal Nanoclusters in Catalysis and Materials Science: The Issue of Size Control,* Corain, B., Schmid, G., and Toshima, N., Eds., Amsterdam: Elsevier, 2008, p. 167.
5. Van Santen, R.A., *Acc. Chem. Res.*, 2009, vol. 42, p. 57.
6. Murzin, D.Yu., *J. Mol. Catal. A: Chem.*, 2010, vol. 315, p. 226.
7. Murzin, D.Yu., *Chem. Eng. Sci.*, 2009, vol. 64, p. 1046.
8. Parmon, V.N., *Dokl. Phys. Chem.*, 2007, vol. 413, p. 42.
9. Binder, A., Seipenbusch, M., Muhler, M., and Kasper, G., *J. Catal.*, 2009, vol. 268, p. 150.
10. Simakova, I., Simakova, O., Mäki-Arvela, P., Simakov, A., Estrada, M., and Murzin, D.Yu., *Appl. Catal., A*, 2009, vol. 355, p. 100.
11. Temkin, M.I., *Adv. Catal.*, 1979, vol. 28, p. 173.
12. Brønsted, J.N., *Chem. Rev.*, 1928, vol. 5, p. 231.
13. Samsonov, C.V. and Krasnov, A.N., *Mater. Sci.*, 1967, vol. 2, p. 348.