Incorporation of size effect in kinetic modeling of catalytic reactions on nanoclusters

Dmitry Yu. Murzin*

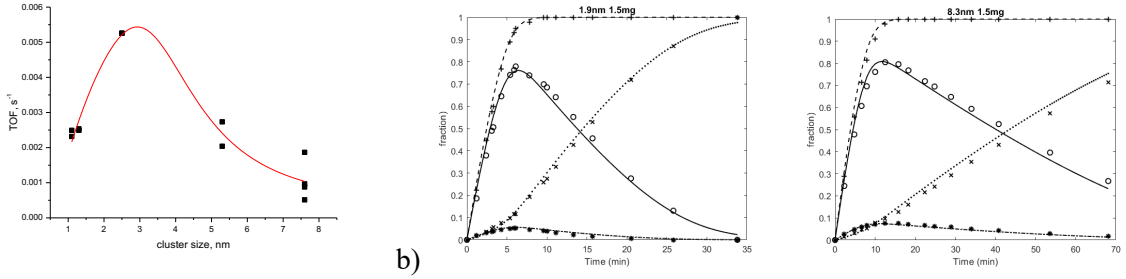
Åbo Akademi University, Turku/Åbo, 20500, Finland, : dmurzin@abo.fi

In the lecture mechanistic concepts leading to kinetic expressions, which explicitly incorporate cluster size, will be discussed. Classical kinetic approach to heterogeneous catalytic reactions often neglects the dimensions of clusters as well as the reacting molecules. This is a very crude approximation in the case of organic catalytic reactions over nanometer-sized transition metal clusters.

The size of the metal clusters can be directly incorporated in the rate equations using either the continuous or discrete distribution of active sites of different reactivity. For example, in the case of a two-step sequence an expression for turnover frequency is

$$v(d) = \frac{p_1 e^{(1-\alpha)\chi / d_{cluster}}}{1 + p_2 e^{\chi / d_{cluster}}} \qquad (1)$$

where p_1 and p_2 are lumped combinations of constants and partial pressures of reactants, α is Polanyi parameter and χ reflects differences in the Gibbs energy of adsorption of terraces and edges. Illustrations are presented in Figure 1 showing applicability of this concept to explain experimental data not only for TOF (Figure 1a, hydrogenation of sugars on supported Ru catalysts) but also for concentration dependencies in complex reactions (Figure 1b, hydrogenation of phenylacetylene on Pd).



a) b)

Figure 1. Dependence of a) TOF on the cluster radius in hydrogenation of arabinose, b) concentration vs time in hydrogenation of diphenylacetylene on Pd catalysts with different dispersion.

Other examples will be discussed, comprising different kinetics models for oxidation, oxidative dehydrogenation, dehydrogenation and hydrogenation reactions [1-12].

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