Full paper/Mémoire

Structure sensitivity in heterogeneous catalysis with noncompetitive adsorption of reactants: Selective oxidation of lignan hydroxymatairesinol to oxomatairesinol over gold catalysts☆

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ABSTRACT

Structure sensitivity in heterogeneous catalytic oxidative dehydrogenation of lignan hydroxymatairesinol (HMR) extracted from Norway spruce knots was investigated over a series of alumina-supported gold catalysts. A mathematical model was developed based on the concept of noncompetitive adsorption of reactants. The model, being consistent with kinetic regularities, such as reaction orders in reactants, explains well the dependence of catalytic activity on the gold cluster size.

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1. Introduction

A significant amount of experimental data was generated along the years, demonstrating that catalytic activity in transition metal catalysis shows a strong dependence on the cluster size in the nanometer range (e.g., the domain of the cluster sizes between 2 and 20 nm) [1–10].

The catalytic activity as such calculated per total amount of catalytic phase should decline with the increase of cluster size. Since the ratio between surface and volume increases with a decrease in size of nanoclusters and the fraction of surface atoms is increasing, fewer exposed sites are available [1].

Turnover frequency (TOF), defined as the activity per unit of exposed surface, could behave differently with alterations of the cluster size (coined structure sensitivity) [2]. For various systems, it has been shown that TOF not only increases or decreases with the cluster size, but can also pass through a maximum. Several explanations for this phenomenon were put forward in the literature, involving changes in the electronic state, alteration of resistance to deactivation as well as different activities of edges, corners, and terrace atoms. The latter one is based on the fact that the relative ratio between these atoms depends on the cluster size [1]. Therefore the difference in clusters reactivity would be anticipated.

Despite a large number of studies, surprisingly little modeling was done, which explains structure sensitivity from a kinetic viewpoint, incorporating the cluster size in the rate expression.

One of the simplest approaches implementing the cluster size dependence in reaction kinetics would be to view reaction constants as size independent. Therefore, each type of sites (terraces and edges) contributes to the overall rate according to:

$$v(d) = r_{terraces} f_{terraces} + r_{edges} f_{edges} \qquad (1)$$

where $f_{terraces}$ and f_{edges} are fractions of the cluster terraces and edges respectively; $r_{terraces}$ and r_{edges} are the reaction rates over the corresponding surface sites.

This approach was reported before to calculate the turnover frequency [5,11]. In a similar fashion, differences in the reactivity of edges, corners and terraces were considered theoretically for a two-step sequence using as a model *fcc* cubic and cubo-octahedron clusters [12]. The theoretical concept led to kinetic equations with the rate constants dependence on the cluster size or (?) directly incorporated in the model.

The alternative way is to utilize the thermodynamic approach [13–15] considering variations of the Gibbs energy $\Delta G_r = -RT\ln K_r = f'(r)$, where variations of the chemical potential of nanoclusters compared to bulk metal are dependent on the cluster size and the presence of adsorbates. A similar description can be obtained based on the explicit difference between the activation energy values for reactions catalyzed by edges and terraces [16,17], leading to different activities of edges and terraces in terms of reaction rates and selectivity.

For the latter approach, which is more chemically sound than the one based on chemical potential variations, mainly a two-step sequence and its special case (Eley–Rideal mechanism) were considered [16,17]. The two-step mechanism described in [18] involves the transformation of one of the most abundant surface intermediates, where two kinetically significant steps are:

1. $Z + A_1 \leftrightarrow ZI + B_1$
2. $\underline{ZI + A_2 \leftrightarrow Z + B_2}$ (2)
   $A_1 + A_2 \leftrightarrow B_1 + B_2$

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

The aim of the current work is to extend this treatment on the cluster size dependence of the reaction rate for a heterogeneous catalytic reaction with noncompetitive adsorption of reactants.

As an example, selective oxidation of lignan hydroxymatairesinol (HMR) via oxidative dehydrogenation over heterogeneous gold catalysts resulting in the formation of oxomatairesinol (oxoMAT) was selected. Valuable lignans presented in the waste from pulping industry demonstrated anticarcinogenic and antioxidative properties [19]. The substrate HMR is found in large amounts in the knots of Norway spruce (*Picea abies*), while the lignan oxoMAT cannot be extracted in considerable amounts from woody biomass. The selective oxidation of HMR to oxoMAT is in fact selective oxidation of a secondary alcohol into a corresponding ketone. This reaction was previously investigated by our research group using gold catalysts, which demonstrated the 100% selectivity in favor of the desired product [20–24]. The reaction kinetics (Scheme 1) is somewhat complicated by the existence of HMR as a mixture of two diastereomers: (7R,8R,8′R)-(–)-7-allo-hydroxymatairesinol (HMR 1) and (7S,8R,8′R)-(–)-7-allo-hydroxymatairesinol (HMR 2). Recent investigation of the reaction kinetics demonstrated that isomer HMR 2 is much more reactive compared to HMR 1 [24].

Kinetic modeling [24] demonstrated good correspondence between experiments and theoretical predictions. The mathematical treatment included also deactivation, which for the sake of simplicity is omitted in the present work, since only initial activity would be considered.
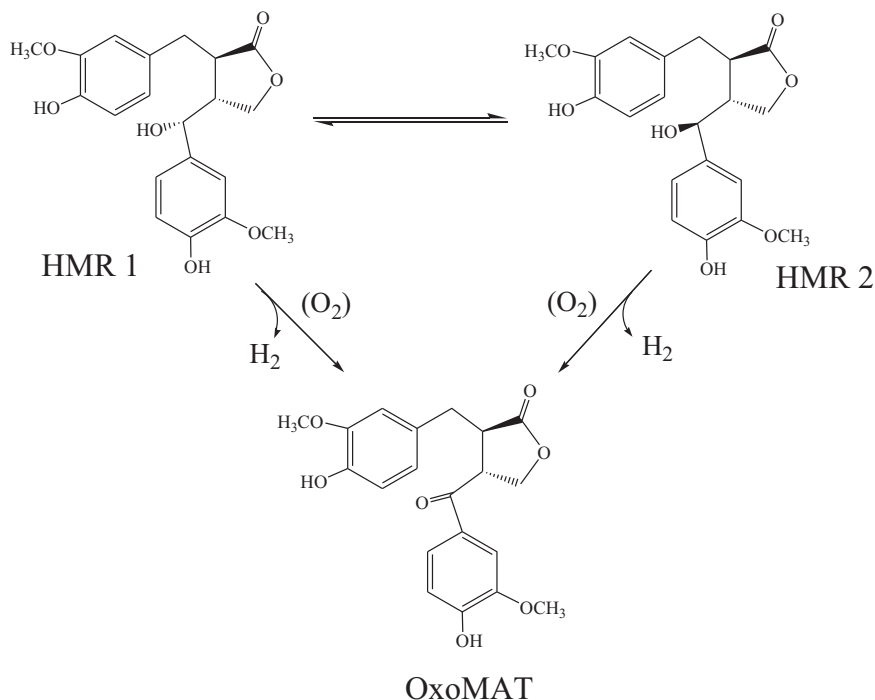
Scheme 1. Reaction pathway of lignan hydroxymatairesinol selective oxidation.