Catal Lett (2012) 142:1279–1285
DOI 10.1007/s10562-012-0896-z

ORIGINAL ARTICLE

On Cluster Size Dependent Activity and Selectivity in Heterogeneous Catalysis

Dmitry Yu. Murzin

Received: 31 May 2012 / Accepted: 17 August 2012 / Published online: 11 September 2012

Abstract The impact of nanoparticle size effects in heterogeneous catalytic kinetics over supported metal catalysts is discussed for clusters having several distinct active sites. Theoretical analysis demonstrates that considerations of different activity for such sites not only allow a description of a smooth increase or decrease of turnover frequency as a function of cluster size, but also can in principle account for maxima in turnover frequency. Several examples are presented addressing advantages and shortcomings of the model (in some cases giving physically unreasonable values of parameters during numerical data fitting). Comparison with a rival model with a continuous variation of activity is presented.

Keywords Cluster size · Structure sensitivity · Kinetic modelling · Selectivity

1 Introduction

Kinetic analysis of catalytic activity in transition metal catalysis as a function of cluster size in the nanometer range, e.g. in the domain between 2 and 20 nm is currently of substantial interest in academic and industrial research.

It is very well known that the ratio between the surface and volume increases with a decrease in size of nanoclusters, and the fraction of surface atoms is increasing [1]. It is thus logical to expect that catalytic activity calculated per total amount of catalytic phase usually declines with the increase of cluster size as fewer exposed sites are available for catalysis. On the other hand changes in the cluster size result in modifications of the relative ratio between edges, corners and terrace atoms. This is one of the explanations (in addition to changes in the electronic state, alteration of resistance to deactivation, etc.) of turnover frequency (TOF), defined as the activity per unit of exposed surface, dependence in some cases on the cluster size (so-called structure sensitivity) [2–5]. For various systems it has been shown, that TOF cannot only increase or decrease with cluster size, but also pass through a maxima.

Quantitative analysis of activity and selectivity for a number of simple reaction mechanisms based on a thermodynamic approach was reported recently [6–9]. Comparison of experimental data with theory presented in a review [9] and in more detail in original publications [10–12] demonstrated applicability of this approach, which is able to describe even maxima in TOF as a function of cluster size.

In [13] the thermodynamic (and thus rather formal) approach from [6–9], based on variations of the chemical potential of nanoclusters in comparison with bulk metal depending on the cluster size and presence of adsorbates, was reassessed. The theoretical analysis in [13] took into account differences in the activation energy between edges and terraces, leading to different activities of edges and terraces in terms of reaction rates and selectivity.

In [13] only terraces and edges as sites with different reactivity were considered and Gibbs energy of adsorption was expressed in the following way

$$\begin{aligned}\Delta G_{ads} &= \Delta G_{ads,terraces} f_{terraces} + \Delta G_{ads,edges} f_{edges}\\ &= \Delta G_{ads,terraces}(1 - f_{edges}) + \Delta G_{ads,edges} f_{edges}\\ &= \Delta G_{ads,terraces} + f_{edges}(\Delta G_{ads,edges} - \Delta G_{ads,terraces})\end{aligned} \tag{1}$$

where $\Delta G_{ads,terraces}$ and $\Delta G_{ads,edges}$ correspond respectively to adsorption on terraces and edges, while $f_{terraces}$, f_{edges}

D. Yu. Murzin (✉)
Åbo Akademi University, Turku, Finland
e-mail: dmurzin@abo.fi

denote fractions of these surface sites, which sum is obviously equal to unity.

Cubo-octahedral shape of nanoparticles was discussed in [13] and the fractions of edges to the total number of atoms on the surface, which includes besides edges also square and triangular faces were calculated following [14] as

$$f_{edges} = \frac{N_{edges}}{N_{edges} + N_{square\_faces} + N_{triangular\_faces}} \tag{2}$$

After implementing a relationship between equilibrium constants and Gibbs energy of adsorption

$$K_{ads} = e^{-\frac{\Delta G_{ads,terraces} + f_{edges}(\Delta G_{ads,edges} - \Delta G_{ads,terraces})}{RT}} \tag{3}$$

and linear free energy (or Brønsted-Evans-Polanyi) relationship between reaction constants k and equilibrium constants K in a series of analogous elementary reactions $k = g K^{\alpha}$ where g and α (Polanyi parameter, $0 < \alpha < 1$) are constants, the rate constant of adsorption is expressed.

$$k_{ads} = k'_{ads} e^{\frac{-\alpha f_{edges}(\Delta G_{ads,edges} - \Delta G_{ads,terraces})}{RT}} \tag{4}$$

In [13] it was shown, that the fraction of edges can be described in a simplified way as $f_{edges} \approx 1/d_{cluster}$ when d is given in nm. Equation (4) can be implemented in various kinetic equations giving a possibility to describe reaction rates (or turnover frequency) dependencies on cluster size.

For example in case of the two-step mechanism with two kinetically significant steps [15, 16], and one most abundant surface intermediates

$$\begin{aligned} &1.\ Z + A_1 \leftrightarrow ZI + B_1 \\ &2.\ ZI + A_2 \leftrightarrow Z + B_2 \end{aligned} \tag{5}$$

$$A_1 + A_2 \leftrightarrow B_1 + B_2$$

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 rate expression is given by

$$v(d) = \frac{(k_1 k_2 P_{A_1} P_{A_2} - k_{-1} k_{-2} P_{B_1} P_{B_2}) e^{(1-2\alpha)\chi/d_{cluster}}}{(k_1 P_{A_1} + k_{-2} P_{B_2}) e^{-\alpha\chi/d_{cluster}} + (k_2 P_{A_2} + k_{-1} P_{B_1}) e^{(1-\alpha)\chi/d_{cluster}}} \tag{6}$$

For an irreversible reaction ($k_{-2} \approx 0$) Eq. (6) can be rearranged into

$$v(d) = \frac{p_1 e^{(1-\alpha)\chi/d_{cluster}}}{1 + p_2 e^{\chi/d_{cluster}}} \tag{7}$$

where p_1 and p_2 are lumped combinations of constants and partial pressures of reactants.

An alternative way of implementing the cluster size dependence in reaction kinetics is to view reaction constants as size independent. Then each type of sites (terraces and edges) contributes to the overall rate according to

$$v(d) = r_{terraces} f_{terraces} + r_{edges} f_{edges} \tag{8}$$

In the current contribution we would like to consider this case and analyze cluster size dependent turnover frequency and selectivity within the framework of this approach.

2 Geometrical Considerations

A simplified cubic geometrical model (Fig. 1a) is selected to represent metal clusters, which is still sufficient for analysis of cluster size kinetics.

In Fig. 1 only corners, edge atoms and atoms in terraces are considered. Number of corners, edges and terraces corresponding to C_3^9, C_5^7, $C_8^{4.5}$ in the notation used in [1] is given respectively for $m > 3$ by eight; $12(m - 2)$ and $[6(m - 1)^2 + 6(m - 2)^2]$, where m is the number of atoms in one edge. The subscript j in the symbol C_j denotes the nearest neighbors, while the upper indices were introduced in [1] to differentiate between atoms whose nearest neighbors are equal in numbers but different in arrangement.

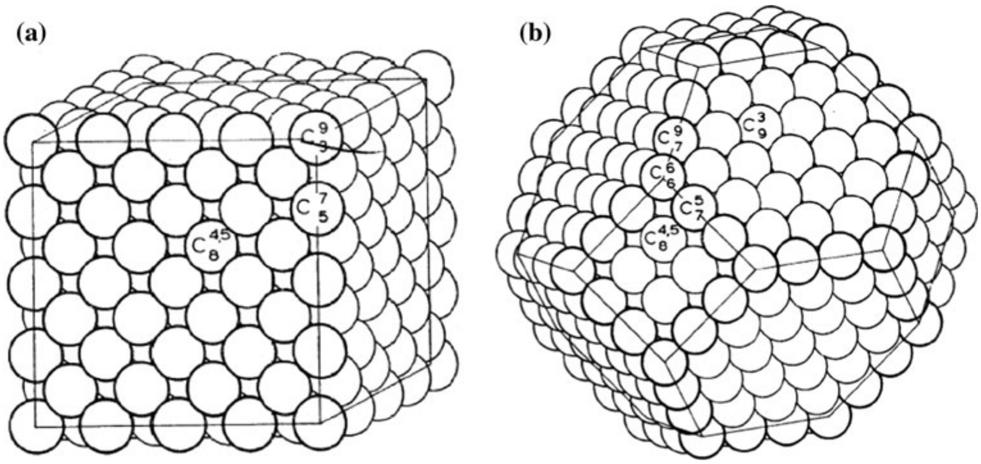

Fig. 1 Fcc **a** cube (m = 5), **b** cubo-octahedron (m = 4). Reprinted from [1] with permission from Elsevier

The total number of surface sites [1] can be expressed by $12m^2 - 24m + 14$, thus the equation for the turnover frequency is

$$\begin{aligned} v(d) &= r_{corners} f_{corners} + r_{edges} f_{edges} + r_{terraces} f_{terraces} \\ &= r_{corners} \frac{8}{12m^2 - 24m + 14} + r_{edges} \frac{12(m-2)}{12m^2 - 24m + 14} + r_{terraces} \frac{6(m-1)^2 + 6(m-2)^2}{12m^2 - 24m + 14} \\ &= \frac{12m^2 r_{terraces} + m(12r_{edges} - 36r_{terraces}) + 8r_{corners} - 24r_{edges} + 30r_{terraces}}{12m^2 - 24m + 14} \end{aligned} \tag{9}$$

For cubic geometry we will consider the size of clusters as a face diagonal, which could be easily related to the number of atoms in one edge and the atom diameter through the following relationship

$$d_{cluster} = m2d_{at} \tag{10}$$

leading to the dependence of TOF on the cluster size.

$$v(d) = \frac{3(\frac{d_{cluster}}{d_{at}})^2 r_{terraces} + \frac{d_{cluster}}{d_{at}}(6r_{edges} - 18r_{terraces}) + 8r_{corners} - 24r_{edges} + 30r_{terraces}}{3(\frac{d_{cluster}}{d_{at}})^2 - 12\frac{d_{cluster}}{d_{at}} + 14} \tag{11}$$

It should be mentioned here that Eq. (11) is valid independent on reaction kinetics types, contrary to the approach, developed in [13].

An approach somewhat similar to Eq. (11) was utilized in [4, 5] when TOF dependence on the cluster size was presented as a sum over contributions of terraces (*t*), steps (*s*) and corners (*c*) with corresponding geometrical factors (*g*) in an approximate way: TOF $\approx k_t + k_s g_s/d + k_c g_c/d^2$. Note that this approach can only account for TOF decrease with cluster size.

On the contrary Eq. (11) can explain not only this case and increase of TOF with cluster size, but in fact it could be demonstrated that Eq. (11) has a maximum in TOF, sometimes observed in the literature.

Analysis of boundary cases could be done for Eq. (11), assuming for example that the rate on terraces is much smaller than on edges or corners. In addition if edges and corners display the same activity one gets

$$v(d) = \frac{r_{edges}(6\frac{d_{cluster}}{d_{at}} - 16)}{3(\frac{d_{cluster}}{d_{at}})^2 - 12\frac{d_{cluster}}{d_{at}} + 14} \tag{12}$$

3 Analysis of TOF on Cluster Size

Numerical analysis of Eq. (12) for a case of metal–metal distance equal to 0.28 nm (platinum) shows, that after an initial obvious spike (no reaction when d = 0), the reaction rate (or the ratio between $v_{(d)}$ and r_{edges} as in Fig. 2) is declining in line with a large body of experimental data demonstrating that for many catalytic reactions decline in TOF follows a reciprocal value of the cluster size.

Another boundary case is the situation when the rate on terraces is much larger than on edges or corners. This case gives a following rate expression

$$v(d) = \frac{(3(\frac{d_{cluster}}{d_{at}})^2 - 18\frac{d_{cluster}}{d_{at}} + 30) r_{terraces}}{3(\frac{d_{cluster}}{d_{at}})^2 - 12\frac{d_{cluster}}{d_{at}} + 14} \tag{13}$$

Numerical analysis for Eq. (13) clearly demonstrates (Fig. 3) that with a cluster size increase TOF will increase also in line with expectations.

It was interesting to compare the experimental data on allylic isomerization of allylbenzene to *trans*-*β*-methylstyrene [17] on gold with the theoretical expression developed in the current work. To this end Eq. (11) was modified and activities of terraces and corners were related to activities of edges

$$v(d) = \frac{3(\frac{d_{cluster}}{d_{at}})^2 r_{edges} a_{t/e} + \frac{d_{cluster}}{d_{at}}(6r_{edges} - 18r_{edges} a_{t/e}) + 8r_{edges} a_{c/e} - 24r_{edges} + 30r_{edges} a_{t/e}}{3(\frac{d_{cluster}}{d_{at}})^2 - 12\frac{d_{cluster}}{d_{at}} + 14} \tag{14}$$

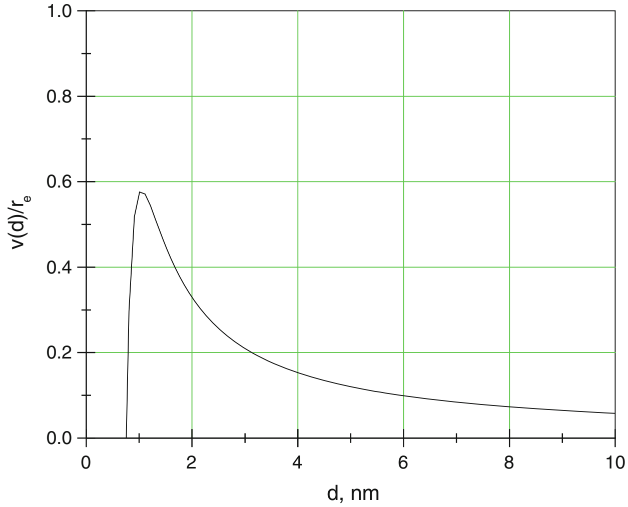

Fig. 2 Normalized TOF as a function of cluster size according to Eq. (12)

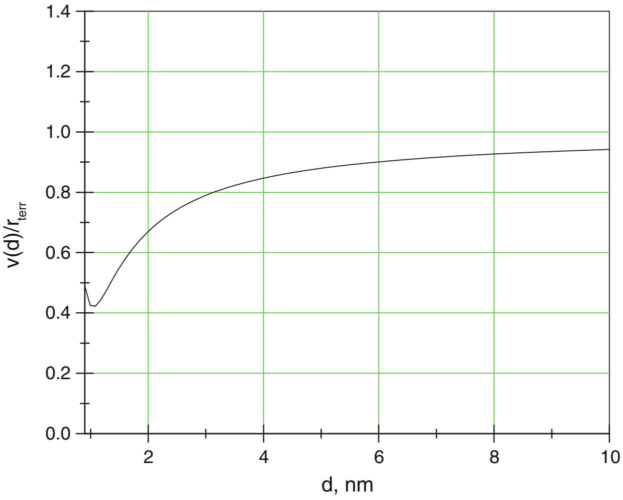

Fig. 3 Normalized TOF as a function of cluster size according to Eq. (13)

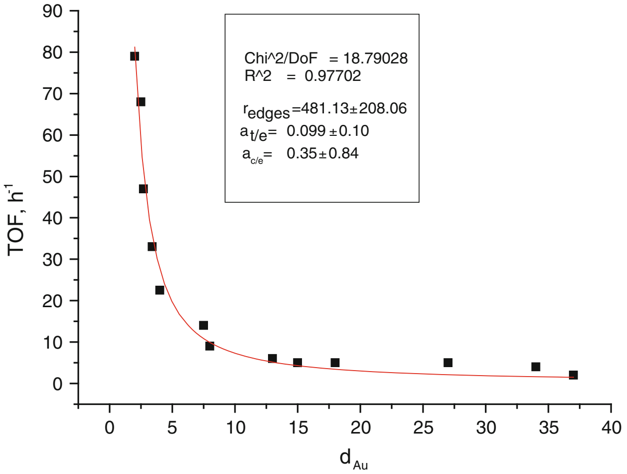

Fig. 4 Measured [17] and calculated (Eq. 14) TOF in allylic isomerization of allylbenzene over gold catalysts

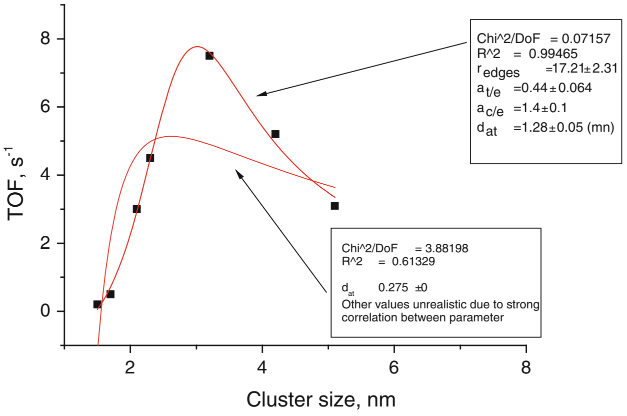

Fig. 5 Measured [18] and calculated (Eq. 14) TOF in hydrogenation of ethyne over palladium catalysts

with

$$a_{t/e} = \frac{r_{terraces}}{r_{edges}}, \quad a_{c/e} = \frac{r_{corners}}{r_{edges}} \tag{15}$$

Equation (14) has then three parameters, which could be determined by numerical data fitting (r_{edges}, $a_{c/e}$, $a_{t/e}$), while the gold metal–metal distance could be fixed to 0.288 nm. Comparison between calculations and experimental data is given in Fig. 4.

The data fitting was a bit challenging due to over-parametrization, thus the errors are rather big especially for $a_{c/e}$. From Fig. 4 the value of this parameter is 0.35 ± 0.84, however, a similar description of the data can be obtained (with different values of other parameters), when $a_{c/e}$ is assumed even equal to unity (not shown). According to the calculated results activities of gold atoms in edges are more than one order of magnitude higher than on terraces. Within the framework of transition state theory the differences in the rate constants could be associated with either pre-exponential factor or activation energy on edges and terraces. Detailed microkinetic analysis could be thus incorporated in Eq. (14) for modeling of cluster size dependence.

It should be noted here that although the general form of Eq. (11) allows even modeling of maxima in TOF as a function of cluster size parameter estimation could be quite challenging. As an example in Fig. 5 calculations are presented for hydrogenation of ethyne over supported palladium on titania catalyst at stoichiometric ratio of reactants [18].

Although a good description was obtained (Fig. 5) in order to have reasonable values of the rate parameters (e.g. positive values of $a_{c/e}$, $a_{t/e}$) the value of metal atom diameter was let floating. As could be seen from Fig. 5 although the fit was improved and the values of rate parameters are positive and reasonable, d_{at} is unrealistically large.

It might be argued that the cubic cluster model is too simplistic and does not represent palladium nanoparticles, which have cubo-octahedral shape. For such geometry (Fig. 1b) number of corners, edges and terraces corresponding to C_6^6, $C_7^5 + C_7^9$, $C_9^3 + C_8^{4,5}$ in the notation used in [1] is given respectively for $m > 4$ by 24; $36(m - 2)$ and $[8(3m^2 - 9m + 7)^2 + 6(m - 2)^2]$. Taking into account the total number of surface sites [1] for cubo-octahedron, which is $30m^2 - 60m + 32$, and validity of the relationship (10), the dependence of TOF on the cluster size for cubo-octahedron is

$$v(d) = \frac{7.5(\frac{d_{cluster}}{d_{at}})^2 r_{edges} a_{t/e} + \frac{d_{cluster}}{d_{at}}(18 r_{edges} - 42 r_{edges} a_{t/e}) + 24 r_{edges} a_{c/e} - 36 r_{edges} + 80 r_{edges} a_{t/e}}{7.5(\frac{d_{cluster}}{d_{at}})^2 - 30\frac{d_{cluster}}{d_{at}} + 32} \tag{16}$$

Figure 6 showing calculations for hydrogenation of ethyne [18] demonstrates an overall good description of the data still with an unrealistically large value of d_{at}.

Note that in Eq. (11) or Eq. (16) no dependence of the rate constant on the cluster size was assumed, thus it was supposed that adsorption/desorption and reaction rates on terraces, edges and corners are always the same independent on the d_{cl}. This might be a too unrealistic view, and such type of dependences might be needed to incorporate in the analysis of cluster size dependent kinetics as was done for example in [13].

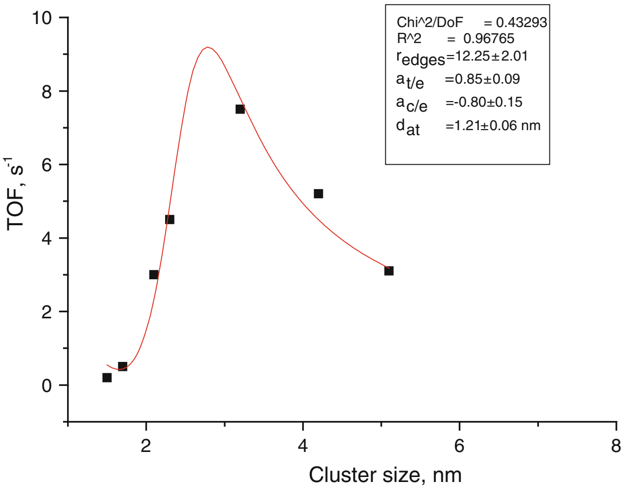

Fig. 6 Measured [18] and calculated (Eq. 16) TOF in hydrogenation of ethyne over palladium catalysts

For example multi-centered adsorption of large organic molecules, requiring an ensemble of sites [8, 19], could be a reason that even for terraces reactivity can depend on the cluster size. A particular case of phenylacetylene hydrogenation was discussed in [20], where it was demonstrated that TOF increases almost three fold with an increase in Rh particle size from 3.5 to 11.4 nm. One of the explanations put forward in [20] was related with a requirement of planar adsorption of benzene ring requiring larger terrace surfaces. Earlier similar reasoning was utilized in [21] for explanation of structure sensitivity and enantioselectivity dependence on the cluster size in case of hydrogenation of diketones, containing a phenyl group. Contrary to phenyacetylene, adsorption of 1-octene, also investigated in [20], requires a small ensemble, thus it is not surprising that hydrogenation of this olefin is a structure insensitive reaction.

It can be thus preliminary concluded that since even on terraces adsorption modes of mainly complex organic molecules can depend on the terrace size, leading also to changes in the binding energy, and subsequently reactivity in catalytic reactions, an approach developed in [13], based on the variation of reactivity with the cluster size, might be more fruitful for modeling of cluster size dependent reaction rates.

4 Selectivity Dependence on the Particle Size

Let us consider now dependence of selectivity on the particle size within the framework of the geometrical concept for a cube discussed above. This concept, if applicable, allows to separate reactions on edges, terraces and corners each having distinct values of rates towards a particular reactant. Let us consider as an example a parallel reaction mechanism A → B, A → C where the rates towards the reactants are given by

$$r_B(d) = r_{corners,B} f_{corners} + r_{edges,B} f_{edges} + r_{terraces,B} f_{terraces} \tag{17}$$

$$r_C(d) = r_{corners,C} f_{corners} + r_{edges,C} f_{edges} + r_{terraces,C} f_{terraces} \tag{18}$$

From (17) and (18) one gets

$$\frac{r_B}{r_C}=\frac{8r_{corners,B}+12(m-2)r_{edges,B}+(6(m-1)^2+6(m-2)^2)r_{terraces,B}}{8r_{corners,C}+12(m-2)r_{edges,C}+(6(m-1)^2+6(m-2)^2)r_{terraces,C}} \tag{19}$$

and finally taking into account the relationship between the rates on terraces, corners and the rates on edges

$$\frac{r_B}{r_C}=\frac{r_{edges,B}(3(\frac{d_{cluster}}{d_{at}})^2a_{t/e,B}+\frac{d_{cluster}}{d_{at}}(6-18a_{t/e,B})+8a_{c/e,B}-24+30a_{t/e,B})}{r_{edges,C}(3(\frac{d_{cluster}}{d_{at}})^2a_{t/e,C}+\frac{d_{cluster}}{d_{at}}(6-18a_{t/e,C})+8a_{c/e,C}-24+30a_{t/e,C})} \tag{20}$$

Let us analyze Eq. (20) using allylic isomerization of allylbenzene over gold catalysts [17]. As mentioned above when the size of gold nanoparticles increased from 2 to 40 nm, TOF decreased from 110 to 0.5 h^{-1}, with particles larger than 40 nm being practically inactive.

The *cis/trans* ratio was influenced in a less prominent way, e.g. it was almost constant in the region 13–34 nm being equal to 0.21, although increasing to 0.45 at smaller particles sizes.

For quantitative analysis of data given in [17] and showing very low TOF on terraces, it can be assumed that $a_{t/e,C}\approx 0$ and $a_{t/e,B}\approx 0$.

Instead of (20) one then arrives at

$$\frac{r_B}{r_C}=\frac{r_{edges,B}(6\frac{d_{cluster}}{d_{at}}+8a_{c/e,B}-24)}{r_{edges,C}(6\frac{d_{cluster}}{d_{at}}+8a_{c/e,C}-24)} \tag{21}$$

At sufficiently large cluster size the ratio between the rates is given by just

$$\frac{r_B}{r_C}=\frac{r_{edges,B}}{r_{edges,C}} \tag{22}$$

This expression should be corrected at smaller sizes (when $d_{cluster}/d_{at}$ is of the same order of magnitude as other terms, especially $a_{c/e,B}$ and $a_{c/e,C}$) giving deviations in selectivity at smaller sizes.

Equation (21) was compared with experimental data from [17] showing rather good correspondence between the theory and experiments (Fig. 7).

This analysis is in line with commented in [9] literature, showing that for many hydrogenations or oxidations of various organic molecules containing similar functional groups (e.g. C=C or C–OH respectively) only a minor dependence of selectivity on the cluster size was observed.

Similar type of analysis could be made for consecutive reactions A → B → C. The selectivity towards the intermediate product B is given by

$$S_B=\frac{r_B}{r_A}=\frac{r_A-r_C}{r_A}=1-\frac{r_C}{r_A}=1-\frac{r_{edges,C}(3(\frac{d_{cluster}}{d_{at}})^2a_{t/e,C}+\frac{d_{cluster}}{d_{at}}(6-18a_{t/e,C})+8a_{c/e,C}-24+30a_{t/e,C})}{r_{edges,A}(3(\frac{d_{cluster}}{d_{at}})^2a_{t/e,A}+\frac{d_{cluster}}{d_{at}}(6-18a_{t/e,A})+8a_{c/e,A}-24+30a_{t/e,A})} \tag{23}$$

Equation (23) provides a possibility to evaluate dependence of selectivity on the cluster size. Detailed numerical analysis of various cases is beyond the scope of the current paper, however, it should be stated, that in some instances, like glycerol oxidation [22] selectivity to the intermediate glycerate increased significantly within the range from 3 to 17 nm, while selectivity in hydrogenation of triple bonds (acetylene [23] or 1-hexyne [24]) over Pd was seen to be independent on the cluster size.

5 Conclusions

Differences in the reactivity of edges, corners and terraces was considered to be responsible for cluster size effects in heterogeneous catalysis using as a model *fcc* cubic and cubo-octahedron clusters. The theoretical concept advanced in the present contribution leads to kinetic equations, somewhat different from previously derived [13] when dependence of the rate constants on the cluster size was directly incorporated in the model. Comparison between experimental and

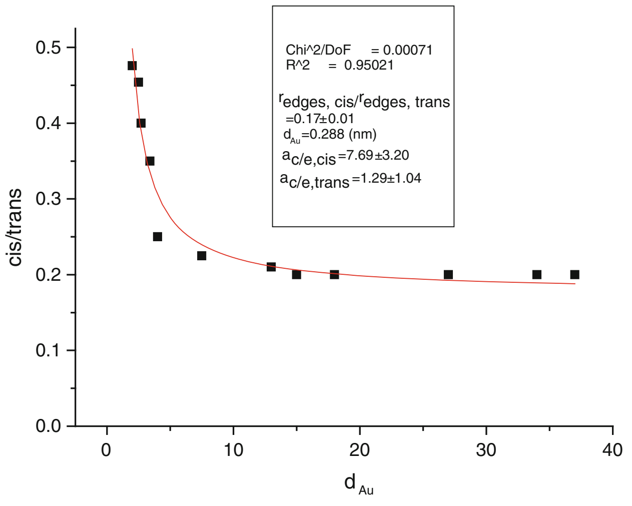

Fig. 7 Measured [17] and calculated (Eq. 21) *cis/trans* ratio in allylic isomerization of allylbenzene over gold catalysts

calculated data demonstrated applicability of the kinetic equations to explain various TOF behavior as a function of cluster size. There exists, however, some challenges in parameter estimation calling for utilization of microkinetic analysis in addition to kinetic analysis of cluster size effects based only on geometrical considerations. Quantitative analysis of selectivity could be also made within the framework of the proposed approach.

Acknowledgments The paper was inspired by several suggestions from Prof. J. A. Dumesic, which are highly appreciated.

References

1. van Hardeveld R, Hartog F (1969) Surf Sci 15:189
2. Boudart M (1969) Adv Catal 20:153
3. van Santen RA (2009) Acc Chem Res 42:57
4. Ligthart DAJM, van Santen RA, Hensen EJM (2011) J Catal 280:206
5. Jones G, Jakobsen JG, Shim SS, Kleis J, Andersson M, Rossmeisl J, Bligaard T, Helveg S, Hinnemann B, Rostrup-Nielsen JR, Chorkendorff I, Sehested J, Nørskov JK (2008) J Catal 259:147
6. Murzin D Yu (2009) Chem Eng Sci 64:64
7. Murzin D Yu (2010) J Mol Catal A Chem 315:226
8. Murzin D Yu (2011) Catal Sci Technol 1:380
9. Murzin D Yu, Parmon VN (2011) Catal Spec Period Rep RSC 23:179
10. Simakova O, Kusema B, Campo B, Leino A-R, Kordas K, Pitchon V, Mäki-Arvela P, Murzin D Yu (2011) J Phys Chem C 115:1036
11. Kusema BT, Campo BC, Simakova OA, Leino A-R, Kordas K, Mäki-Arvela P, Salmi T, Murzin D Yu (2011) ChemCatChem 3:1789
12. Simakova I, Simakova O, Mäki-Arvela P, Simakov A, Estrada M, Murzin D Yu (2009) Appl Catal A Gen 355:100
13. Murzin D Yu (2010) J Catal 276:85
14. Montejano-Carrizales JM, Aguilera-Granja F, Moran-Lopez JL (1997) Nanostruct Mater 8:269
15. Temkin MI (1984) Kinet Catal 25:299
16. Boudart M, Tamaru K (1991) Catal Lett 9:15
17. Smirnov VV, Nikolaev SA, Murav'eva GP, Tyurina LA, Vasil'kov A Yu (2007) Kinet Catal 48:281
18. Binder A, Seipenbusch M, Muhler M, Kasper GJ (2009) J Catal 268:150
19. Murzin D Yu (2010) Langmuir 26:4854
20. Quek X-Y, Guan Y, Hensen EJM (2012) Catal Today 183:72
21. Murzin D Yu, Toukoniitty E (2007) React Kinet Catal Lett 90:19
22. Dimitratos N, Lopez-Sanchez JA, Lennon D, Porta F, Prati L, Villa A (2006) Catal.Lett 108:147
23. Ruta M, Semagina N, Kiwi-Minsker L (2008) J Phys Chem C 12:13635
24. Semagina N, Renken A, Kiwi-Minsker L (2007) J Phys Chem C 111:13933