

# Giant Pd-561 clusters: onset to new catalytic properties

Mykhailo K. Starchevsky <sup>a</sup>, Serhiy L. Hladiy <sup>a,\*</sup>, Yuriy A. Pazdersky <sup>a</sup>,  
Mikhail N. Vargaftik <sup>b</sup>, Illia I. Moiseev <sup>b</sup>

<sup>a</sup> *SynteZ Research Institute, Joint-Stock, 293760 Boryslav, Ukraine*

<sup>b</sup> *N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Federation*

## Abstract

Remarkable catalytic properties have been exhibited by giant Pd-561 clusters (GPC) employed in oxidation reactions. Lower alcohol oxidation can easily occur in GPC solution at 293–323 K giving wide product spectrum: aldehydes, esters, anhydrides, carboxylic acids and acetals. Moreover hydrocarbons and carbon dioxide have been found as gaseous products. Actually GPC imply some reactivity of both bulk Pd and Pd complexes. This reactivity, however, acquires new unique features unknown for any other clusters or Pd compounds. Reaction mechanism involves formation of two kinds of activated species. It also assumes the reaction medium as well as ligand sphere to be of significant importance for GPC reactivity. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Cluster chemistry; Palladium clusters; Giant clusters; Lower alcohol oxidation; Lower aldehyde oxidation; Surface catalysis

## 1. Introduction

In a series of works, chemistry of clusters has been extensively studied. Actually for each reaction of great industrial importance, at least one cluster catalyst is known [1] (Table 1). Among these clusters, however hardly any large cluster could be found. Preferentially structural features and analytical aspects have been reported about high nuclear clusters.

A term ‘giant cluster’ appeared in the literature in the mid-1980s [2]. The work reported that in the lab of Moiseev a giant cluster of palladium had been prepared. Antecedent work of Schmid et al. [3] appeared to be an auspicious background for understanding nature of

this compound. Framework of the synthesized cluster is built of 561 Pd atoms and that authorized the conception of Chini about similarity of large clusters to small metal crystallites [4,5]. So, the giant palladium cluster (GPC) spotted the fifth position in Chini’s succession. The GPC core has icosahedron structure that is tightly fixed with 1,10-phenanthroline (phen) molecules. Anion ligands, namely  $\text{CH}_3\text{COO}^-$  or  $\text{PF}_6^-$ , form an external coordination sphere:  $\text{Pd}_{561}\text{phen}_{60}(\text{OAc})_{180}$  (I) or  $\text{Pd}_{561}\text{phen}_{60}(\text{PF}_6)_{60}(\text{O})_{60}$  (II).

Schmid et al. have obtained, with the use of the same preparation method and a close technique set, the Pd-561 giant cluster formulated as  $\text{Pd}_{561}\text{phen}_{36}\text{O}_{190-200}$  [6,7]. Some differences in the procedure of preparation cause the formula and structure distinctions: X-ray data support a

\* Corresponding author

Table 1  
Reactions catalysed by clusters

Reaction type	Cluster framework
Olefin hydrogenation	Ni <sub>3</sub> , Fe <sub>3</sub> , Ru <sub>4</sub> , Pd <sub>4</sub>
Fischer–Tropsch and hydroformylation	Co <sub>4</sub> , Co <sub>2</sub>
Isomerization	NiRu <sub>3</sub> , Ru <sub>4</sub> , Co <sub>2</sub> Pt <sub>2</sub>
Hydrogenation of CO	Ru <sub>4</sub> , Ru <sub>6</sub>
Oligomerization	Pd <sub>2</sub> , Mo <sub>2</sub> , Pt <sub>2</sub> W <sub>2</sub> , Pt <sub>5</sub>

ccp structure in this case as well as 36 phen ligands fit best on the cuboctahedral surface [8,9].

Assuming catalysis by giant clusters, their similarity to microcrystals of bulk metal should be first highlighted. As to palladium metal, its catalysts belong to the oldest ones known in catalytic chemistry. Hence some catalytic properties of the GPC being close to bulk palladium could be expected. On the other hand, the surface of the cluster core is different from that of bulk metal since the former is modified by ligand molecules. So catalytic properties of the cluster should be altered in some way.

Giant metal clusters, on their structure and size, are positioned between low-nuclear metal clusters and high-disperse metals. By a first approach, such substances could be expected to exhibit catalytic activity typical for both homogeneous and heterogeneous catalysts, being a sort of a link between homogeneous and heterogeneous catalysis [10,11].

Another approach to GPC catalytic activity would say that the shield made with bulky phen ligands should prevent substrates to access the Pd surface. Nevertheless these clusters were found to exhibit unique catalytic properties that had not been revealed for other giant clusters.

Owing to solubility in common solvents (e.g., water, acetic acid, acetonitrile), the Pd giant clusters act as homogeneous catalysts for some reactions, which have been traditionally related to heterogeneous catalysis. This became the way to provide fresh insight into their mechanism.

Oxidation reactions appeared to be most successful for the GPC catalysis so that these reac-

tions have been extensively studied [10,12]. The primary report of the GPC chemistry applied to olefin oxidative acetoxylation reaction. L.Lewis proclaimed this fact in his review [1] as “the most inspiring and exciting result in cluster catalysis”. Really, the known supported Pd catalysts for the oxidative acetoxylation of ethylene to vinyl acetate and propylene to allyl acetate in the vapour-phase process [13,14] which needs 180–200°C at 8–10 atm and the additives of alkali metal acetates as promoters. The giant Pd clusters catalyse these reactions in liquid phase under mild conditions (60–90°C, 1 atm) [15–17] yielding much less by-products being so common for the rigid gaseous process.

In the presence of GPC and a strong acid (aqueous solution) at 50°C propylene is oxidising to give acrylic acid with the yield of 60% [18]. Methanol solution yields 40% of methyl acrylate at the same conditions.

Applying GPC in lower alcohol oxidation has afforded to exhibit more unique properties of this catalyst.

## 2. Experimental

The preparation method for the GPC as well as all the experiment and measurement details is well described in the earlier work [10]. Pure methanol, ethanol, *n*-propanol and *n*-butanol as well as corresponding aldehydes containing water of maximum of 0.2 wt.% were employed as reaction substrates.

A glass reactor of 20 cm<sup>3</sup> capacity with two outlets was firmly fixed on a mixer-set which provided agitation of vibration type. The first outlet was connected directly with a liquid-closed gas system; the second had an embedded plug for taking of syringe probes. Analyses were carried out using gas chromatography with katharometer as well as FID detector. Chromosorb 101 and polyethylene glycol sebacinate supported on teflon were used as two-column packing for matching analyses.

Table 2  
Initial O<sub>2</sub> consumption rate ( $V_0$ ) by lower alcohol oxidation at 323 K. Cluster concentration  $7.2 \times 10^{-5}$  mol dm<sup>-3</sup>

Alcohol	$V_0$ , (c <sup>-1</sup> )	
	Cluster I	Cluster II
Methanol	5.8	3.9
Ethanol	2.4	1.5
<i>n</i> -Propanol	1.3	1.2
<i>n</i> -Butanol	0.3	0.2

In a typical experiment: on alcohol oxidation reactor was inputted with 24.0–25.0 mg of catalyst (cluster I or II) and 5 cm<sup>3</sup> of alcohol. The solution being thermostated at 293–323 K was agitated intensively under oxygen atmosphere within 90–300 min. The reaction system being isolated has given the substrate conversion of maximum of 4–5%. During the experiment the samples of the reaction solution were taken for analyses within the 10–30 min period. Since exact solubility of GPC in alcohols has not been studied, all GPC concentrations and rate figures presented are of comparative value.

### 3. Results and discussion

In the presence of the GPC, methanol and ethanol are oxidized by O<sub>2</sub> with a considerable rate at extremely mild conditions, namely 293–303 K and 0.1 MPa [19,20]. The oxidation rates of *n*-propanol and *n*-butanol are significantly lower (Table 2). Except methanol, all the em-

ployed alcohols yielded the identical product sequence: aldehydes, esters, anhydrides, carboxylic acids and acetals (Table 3). Despite very common succession, this is a remarkable fact because hardly any catalyst could be found to yield all these products simultaneously within a single reaction run. From the classical view, to obtain any of the mentioned products by liquid phase oxidation of the corresponding alcohol or aldehyde special catalysts and conditions (quite rigid) is necessary in each case.

The distinction of methanol oxidation consists in formation of only methyl formate and carbon dioxide (see Table 3). No other product was revealed in the reaction medium. A considerable yield of methyl formate given by GPC in this banal reaction implies a certain perspective. A series of attempts to produce methyl formate through oxidation or dehydrogenation of methanol [21] has actually failed owing to burning of a significant part of methanol.

The importance of methyl formate as a feedstock has been widely discussed and the commercial interest upon this trend has been gradually rising [22–25]. The most common method of methyl formate production is based on the base-catalysed carbonylation of methanol. On the background of heavy capital outlays, being involved for this commercial process, simple methanol oxidation provided the proper catalyst which is available, looks much set off and attractive.

When ethanol, propanol and butanol are oxidizing, aldehydes and esters form in prevailing

Table 3  
Oxidation product yield ( $Y = Y_{\text{Cluster I}} | Y_{\text{Cluster II}}$ ) by lower alcohol oxidation at 323 K. The data are of equal oxygen consumption value of 0.230 mol dm<sup>-3</sup>. Cluster concentration of  $7.2 \times 10^{-5}$  mol dm<sup>-3</sup>

Alcohol	Y (%)											
	RCHO		RCOOR'		(RCO) <sub>2</sub> O		RCOOH		CO <sub>2</sub>		Acetal	
	Cluster I	Cluster II	Cluster I	Cluster II	Cluster I	Cluster II	Cluster I	Cluster II	Cluster I	Cluster II	Cluster I	Cluster II
Methanol			96.4	92.8					3.6	7.2		
Ethanol	44.7	18.2	37.4	23.5	7.5	8.8	5.2	5.5	5.2	4.9	–	39.1
<i>n</i> -Propanol	49.2	31.4	33.0	37.9	5.2	2.9	6.8	6.5	5.8	6.0	–	15.3
<i>n</i> -Butanol	89.3	89.1	3.3	2.6	–	–	4.7	5.2	2.7	3.1	–	–

quantity. The other products accumulate up to much less amount. Unlike the classical process, acetaldehyde was found to rise without initiation period [20]. Ethyl acetate and methyl formate [19] also form with constant rates. Thus aldehyde and ester may be suggested to be primary oxidation products forming directly from ethanol. Such unique kinetics rules out any radical approach to the GPC catalysed oxidation. This concept was supported with a single test [20]. Anhydrides, carboxylic acids and acetals are obviously the secondary products.

It is well seen (Table 3) that lengthening of carbon chain results in the rise of aldehyde yield and decrease of that of ester. So in the case of butanol, the yield of ester becomes equivalent to that of the secondary products. Butyric anhydride and corresponding acetal were not found by butanol oxidation. Presumably, the phenyl ligand shield that we mentioned above controls, to a certain extent, molecule size and configuration so that bulk substrates can rarely penetrate the metal surface.

Unlike the other alcohols, ethanol oxidation rate was noticed to lower quickly during the reaction. Single test where some amount of acetaldehyde was inputted to the initial ethanol solution clearly showed reduction of the initial oxidation rate  $V_0$ . Hence acetaldehyde itself causes the deceleration of ethanol oxidation. As to propanol and butanol, no sufficient influence of the corresponding aldehydes was found.

Interesting feature arises when comparing the reactivity of clusters I and II. Cluster I seems to be more active as it is seen from the oxidation rate data (Table 2). However, considering total ethanol conversion (see Table 3), cluster II even appears a bit more productive. The bold distinction of cluster II consists in catalysis of acetal formation. Cluster I was not found to catalyse this reaction. Generally the catalytic activities of both clusters may be assumed as quite equal, though their directions are obviously different.

Initial rate data (Table 4) apparently show that cluster II has considerably high activity in the acetal formation, being actually of the same

Table 4  
Initial rate values ( $V_0'$ ) of aldehydes, esters (catalysed by cluster I) and acetals (by cluster II) at 323 K

Alcohols	$V_0'$ ( $\text{c}^{-1}$ )		
	Aldehyde <sub>I</sub>	Ester <sub>I</sub>	Acetal <sub>II</sub> ( $\text{c}^{-1} \text{M}^{-1}$ )
Methanol	–	5.6	–
Ethanol	2.0	0.3	5.0
<i>n</i> -Propanol	1.9	0.1	1.1
<i>n</i> -Butanol	0.7	0.01	–

range as activity of cluster I in the oxidation. It is also well seen, however, that the acetal formation rate abruptly lowers from ethanol to propanol. The same tendency, though to less extent, exists for the ester formation. Concurrent deducing of the rate values for aldehydes is quite moderate. This assumes the steric factor to be of significant part in the reaction rate.

The column with  $\text{CO}_2$  data (see Table 3) is worth a separate discussion. When revealed first in the gaseous phase above the reaction medium, carbon dioxide was treated as a common product being so inherent for any oxidation process. Thorough analysis of the post-reaction gas has discovered hydrocarbons. By methanol oxidation, however,  $\text{CO}_2$  is the only gaseous product. During ethanol reacting methane is producing besides  $\text{CO}_2$ . The *n*-propanol and *n*-butanol conversion gives olefins: ethylene and propylene correspondingly as well as small amount of alkanes—ethane and propane. In all cases the mole number of hydrocarbon was equal to that of carbon dioxide. This suggested that the gaseous product yield owing to breaking of the carbon–carbon bond of the initial alcohol and  $\text{CO}_2$  is not a result of entire alcohol oxidation. Basing on this suggestion, aldehydes were suspected to undergo oxidative degradation catalysed by GPC.

In special experiments, aldehyde oxidation has been studied in isopropanol solution with the GPC concentration of  $4.5 \times 10^{-5} \text{ mol dm}^{-3}$  at 333 K (0.1 MPa of oxygen). Aliphatic aldehydes  $\text{C}_2$ – $\text{C}_4$  were employed as substrates. Hy-

drocarbons and carbon dioxide have been revealed to be present in significant amount under the said conditions (Table 5). Oxidation of propanol and butanol gives the gaseous products with prevailing yields. Thus each hydrocarbon is formed from its corresponding aldehyde through degradation of one carbon atom.

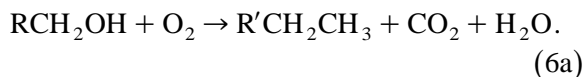
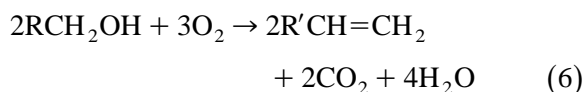
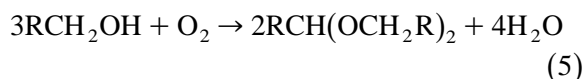
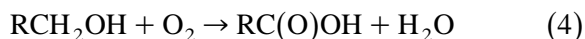
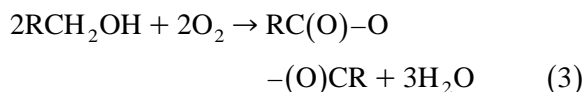
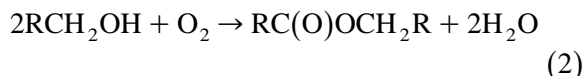
Metallic Pd has been widely reported to catalyse decarbonylation of aldehydes [26–28]. This reaction, however, can proceed freely if the temperature is at least 473 K. Related hydroformylation reaction was reported to be catalysed by Co<sub>4</sub> clusters at 413 K [29,30]. As a fact, giant Pd clusters release degradation with a noticeable rate at 293 K and the temperature of 333 K makes this reaction most auspicious for lower aldehydes [31].

Another remarkable feature of the catalyzed by GPC aldehyde oxidation is formation of anhydrides. Carboxylic acids being considered as so ordinary product of aldehyde oxidation form in very small quantity. Well-known industrial process on acetic anhydride production applies Co and Cu compounds in radical oxidizing of acetic aldehyde [32]. No other metal compound clusters have been implied to produce anhydride by an aldehyde oxidation. GPC has been proven to catalyse formation of acetic anhydride through non-radical oxidation [33].

Each of the employed aldehydes gives a considerable amount of corresponding isopropyl ester (see Table 5). At the same time no ester derived from recombination of aldehyde was detected. This fact supports well some points of suggested mechanism.

#### 4. Reaction mechanism

It is apparently seen that by the GPC catalysis of alcohol oxidation the following reactions occur:



Some general aspects of this reaction mechanism have been discussed earlier [20,31,33]. It implies formation of two active species on the Pd surface (Scheme 1). Two different values of isotopic effect for acetic aldehyde ( $V'_0(\text{CH}_3\text{CHO})/V'_0(\text{CD}_3\text{CDO}) = 4.2 \pm 0.3$ ) and ethyl acetate ( $V'_0(\text{CH}_3\text{COOC}_2\text{H}_5)/V'_0(\text{CD}_3\text{-COOC}_2\text{D}_5) = 8.7 \pm 0.3$ ) obtained by oxidation of  $\text{CD}_3\text{CD}_2\text{OD}$  in acetonitrile solution supports this suggestion.

On the first stage an alcohol molecule absorbing on the Pd core surface transforms to

Table 5

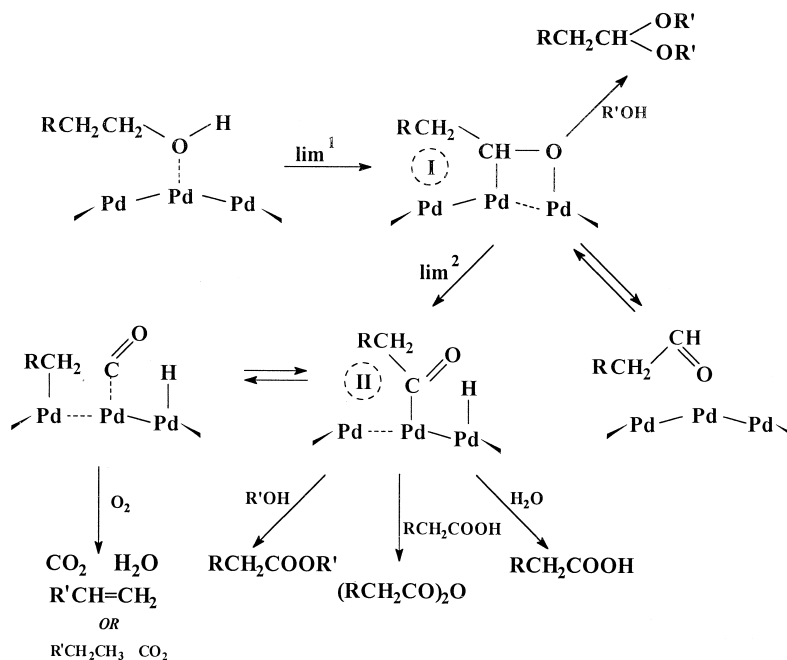
Initial aldehyde oxidation rate ( $V''_0$ ) and product yield ( $Y = Y_{\text{cluster I}} | Y_{\text{cluster II}}$ ) in isopropanol solution at 333 K. Cluster concentration  $4.5 \times 10^{-5} \text{ mol dm}^{-3}$

Aldehyde	$V''_0$ ( $\text{dm}^3 \text{ mol}^{-1} \text{ c}^{-1}$ )	Y (%)			
		RCOOH	(RCO) <sub>2</sub> O	CO <sub>2</sub> + C <sub>n</sub> H <sub>m</sub>	(CH <sub>3</sub> ) <sub>2</sub> CHOOCR
Ethanal	4.0 3.2	8.6 5.3	34.7 34.9	24.5 24.9	32.2 34.9
<i>n</i> -Propanal	5.7	3.8	26.9	52.0	17.3
<i>n</i> -Butanal	1.0	9.0	8.4	76.0	6.6

active particle of kind **I** (see Scheme 1). This particle can release from the surface forming *aldehyde* (see Scheme 1 and Eq. (1)) or being attacked by an alcohol molecule gives *acetal* (Eq. (5)). Another route of particle **I** suggests its transformation to acyl fragment of kind **II**. Acyl species is a well-known entity on Pd surface that has been often reported regarding reaction mechanism on both bulk Pd [27] and Pd complexes [34,35]. This is a key particle that can undergo a series of conversions depending on external substrate. If the latter is an alcohol molecule *ester* will be reaction product (Eq. (2)). When carboxylic acid attacks species **II**, it forms *anhydride* (Eq. (3)). Water molecule results in *carboxylic acid* formation (Eq. (4)). On Pd surface, acyl fragment is also enabled to dissociate into CO and hydrocarbon fragments that involves equilibrium with the precursor form. This fact has been reported for the decarbonylation process on bulk Pd [27]. Only rarely did our attempts on ethanol oxidation resulted in detectable trace of CO. No hydrocarbon or carbon monoxide was found in the tests with alde-

hydes under Ar atmosphere. According to classical view, Pd atoms have a tremendous affinity to CO and H species. Thus in our case the particles of carbon monoxide forming on Pd core are suggested to stick firmly to the surface so that it becomes inactive. No reaction can occur at such conditions. In the presence of oxygen, however, CO and H are easily swept being transformed into CO<sub>2</sub> and H<sub>2</sub>O. Then hydrocarbon species generate *olefins* or partially *alkanes* can be produced due to transferring of H-particles. The latter step rarely occurs because the oxidation of H-particles is an apparently quick process.

Unlike alcohol oxidation catalysed by cluster Pd<sub>4</sub> [35], diacyl derivatives have not been detected in the presence of GPC. This assumes that acyl fragments (**II**) is isolated on the Pd<sub>561</sub> surface whereas on Pd<sub>4</sub> cluster they are situated close enough to form dimers. Basing on formation of diacyl GPC stability can be presumed. In the case of degradation of Pd-561-clusters other products, which are proper for low-nuclear Pd clusters, namely diacyl, would accumulate in



Scheme 1. Reaction mechanism of the lower alcohol oxidation catalysed by giant Pd-561 clusters.

reaction medium. On the other hand, had aggregation occurred then a quick fall of catalyst activity would have been observed.

## 5. Concluding remarks

Summarising, it can be stated that the giant Pd-561 clusters exhibit the onset of principally new catalytic properties. And this is clearly displayed from the above given reactions. First, there is some reactivity inherent to both bulk Pd and Pd complexes. However, neither complexes nor bulk Pd has been ever known to catalyse oxidation of alcohols and aldehydes yielding the said products with even approaching efficiency. Moreover, extremely mild conditions being provided by the GPC, where at 293 K and 0.1 MPa, breaking and transformation of habitually strong bonds smoothly occurs, is really a remarkable fact about the giant Pd clusters.

The said distinction of Pd<sub>561</sub> reactivity from that of bulk Pd and Pd low-nuclear complexes supports catalysis by giant cluster. It was proven in earlier works on oxidative acetoxylation of olefins [10] that GPC does not undergo any substantial changes in the reaction course. During single studies of ethanol oxidation, we separated the GPC sample after completion of the reaction and employed it in another experiment. No considerable deviation of reactivity was noticed.

Another speculation appears about ligand shielding. Once, an allusion was said about romantic naked clusters of uniform size and structure [8]. Such an active particle of metal catalyst being entirely accessible for any substrate seems rather to be an inaccessible ideal of catalysis. Actually, however, this ideal particle might be approachable close enough. In the present case, the GPC can be obtained using various amounts of initial phen for synthesis, as can be seen from Refs. [2,6]. Therefore developing this direction the giant clusters could be obtained with definite surface covering, e.g.,

within of abovementioned 36 and 60 phen molecules.

External ligand set is also proven to be of tremendous importance. Abrupt shift of cluster II reactivity to acetal formation, as a result of ligand substitution (AcO<sup>-</sup> for PF<sub>6</sub><sup>-</sup>), firmly supports this concept. So ligand shell, that is often treated as a hindrance for metal surface reactivity, can be turned as implement for reaction control.

## References

- [1] L.N. Lewis, *Chem. Rev.* 93 (1993) 2693.
- [2] M.N. Vargaftik, V.P. Zagorodnikov, I.P. Stolarov, I.I. Moiseev, V.A. Likholobov, D.I. Kochubey, A.L. Chuvilin, V.I. Zaikovskiy, K.I. Zamaraev, G.I. Timofeeva, *J. Chem. Soc., Chem. Commun.* 937 (1985).
- [3] G. Schmid, R. Pfeil, R. Boese, F. Bandermann, S. Meyer, G.H.M. Calis, J.W.A. van der Velden, *Chem. Ber.* 114 (1981) 3634.
- [4] P. Chini, *Gazz. Chim. Ital.* 109 (1979) 225.
- [5] P. Chini, *J. Organometal. Chem.* 200 (1980) 37.
- [6] G. Schmid, *Chem. Rev.* 92 (1992) 1709.
- [7] G. Schmid, V. Maihack, F. Lantermann, S. Peshel, *J. Chem. Soc., Dalton Trans.* 589 (1996).
- [8] G. Schmid, *Polyhedron* 7 (1988) 2321.
- [9] G. Schmid, *Mater. Chem. Phys.* 29 (1991) 133.
- [10] M.N. Vargaftik, V.P. Zagorodnikov, I.P. Stolarov, I.I. Moiseev, D.I. Kochubey, V.A. Likholobov, A.L. Chuvilin, K.I. Zamaraev, *J. Mol. Catal.* 53 (1989) 315.
- [11] G. Schmid, *Chem. Rev.* 92 (1992) 1709.
- [12] I.I. Moiseev, M.N. Vargaftik, in: J.A. Thomas, K.I. Zamaraev (Eds.), *Perspectives in Catalysis*, Blackwell, Oxford, 1992, p. 91.
- [13] T. Shimidzu, M. Tamura, *Shokubai* 16 (1974) 84.
- [14] S. Nakamura, T. Yasui, *J. Catal.* 23 (1971) 315.
- [15] I.P. Stolarov, M.N. Vargaftik, O.M. Nefedov, I.I. Moiseev, *Kinet. Katal.* 28 (1987) 1359.
- [16] V.P. Zagorodnikov, M.N. Vargaftik, *Izk. Akad. Nauk. Ser. Khim.* (1985) 2652.
- [17] I.I. Moiseev, in: A.E. Shilov (Ed.), *Fundamental Research in Homogeneous Catalysis*, Vol. 4, Gordon and Breach, New York, 1986, p. 12.
- [18] P.I. Pasichnyk, M.K. Starchevsky, Yu.A. Pazdersky, V.P. Zagorodnikov, M.N. Vargaftik, I.I. Moiseev, *Mendelev Comm.* (1994) 1.
- [19] Ya.V. Lastoviak, S.L. Hladiy, P.I. Pasichnyk, M.K. Starchevsky, Yu.A. Pazdersky, M.N. Vargaftik, I.I. Moiseev, *Kinet. Kat.* 35 (1994) 559.
- [20] M.K. Starchevsky, S.L. Hladiy, Ya.V. Lastoviak, P.I. Pasichnyk, Yu.A. Pazdersky, M.N. Vargaftik, I.I. Moiseev, *Kinet. Kat.* 37 (1996) 408.

- [21] D.J. Darensbourg, R.L. Gray, C. Ovalles, *J. Mol. Catal.* 41 (1987) 329.
- [22] M.K. Starchevsky, Yu.A. Pazdersky, I.I. Moiseev, *Methyl Formate, Properties, Synthesis, Application, Outlook*, VAT Hallak, Boryslav (Ukr), 1997, p. 229.
- [23] G. Jenner, *Appl. Catal. A: General* 121 (1995) 25.
- [24] M.K. Starchevsky, Yu.A. Pazdersky, I.I. Moiseev, *Chem. Prom. (Russ.)* 387 (1991) 3.
- [25] J.S. Lee, J.C. Kim, Y.G. Kim, *Appl. Catal.* 57 (1990) 1.
- [26] J.F. Hemidy, F.G. Gault, *Bull. Soc. Chim. France* 6 (1965) 1710.
- [27] J. Tsuji, K. Ohno, *J. Am. Chem. Soc.* 90 (1968) 94.
- [28] J. Falbe, H. Tummes, H. Hahn, *Angew. Chem.* 82 (1970) 181.
- [29] M.-J. Don, M.G. Richmond, *J. Mol. Catal.* 73 (1992) 181.
- [30] C.U. Pittman, H. Hilal, M.-J. Don, M.G. Richmond, *Chem. Ind.* 47 (1992) 307.
- [31] S.L. Hladiy, M.K. Starchevsky, Ya.V. Lastoviak, Yu.A. Pazdersky, M.N. Vargaftik, I.I. Moiseev, *Dop. Naz. Akad. Nauk Ukr.* 1 (1998) 174.
- [32] J.Y. Nedelec, L. Gefort, *Tetrahedron Lett.* 51 (1971) 5037.
- [33] M.K. Starchevsky, S.L. Hladiy, Ya.V. Lastoviak, Yu.A. Pazdersky, M.N. Vargaftik, I.I. Moiseev, *Dokl. Akad. Nauk (Russ.)* 342 (1995) 772.
- [34] T.A. Stromnova, N.Yu. Tikhonova, L.K. Shubochkin, I.I. Moiseev, *Koord. Chem. (Russ.)* 19 (1993) 450.
- [35] T.V. Chernyshova, T.A. Stromnova, M.N. Vargaftik, I.I. Moiseev, *Dokl. Akad. Nauk (Russ.)* 348 (1996) 780.