

Palladium(+1) Carbonyl Clusters in the Catalytic Oxidation of Unsaturated Compounds

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Some palladium carbonyl clusters containing the palladium in the (+1) formal oxidation state, and derivatives of these clusters investigated in our laboratories are examined in this paper. In particular, tetranuclear carbonyl carboxylates of palladium are discussed as a model of key intermediates in various processes, including CO oxidation by a palladium catalyst with molecular oxygen as the oxidant. A second type of cluster, a palladium cationic cluster which contains N-donor ligands acts as a catalyst precursor for processes such as exhaust gas purification. A third type of palladium carbonyl cluster includes bimetallic compounds which catalyse new reactions, such as the low-temperature dehydration of alcohols.

Palladium (Pd) carbonyl complexes are of interest to chemists due to their role in industrially important catalytic processes involving carbon monoxide (CO), such as CO oxidation, the synthesis of dialkyl oxalates and dialkyl carbonates, and the carbonylation of alcohols, unsaturated hydrocarbons, nitroaromatic compounds and others (1–5). To understand the mechanism of Pd-catalysed reactions involving CO, the properties and reactivities of palladium carbonyl complexes have to be studied.

Complexes that contain palladium atoms in the (+1) formal oxidation state are not as abundant and stable as complexes containing palladium in the (+2) and (0) oxidation states (6). Pd(+1) complexes have often been postulated as the active intermediates in reactions, such as the Pd-catalysed isomerisation and carbonylation of alkenes. The first evidence of the participation of Pd(+1) complexes in the catalytic and stoichiometric transformation of unsaturated compounds came from the work of Moiseev and coworkers as early as the 1960s (7).

A group at the N. S. Kurnakov Institute in Moscow has developed methods for the synthesis of Pd(+1) complexes containing carbonyl ligands. These methods (8–11) have allowed a range of new complexes in platinum metals chemistry to be produced, such as, principally:

- tetranuclear neutral carbonyl carboxylate clusters

of composition $\text{Pd}_4(\text{CO})_4(\text{OCOR})_4$ (I), with a closed structure, where R = Me, Et, Ph, CMe_3 , CF_3 , CCl_3 , CH_2Cl (8, 9). Figure 1 shows the planar metal framework (rectangle, square or rhombus), with bridging carbonyl and carboxylate ligands coordinated on the sides of the metal frame.

- cationic carbonyl clusters of composition $[\text{Pd}_4(\text{CO})_2\text{L}_4]\text{X}_4$ (II), where L = 1,10-phenanthroline (phen) or 2,2'-bipyridyl (bipy); X = OAc, ClO_4 , CF_3COO . Figure 2 shows the tetrahedral metal core (L = phen; X = OAc). In these clusters the tetrahedral metal core forms from two mutually perpendicular fragments, $\text{Pd}(\mu\text{-CO})\text{Pd}$, which lie in parallel planes and are bonded by a direct metal-metal bond (10), and

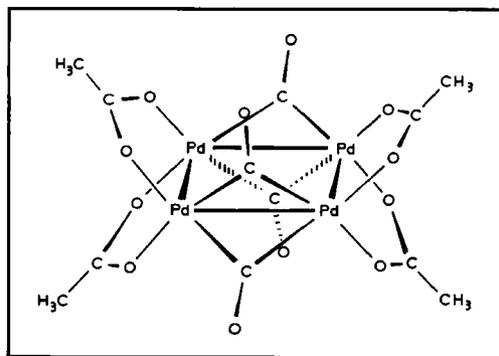


Fig. 1 Structure of cluster $\text{Pd}_4(\mu\text{-CO})_4(\mu\text{-OCOR})_4$ (I), where R = CH_3 . Carbonyl and carboxylate ligands bridge the four metal atoms

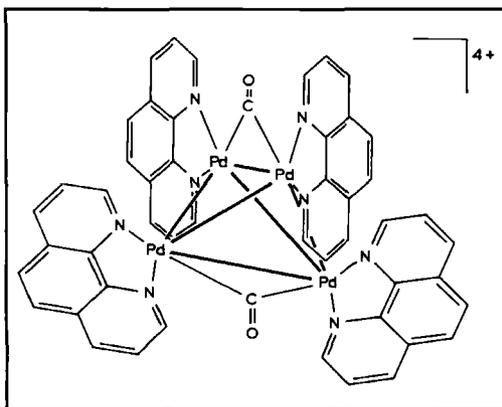


Fig. 2 Structure of the palladium cation cluster $[Pd_4(\mu-CO)_2phen_4](OCOCH_3)_4$ (II). The four metal atoms form a tetrahedral core

- a heterobimetallic palladium-molybdenum (Pd-Mo) cluster of composition $Na_2\{Pd_4[CpMo(CO)_3]_4\}$ (III) where the Pd atoms are in the +0.5 formal oxidation state and the four Pd atoms in the cluster anion form a square with a bridging $CpMo(CO)_3$ group on each side, see Figure 3. The main features of the cluster anion are that all the eight metal atoms (of Pd and Mo) lie in the same plane (11), and that the cluster does not show any tendency to exist in the closo-polyhedral form characteristic of the majority of clusters. Using CpMo allowed the creation of bimetallic compounds with metal-metal bonds.

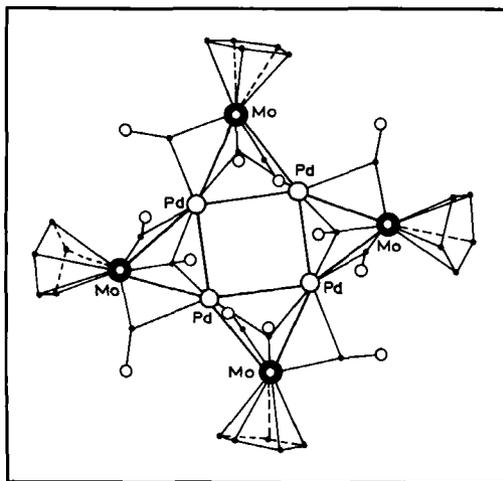


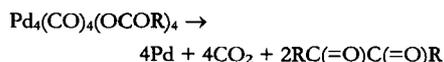
Fig. 3 Structure of an anion of the Pd-Mo cluster (III) $Na_2\{Pd_4[CpMo(CO)_3]_4\}$. The sodium atoms are not present

The main question to be considered here is: what role do these clusters, with the palladium atoms in unstable formal oxidation states, play in catalytic reactions (mainly oxidations)? There are three interesting aspects to this question:

- The first is what is the behaviour of the synthesised palladium clusters under conditions that are very similar to those of the key stage of the catalytic process?
- The second aspect is the search for new reactions where the synthesised clusters could be a catalyst (or a precursor that would easily transform into a catalyst).
- The third is what are the clusters that are involved in the catalysis of known reactions, including industrially important processes?

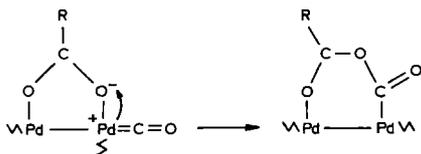
Palladium Carbonyl Clusters as a Model of Key Intermediates

The oxidation of the coordinated CO group is a key stage in redox reactions involving CO that are catalysed by palladium and its compounds. The most likely intermediates of such processes are complexes containing palladium in the intermediate oxidation state between (+2) and (0). It is known that the thermolysis of transition metal carbonyl complexes includes CO elimination or the disproportionation of two molecules of CO to give CO₂ and carbide cluster formation (12). However, in contrast to this, the thermolysis of palladium carbonyl carboxylate clusters (I) proceeds principally by a different route (13). We have found that the thermolysis of clusters (I) at 110–120°C in an inert atmosphere (argon) gives Pd metal, CO₂ and a diacyl $RC(=O)C(=O)R$, according to the equation:

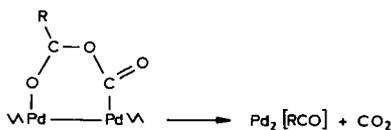


The process includes oxygen atom transfer from the carboxylate group to the carbonyl, that is, the carboxylate group is an oxygen atom donor. It is proposed that this oxidation process includes the rupture of the Pd-O bond accompanied by an increase of negative charge on the oxygen atom and an attack by the oxygen atom on the carbon atom of the CO group (it can be formally shown

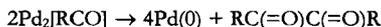
as CO insertion into the Pd-O bond) to give the unstable intermediate:



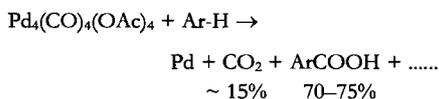
Decomposition of this unstable intermediate leads to CO₂ elimination and the formation of the coordinated acyl group:



Recombination of two of the coordinated acyl radicals gives diacyl:



The thermolysis of cluster (I) where (OCOR) = (OAc), in benzene or toluene in an argon atmosphere produces CO₂ of less than 15 per cent from the stoichiometric amount. The main product of oxidation of the coordinated CO groups was found to be the corresponding aryl carboxylic acid (benzoic acid in the case of benzene and tolylic acid in the case of toluene):

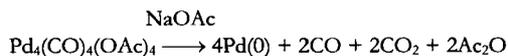


where OAc = acetate; Ac = CH₃CO; Ar = aryl.

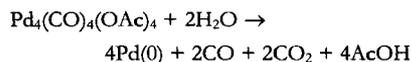
It is proposed that the formation of the unstable intermediate in this reaction is accompanied by the oxidative addition of an arene molecule proceeding via Ar-H bond rupture. The next transformation includes CO₂ insertion into the Ar-Pd bond and the reductive elimination of a molecule of aryl carboxylic acid.

The above mentioned process of inner-sphere oxidation of coordinated CO groups proceeds at 110–120°C. However, the oxidation of coordinated carbonyl groups by nucleophiles containing an oxygen atom, such as water molecules, acetate ions, aliphatic alcohols or phenol, proceeds at room temperature (14, 15). The carbonyl carboxy-

late complexes (I) are decomposed in the presence of OAc anions as:



A kinetic investigation of this reaction showed that the mechanism includes a repeated step of CO insertion into the Pd-O bond, CO₂ elimination, followed by Ac₂O formation. It can be assumed that the interaction of clusters (I) with water proceeds via the same mechanism, according to:



The reaction of clusters of (I) with C₁–C₃ aliphatic alcohols (methanol, ethanol, *i*-propanol) proceeds by a few paths (16) to give the products of oxidation of coordinated CO (CO₂ and dialkylcarbonates) and organic products of alcohol oxidation (acetaldehyde in the case of ethanol). Thus, the reaction of clusters (I) with nucleophiles containing an oxygen atom (both inner-sphere carboxylate groups coordinated in clusters and outer-sphere molecules of alcohols, water and acetate ions) results in the reduction of Pd(+1) to Pd(0) metal and the oxidation of the coordinated CO to CO₂ or dialkylcarbonates. This reaction may be considered as a model of the key stage of processes that proceed with the participation of CO and the substrates mentioned above.

The interaction of carbonyl carboxylate clusters (I) with a nitrosoarene molecule, ArNO, which contains two potential donor atoms, oxygen and nitrogen, proceeds via an oxygen atom transfer from the nitrosoarene molecule to the coordinated CO to give CO₂ and the very active arylnitrene species [ArN:]. Transformation of [ArN:] then depends on the composition of the aryl radical.

In the case of nitrosobenzene ArNO (Ar = Ph), a number of products containing the [PhN:] group were obtained. These were: azoxybenzene PhN=N(O)Ph, azobenzene PhN=NPh, aniline PhNH₂ and a palladium complex of composition Pd₂(μ-OCOR)₂(PhNC₆H₄NO)₂ (IV) which contains an amide ligand, see Figure 4 (17). The formation of the amide ligand proceeded with the participation of the phenylnitrene species and may

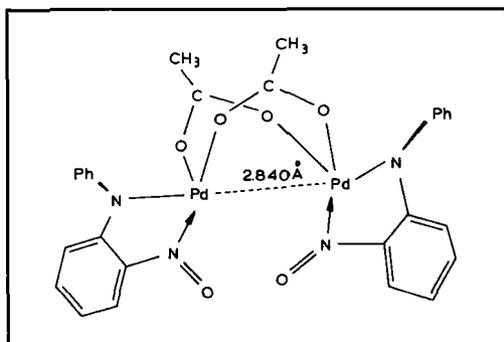
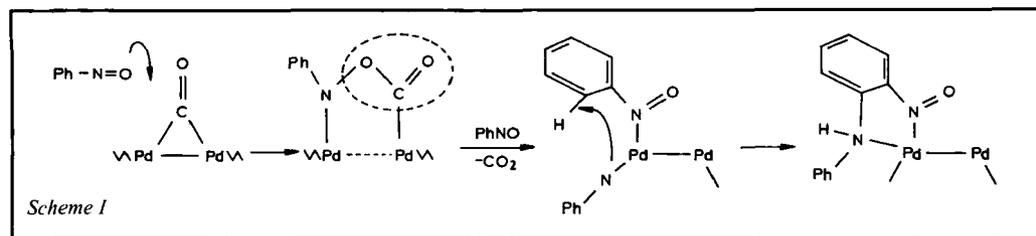
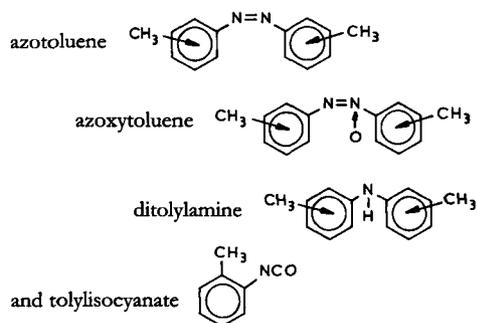


Fig. 4 Structure of the palladium complex $Pd_2(\mu\text{-OCOCH}_3)_2(\eta^2\text{-PhNC}_6\text{H}_4\text{NO})_2$, which contains amide ligands

include the next steps:

- $[\text{PhN:}]$ species formation and simultaneous CO_2 elimination, followed by
- coordination of a second molecule of nitrosobenzene, and
- $[\text{PhN:}]$ species insertion into the C-H bond of the phenyl ring according to the Scheme I below. Deprotonation of the resulting amine leads to the formation of an amide ligand.

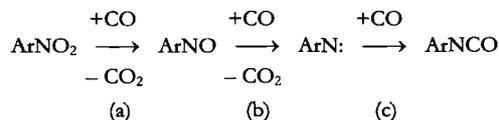
In the case of the reaction of carbonyl carboxylate clusters (I) with *o*-nitrosotoluene ArNO ($\text{Ar} = \text{MeC}_6\text{H}_4$) (18), the formation of tolylnitrene species is also confirmed by CO_2 elimination and the formation of organic products such as:



Thus it can be concluded that the interaction of carbonyl carboxylate clusters (I) with nitrosobenzene and *o*-nitrosotoluene includes the oxidation of the coordinated CO group to give CO_2 and aryl-nitrene species. The aryl-nitrene species can be easily transformed into arylisocyanate (at $P_{\text{CO}} = 1$ atm, 20°C). The oxidation of CO by the oxygen of nitrosoarenes and coordination to the nitrosoarenes is one of the main stages of the reductive carbonylation of nitroarenes:



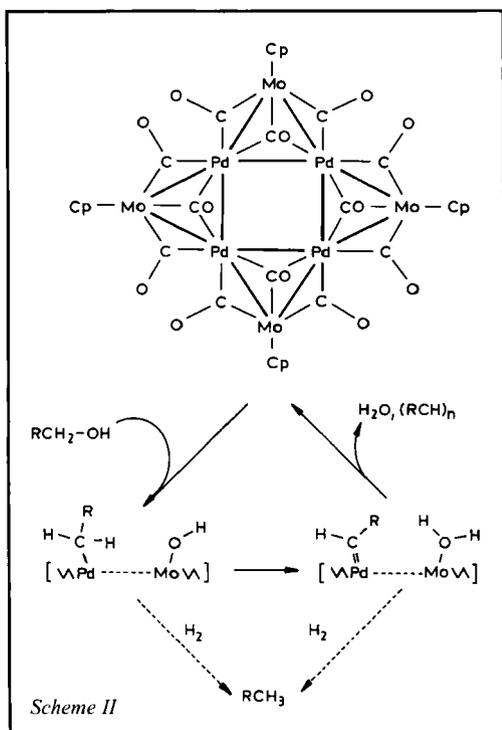
This process allows a wide range of nitrogen-containing organic products to be obtained by an environmentally friendly route. It is postulated in the literature that the mechanism of Reaction (i) includes consecutive reductions of the nitrobenzene molecule:



Palladium and its compounds are the most active catalysts for Reaction (i). The generation of the aryl-nitrene species $[\text{ArN:}]$ (Stage (b)) and the formation of arylisocyanates ArNCO (Stage (c)) is one possible mechanism.

Reactions Catalysed by Palladium Carbonyl Clusters and Derivatives

Some of the compounds synthesised were found to be efficient catalysts for redox reactions. Among these compounds, the Pd-Mo cluster $\text{Na}_2\{\text{Pd}_4[\text{CpMo}(\text{CO})_3]_4\}$ (III) is particularly interesting, for the formation of bimetallic clusters in which the Pd and Mo are connected by metal-metal bonds. This cluster is highly soluble and



Scheme II
The mechanism of dehydration of alcohols catalysed by the Pd-Mo cluster (III)

fairly stable in non-aqueous solvents. It does not contain readily oxidisable phosphine or related ligands. As two metals of different natures, palladium and molybdenum, constitute the cluster metal core, the cluster may simultaneously activate two different molecules or two different functional groups of the same substrate molecule.

Low-Temperature Dehydration of Alcohols via the Carbene Mechanism

It was shown (19) that the Pd-Mo cluster (III) is a good catalyst for the selective oxidation of alcohols in air. In the presence of cluster (III), methanol (MeOH) is transformed into methylformate MeOCHO, ethanol (EtOH) into acetal MeCH(OEt)₂, and benzyl alcohol (PhCH₂OH) is changed into benzaldehyde PhCHO.

In the absence of oxygen, the Pd-Mo cluster (III) catalyses an unusual reaction, the low-temperature (60–80°C) dehydration of alcohols (20). In the presence of the Pd-Mo cluster both aliphatic (MeOH, EtOH, *i*-PrOH, Me₃CCH₂OH) and

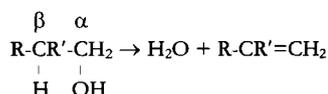
aromatic (PhCH₂OH, Ph₂CHOH) alcohols are dehydrated. Dehydration of benzyl alcohol yields *trans*-stilbene and water. In the case of aliphatic alcohols the dehydration results in the formation of water and a wax-like hydrocarbon. The rate of dehydration of aromatic alcohols exceeds by twice that for aliphatic ones.

What Is the Reaction?

Acid catalysts are known to promote an intermolecular dehydration of alcohols to form ethers, according to:



Ethers were not found in the reaction mixture. A more unusual peculiarity of the reaction is the dehydration of alcohols that do not have a hydrogen atom in the β position to the hydroxyl group in their molecules, for example, methanol, neopentyl alcohol, benzyl alcohol and diphenylcarbinol. In these cases the β -elimination of water:



is not possible. Hence this reaction might be assumed to proceed by the mechanism of α -elimination, which includes the removal of the hydroxyl group and a hydrogen atom from the same carbon atom. This assumption was confirmed by the fact that *tert*-butanol did not undergo dehydration because of the absence of α -hydrogen atoms in its molecule. All these facts suggest that the reaction proceeds via a carbene mechanism according to Scheme II.

Probably, according to Scheme II, the first stage of the reaction includes the oxidative addition of an alcohol molecule to the Pd-Mo bond. This is followed by the formation of an intermediate which contains the alkyl group σ -bound to a Pd atom. Proton transfer from the alkyl group to the hydroxyl produces a complex containing the coordinated water and carbene ligands. Further transformation of the complex includes the elimination of a water molecule and the dimerisation or oligomerisation of the carbene species into the hydrocarbon reaction products.

Additional evidence for the formation of coordinated carbene species was obtained from the experiment on reaction mixture hydrogenolysis. A solution of the Pd-Mo cluster was exposed to an alcohol for some days at 60°C, and after cooling to 20°C was reacted with molecular hydrogen (1 atm, 20°C). After the last procedure, the corresponding hydrocarbons (methane from methanol and toluene from benzyl alcohol) were found in the reaction mixture.

Palladium Carbonyl Clusters as Catalysts (or Precursors) of Known Processes

Homogeneous Catalysts

Palladium carbonyl carboxylate complexes have no potential as homogeneous catalysts in oxidation reactions because they have low solubility in organic solvents and poor stability in the presence of oxygen-containing nucleophiles. However, Pd carbonyl complexes with additional ligands that have N- and P-donor atoms have more prospects in homogeneous catalysis.

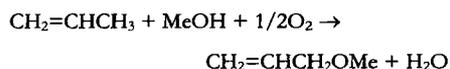
(a) Oxidative Acetoxylation and Oxidative Alkoxylation of Alkenes

The oxidation of alkenes proceeds via two different routes in the presence of Pd and its compounds:

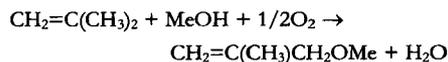
- (a) A 'classical' mechanism consisting of alternating stages in which Pd(II) is reduced to Pd(0) by olefin, and the Pd(0) is reoxidised by an oxidant.
- (b) A 'cluster' mechanism in which olefin oxidation occurs at the surface of a low-valence palladium cluster, such as a giant Pd₅₆₁ cluster. This mechanism does not suggest alternating oxidation and reduction stages but the nanocluster acts as an 'electron mediator', transferring electrons from the olefin molecule to the oxidant molecule.

Moiseev and coworkers have studied Pd-catalysed olefin oxidation proceeding via the 'classical' and 'cluster' mechanisms (21–25). It was shown that the complexes obtained by interaction of (I) with L (L = phen or bipy, Pd/L > 1) are suitable catalysts for olefin oxidation. In alcohol solutions of these complexes, selective oxidative alkoxylation of alkenes proceeds under mild conditions (60–100°C, P_{alkene} = 0.7 atm, P_{O₂} = 0.3 atm) at a

good rate. Under these conditions propylene is transformed into allyl methyl ether:



and *i*-butylene is transformed to the ether:



Thus, in both cases only alkyl groups of substrates will be oxidising which is evidence of catalysis by Pd in a lower oxidation state.

In the oxidation of propylene in alcohol media, the presence of Pd(II) could be considered to lead to a mixture of ethers including the products of the different groups of the alkene molecule. The nature of the products formed in these reactions is evidence for the 'cluster' mechanism of catalysis that includes the molecular clusters or nanoparticles formed in these systems (26).

Acetic acid solutions of the above complexes are good catalysts for CO oxidation by air:



The velocity of CO oxidation is 10⁻² mol CO₂/l of complex/hour at 20°C, where [Pd] = 0.2 g-atom/l.

This is evidence that the Pd complexes obtained by the interaction of carbonyl carboxylate complexes with N- and P-containing arenes can be used as precursors for the catalyst used for the oxidation of alkenes and CO under mild conditions. In the case of alkenes only their alkyl groups will be oxidising. These complexes can serve as models of the active centres of the catalysts for the oxidation of unsaturated compounds and help search for potential catalytic systems.

Heterogeneous Catalysts

All the catalytic reactions mentioned above occur in the presence of homogeneous catalysts. We would now also like to obtain data about the activity of the synthesised clusters in conditions that are very close to industrial ones. The complexes obtained from cluster (I) and phen or bipy were immobilised on oxide supports. We used commercial supports: silica and α-Al₂O₃, and also TiO₂, where the Ti surface was oxidised electro-

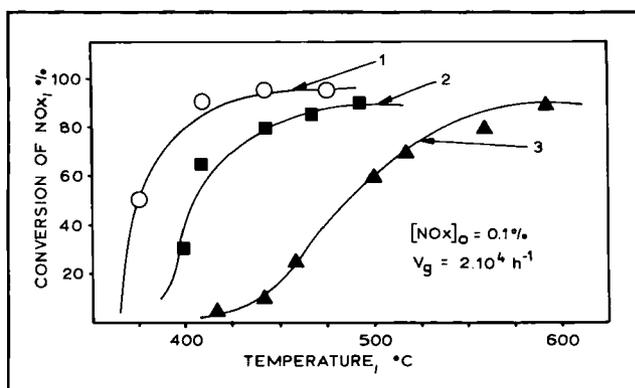


Fig. 5 Comparison of catalytic activity in NOx conversion of three catalysts impregnated onto an industrial α -Al₂O₃ support:

V_g = velocity of gas mixture

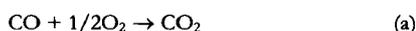
1 - catalyst prepared from cluster (I) and phen. containing 0.1% Pd

2 - catalyst based on the platinum salt, H₂PtCl₆, containing 0.1% Pt

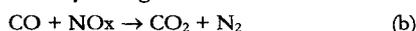
3 - industrial catalyst APK-2; this catalyst contains 2% Pd

chemically. The catalysts all contained 0.1 wt.% Pd. The Pd(I) clusters immobilised on the oxide carriers were found to have high activity in the following reactions:

CO oxidation in air:



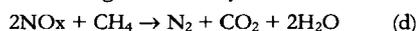
CO oxidation by nitrogen oxides:



Alkane oxidation in air:



Reduction of nitrogen oxides by methane:



Using the data obtained, effective heterogeneous catalysts for exhaust gas purification were developed (27, 28). These catalysts can also be used to help with ecological problems, such as the purification of off-gas from metallurgical or petrochemical plants, or engines.

Catalysts prepared from palladium clusters immobilised on a support of spherical silica particles showed high activity for the oxidation of CO and hydrocarbons. Complete conversion of CO was achieved at 160–180°C ($V_{\text{gases}} = 4000 \text{ h}^{-1}$, 4% CO). This temperature is the lowest for known catalysts. The high activity of the prepared catalyst was achieved by using palladium cluster compounds; the catalyst contains 5 to 10 times less noble metal than the usual industrial catalysts (for example, the Russian catalyst APK-2 contains 2 wt.% Pd).

The catalytic activity of the cluster catalyst immobilised on a *Sibunit* carrier (activated carbon sorbent prepared from coal) was investigated at the Institute of Catalysis, Siberian Branch of the RAS

(Novosibirsk). The complete oxidation of methane and butane in air occurred at a significantly lower temperature than on regular catalysts. For instance, C₄ hydrocarbons were oxidised at ~300°C, instead of at >350°C for the usual industrial catalysts.

Purifying the polluting gases from nitric acid plants may be achieved by using a palladium cluster catalyst. Similarly, decomposition of NO_x is an environmental challenge for the chemical industry. Around 50 UKL-7 plants of capacity 120,000 tonnes per year of nitric acid are now operating in the former Soviet Union and each of them emits 60,000 m³ h⁻¹ of NO_x-containing pollution. All these plants presently use deNO_x catalytic systems to reduce the concentration of NO_x from ~0.1% to less than 50 ppm. The reduction process is based on the reaction of NO_x with natural gas, see Reaction (d).

Therefore, to compare the activity of the palladium cluster catalyst proposed by us with the industrial APK-2 catalyst, both were impregnated on the same industrial α -Al₂O₃ carrier. The catalytic activities were comparable although the amount of palladium in our cluster catalyst (0.1%) was twenty times less than that in APK-2 (2%), see Figure 5. Moreover, the working temperatures of the cluster catalyst appeared to be at least 100°C lower than that of the industrial one.

Conclusions

The current work shows that Pd(+1) complexes can play a role in catalysis. While our work in this area has ended, we believe further work could produce further interesting results.

Acknowledgement

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Alcohol Oxidation by Ruthenium Catalyst

Traditional oxidations of alcohols use heavy metal oxidants, resulting in noxious waste and unwanted coproducts (*Platinum Metals Rev.*, 2002, 46, (1), 26). Alternative homogeneous catalytic systems have been developed, but are limited mostly to oxidation of activated benzylic and allylic alcohols, or large amounts of additives (NaOAc, NaOH and K_2CO_3) are required.

Now, researchers at the University of Tokyo have developed an efficient heterogeneous Ru catalyst that can oxidise alcohols with 1 atm of O_2 or air, without additives (K. Yamaguchi and N. Mizuno, *Angew. Chem. Int. Ed.*, 2002, 41, (23), 4538–4542). The 1.4 wt.% Ru/ Al_2O_3 catalyst was prepared by stirring γ - Al_2O_3 with an aqueous solution of $RuCl_3$ at room temperature, and then treated with aqueous NaOH.

The Ru/ Al_2O_3 system had high catalytic activity for oxidising activated and non-activated alcohols with 1 atm of O_2 ; reaction selectivity was over 97%. Even less reactive primary alcohols (1-octanol and 1-decanol) could be oxidised. The Ru/ Al_2O_3 system is reusable, recoverable and no Ru leaching occurs, which make it a possible system for industrial use.