Study of interfacial reaction of palladium(II) ion and bentonite in the presence of complex forming agents

Palladium(II)-ion és bentonit határfelületi reakciója komplexképző jelenlétében

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Abstract – The sorption of palladium(II) ion on sodium-bentonite was studied. In order to avoid the hydrolysis of Pd(II) and the acidic destruction of clay Pd(II) was applied as positively charged $[Pd(NH_3)_2]^{2+}$ and $[Pd(en)_2]^{2+}$ complexes. In case of $[Pd(NH_3)_2]^{2+}$ the solution contains ammonium ions so a ternary system has to be considered. X-ray diffraction and thermal analytical studies reveal that in the presence of both complex forming agents and palladium ions are mainly sorbed on the deprotonated silanol sites of the clay mineral. Palladium(II) can be reduced to metallic Pd(0) thermally.

Összefoglalás – Palládium(II)-ion szorpcióját tanulmányoztuk nátrium-bentoniton. A Pd(II)-ionok hidrolízisének és az agyag roncsolásának elkerülése érdekében pozitív töltésű $[Pd(NH_3)_2]^{2+}$- és $[Pd(en)_2]^{2+}$-komplexeket alkalmaztunk. A $[Pd(NH_3)_2]^{2+}$-komplex esetén az oldat ammóniumionokat is tartalmazott, így a rendszert három komponensűként kellett kezelni. Röntgendiffrakciós és termoanalitikai vizsgálatok azt mutatták, hogy mindkét komplexképző esetén a palládiumionok főleg az agyagásvány deprotonált szilanol-csoportjain kötődnek meg. A palládium(II)-ionok termikusan fémes Pd(0)-vá redukálódnak.

Key words – adsorption, bentonite, catalyst, complex formation, palladium(II) ion
Tárgyszavak – adszorpció, bentonit, katalizátor, complex képzés, palládium(II)-ion

Introduction

Montmorillonites offer wide-ranging catalytic applications in the fields of organic chemistry (LASZLO 1987). Pd-montmorillonite has been applied as a catalyst for organic reactions, e.g. regiospecific hydroesterification of vinylsilanes (LEE & ALPER 1996), cyclocarbonylation of allylphenols (OREJON & ALPER 1999), hydrocarboxylation of an ethanol derivative (JANG et al. 1999), hydro-isomerization of n-butane (CANIZARES et al. 2001), hydrogenations of alkynes (MASTALIR et al. 2001, 2004). Combined palladium-copper-montmorillonite has been used for the cross-coupling of methyl acrylate with aryl amines (WATERLOT et al. 2000).

Palladium-montmorillonite catalysts have been produced in different ways. In most cases sodium-montmorillonite has been suspended in an aqueous or organic solution of a palladium compound, then after some time the solvent is eliminated by different ways (e.g. evaporation, filtration) (CANIZARES et al. 2001, OREJON & ALPER 1999, LEE & ALPER, 1996). Palladium-copper-montmorillonite has been prepared in a similar way, using a solution containing palladium as well as copper ions (WATERLOT et al. 2000). In other cases sodium-montmorillonite has been treated by HCl solution (formation of H-montmorillonite), then silane-exchanged montmorillonite has been produced and complexed with a palladium-containing solution (JANG et al. 1999).

These examples show that the conditions used for the production of the catalysts are sometimes confused. The products cannot be real cation exchanged montmorillonites, palladium ion is not present in the interlayer space of montmorillonite. The clay mineral often acts just as a supporting material, palladium salt is simply dried onto its surface (CANIZARES et al. 2001, OREJON & ALPER, 1999, LEE & ALPER, 1996). In other cases the acidic medium preventing the hydrolysis of the palladium cation can destroy the crystal structure of the clay (JANG et al. 1999).

Certain authors have produced palladium-montmorillonite in organic media (MASTALIR et al. 2001, 2004). They have characterized the structure of the product, too.

This work studies the sorption of palladium(II) ion on bentonite in an aqueous medium. In order to avoid the hydrolysis of palladium(II) ions and the decomposition of clay by the acid medium, Pd(II)-bentonite was produced by $[Pd(NH_3)_4]^{2+}$ and Pd ethylene diamine complexes. These complexes are positively charged enabling sorption on the negative layer charge of montmorillonite as well as on the negative edge charges of the clay (VAN OLPHEN 1977).

Experimental

Bentonite samples collected at the site Valea Chioarului (Romania) (KOVÁCS-PÁLFFY 1998) were used as a base material for the production of palladium-bentonite. The exchangeable cation is sodium ion which is beneficial because the exchange of monovalent sodium ion to divalent palladium ion can be easily observed by the change of the 001 basal spacing of montmorillonite (cca. 1.2nm for monovalent cations, 1.5nm for divalent cations).

The mineral composition (*Table 1*) was determined by means of X-ray diffraction analysis, using a computer controlled Philips PW1710 diffractometer with a Cu anticathode, operating at 30mA and 40kV with a graphite monochromator. The scanning rate was $2°\Theta min^{-1}$. The mineral composition was calculated on the basis of the relative intensity rates of the reflections characteristic to the minerals, applying the literature or experimental corundum factors on minerals (KLUG & ALEXANDER 1954). The elementary composition of the bentonite samples as well as cation-exchange capacity determined by ammonium acetate method (RICHARDS, L.A. 1957) are shown in *Table 1*.

The number of edge sites (silanol and aluminol) was determined by potentiometric titration. The titration curves were evaluated by the surface complexation model (DAVIS et al. 1978, JAMES & PARKS 1982, NAGY & KÓNYA 2004).

The procedure is not discussed here only the number of the edge sites is given (*Table 1*) and used later for the evaluation of the palladium sorption results.
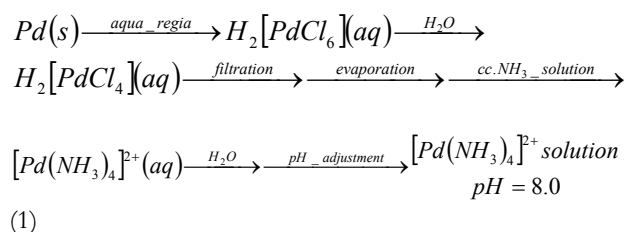
The bentonite samples were air-dried at room temperature and powdered in a porcelain mortar. The specific surface area (*Table 1*) of the samples was determined by static BET adsorption. The static measurement was made by an AUTOSORB-1 instrument (produced by Quantachrome) using nitrogen vapour at 77K. Before the measurement the sample was kept at 80°C for at least 20 hours at a pressure of $1.33*10^{-2}$Pa. The specific surface area was calculated from five points, the regression of the straight line was >0.9990. Three measurements were made and the standard deviation was less than ±5 %.

Mineral, %		Elementary composition, %	
Montmorillonite	48	SiO_2	63.74
Illite	2	Al_2O_3	14.77
Kaolinite	1	Fe_2O_3	1.22
Quartz	5	FeO	0.6
Plagioclase	8	CaO	0.89
Amorphous	5	MgO	4.06
Opal-CT	30	MnO	0.02
Lepidocrocite	1	TiO_2	0.2
Surface caracterization		P_2O_5	0.02
S, m^2/g	15	Na_2O	0.87
CEC, mequ/100 g	40	K_2O	0.16
AlOH (mol/g)	3.3e-5	H_2O	14.09
SiOH (mol/g)	8.5e-5		

Table 1 The elementary and mineral composition, specific surface area (A), cation exchange capacity (CEC) and the number of surface (aluminol and silanol) groups of the bentonite sample from Valea Chioarului (Romania)

1. táblázat A Valea Chioarului (Románia) bentonit minta elemi és ásványos összetétele, fajlagos felülete (A), kationcsere-kapacitása (CEC), valamint a felületi (aluminol és szilanol) csoportok száma

The stock solution containing $[Pd(NH_3)_4]^{2+}$ complex was produced by the reaction scheme (1). Metallic palladium was dissolved in aqua regia. The solution was diluted, filtrated, evaporated and the solid formed was dissolved in concentrated ammonia solution. It was diluted again, pH=8.0 was adjusted with $HClO_4$ solution.

$$Pd(s)\xrightarrow{aqua\_regia} H_2[PdCl_6](aq)\xrightarrow{H_2O}$$
$$H_2[PdCl_4](aq)\xrightarrow{filtration}\xrightarrow{evaporation}\xrightarrow{cc.NH_3\_solution}$$

$$[Pd(NH_3)_4]^{2+}(aq)\xrightarrow{H_2O}\xrightarrow{pH\_adjustment}[Pd(NH_3)_4]^{2+}\ solution\ pH=8.0$$

(1)

The palladium concentration of the solution was measured by a Pye Unicam SP 1900 atomic absorption spectrometer.

Thermodynamic calculations considering the stability constant of $[Pd(NH_3)_4]^{2+}$ complex and the base ionisation constant of ammonia show that at pH=8.0 Pd(II) forms amine complex with coordination number 4 (MARTELL &
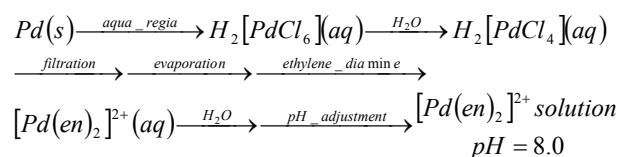
SWITCH 1974). The concentration of the chemical species in this stock solution: $[Pd(NH_3)_4]^{2+}$ = 0.025mol/dm^3, NH_3 = 0.066mol/dm^3, NH_4^+ = 1.57mol/dm^3.

The sorption of palladium complex on sodium-bentonite was studied by batch equilibration technique at constant (25°C) temperature. 200.0mg of air-dried bentonite samples was measured into a beaker, and 20.0cm^3 of double distilled water was added and the mixture stirred at constant rpm for 60min. According to the experiences this time is sufficient to reach solubility equilibrium between the phases. During this process pH was adjusted to 8.0 with NaOH as well. Then 20-500μl of the palladium containing stock solution was added. The suspension was stirred again for 120min. This time was found to be suitable for the sorption equilibrium. The phases were separated by a Universal 16 centrifuge (15min, 2700/min) and the pH of the liquid was measured.

As seen later, ammonium ions also sorb on bentonite, therefore three ions (palladium, sodium and ammonium) are present in the bentonite phase and in the solution as well. The palladium and sodium ion concentration of the solution was measured by a Unicam SP 1900 atomic absorption spectrometer. The concentration of palladium in the bentonite phase was determined by X-ray fluorescence spectrometry. The measurements were accomplished with a Si(Li) detector of 20mm^2 area and 3.5mm thickness and with pressed pellet samples of 10mm in diameter and 200mg in weight. An IBM AT compatible computer with Canberra DSA-1000 digital spectrum analyser together with a Genie-2000 basis spectroscopic software were applied. The excitation was made by a ^{125}I annular radioisotope source prepared in our laboratory.

The structure of the palladium-bentonite was studied by X-ray diffraction (discussed earlier) and by thermal analysis using Derivatograph-PC computer controlled simultaneous TG, DTG, DTA apparatus. The temperature of the furnace was regulated by a linear heating program at a rate of 10°Cmin^{-1}. The analytical conditions are: air atmosphere, ceramic crucible, mass of sample about 100mg, reference material Al_2O_3.

To avoid the exchange of the positively charged ammonium ion, palladium ethylene diamine (en) complex was also produced similarly to Eq.1, where ethylene diamine was applied instead of concentrated ammonia. Palladium forms ethylene diamine complexes with coordination number 2 (MARTELL & SWITCH 1974). The excess of a complexing agent is neutral therefore it has no effect on the cation exchange in the interlayer space of montmorillonite. The scheme of the production of $[Pd(en)_2]^{2+}$ complex is described by Eq.2.

$$Pd(s)\xrightarrow{aqua\_regia} H_2[PdCl_6](aq)\xrightarrow{H_2O} H_2[PdCl_4](aq)$$
$$\xrightarrow{filtration}\xrightarrow{evaporation}\xrightarrow{ethylene\_diamine}$$
$$[Pd(en)_2]^{2+}(aq)\xrightarrow{H_2O}\xrightarrow{pH\_adjustment}[Pd(en)_2]^{2+}\ solution\ pH=8.0$$

(2)

The sorption process was studied at the greatest Pd(II) concentration applied in the case of the amine complex. The structure of the produced Pd-bentonite was studied by X-ray diffraction and thermal analysis as discussed earlier.

The used chemicals were of pro analysis quality.

Results and Discussions

The sorbed quantity of palladium(II) as a function of the equilibrium $[Pd(NH_3)]^{2+}$ concentration is shown in *Fig. 1*.

As seen in *Fig. 1* the isotherm shows not the usual tendencies of the sorption isotherm: a plot with an increasing slope is obtained instead of the usual asymptotic curve. It is caused by the great excess of an additional positive ion (ammonium ion). By comparing the

concentrations of the sorbed and dissolved cations (sodium, ammonium and palladium ions) it reveals that a ternary ion exchange reaction takes place. In *Fig. 2* the quantity of the dissolved sodium ion is plotted as a function of the sorbed quantity of palladium(II) ion. The slope of the straight line is 5.6. In the case of binary Pd(II)-Na(I) exchange this value would be 2. Since the slope is much higher than 2, i.e. the quantity of the dissolved sodium ion is greater than that of the sorbed palladium(II), ammonium-sodium ion exchange has to be supposed.
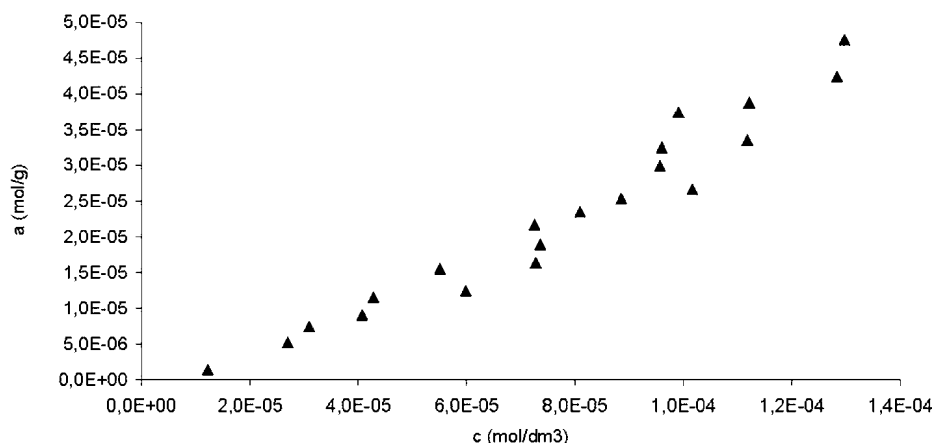

Figure1 The quantity of the sorbed palladium(II) ion (a) on sodium-bentonite as a function of the equilibrium concentration of the solution (c). Complex: $[Pd(NH_3)_2]^{2+}$
1. ábra A nátrium bentoniton megkötött palládium(II)-ion mennyisége (a) az oldat egyensúlyi koncentrációjának (c) függvényében. Komplex: $[Pd(NH_3)_2]^{2+}$
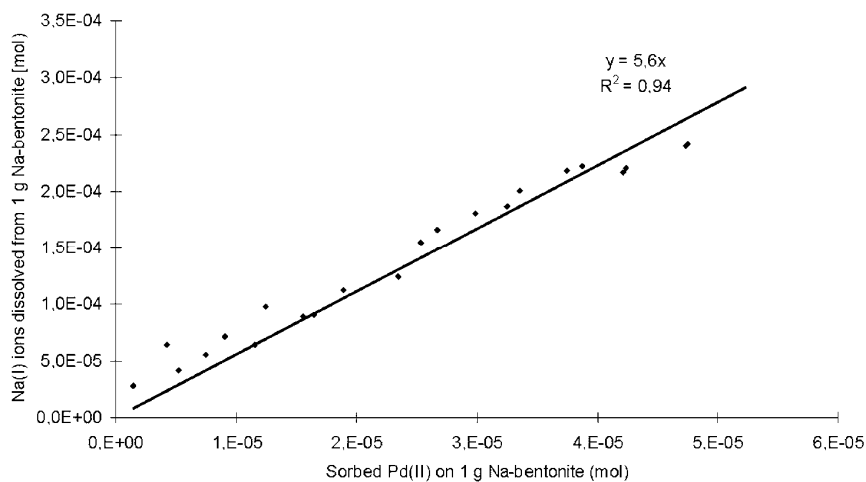

Figure 2 The dissolved quantity of sodium ion as a function of the sorbed palladium(II) ion. Complex: $[Pd(NH_3)_2]^{2+}$
2. ábra Az oldott nátriumion mennyisége a megkötött palládium(II)-ion mennyiségének függvényében. Komplex: $[Pd(NH_3)_2]^{2+}$

However, the sorbed palladium(II) quantity can be considered to be significant, regarding that the concentration of Pd(II) complexes in the stock solution is less by some orders of magnitude than ammonium concentration. Under the experimental conditions the maximum sorbed quantity of palladium(II) is around. 25% of the cation exchange capacity of sodium-bentonite.

The question arises how palladium ion sorbs on bentonite and whether palladium(II) sorption leads to any

changes in crystal structure. X-ray diffraction and thermal analytical studies help to answer these questions.

The result of X-ray diffraction studies of Pd-bentonite and the initial substance (Na-bentonite) are listed in *Table 2*.

The basal spacing of montmorillonite slightly decreases during the sorption of palladium(II). It shows that palladium(II) ions practically do not enter into the interlayer space (the basal spacing of montmorillonite

containing divalent cations in the interlayer space is about 1.5nm).

	Pd-mont.	Na-mont.
2θ (°) (CuK$_\alpha$)	7.36	7.12
d (nm)	1.200	1.240
Width at halfmaximum intensity (2θ °)	1.12	0.65
Intensity (arbitrary units)	223	443

Table 2 Basal reflections of Na- and Pd-montmorillonite
2. táblázat Na- és Pd-montmorillonit bázislap távolsága

Therefore Pd(II) ions can be sorbed on the deprotonated edge sites of the crystal lattice. At pH=8 of the experiments the silanol sites are totally deprotonated.

As seen in *Table 1* the number of silanol sites is about 20% of the cation exchange capacity. It is in a fairly good agreement with the sorbed quantity of palladium(II).

The results of thermal analytical studies are summarised in *Table 3*. As seen Pd-bentonite shows the usual thermal processes of montmorillonites but there are two new exothermic reactions at 338 and 548°C. At the 338°C exothermic reaction a slight weight loss of the sample is also observed in a wide temperature range. It may indicate the partial amorphisation of bentonite. At 548°C the reduction of Pd(II) to Pd(0) can be supposed. The water content of the interlayer space (eliminated at cca. 136°C) of Pd-montmorillonite is about a half of that for Na-montmorillonite.

Sample	Water elimination		Dehydroxilation	New exothermic reactions	
	T_1(°C)	E_1 (kJ/mol)	T_2(°C)	T_3(°C)	T_4(°C)
Average of 16 Na-bentonites	136	41,6			
Na-bentonite used here	138,4	39,8	696		
Pd-bentonite produced	136,3	39,1	686	338	548,5

Table 3 Corrected water elimination and dehydroxilation temperatures as well as the activation energy of water elimination in Na- and Pd-bentonites (kJ/mol)
3. táblázat Na- és Pd-bentonit korrigált vízvesztési és dehidroxilezési hőmérséklete, valamint a vízvesztés aktiválási energiája (kJ/mol)

To avoid the effect of the ammonium ion on the palladium(II) sorption the sorption experiments were repeated with [Pd(en)$_2$]$^{2+}$ complexes. The X-ray diffraction and thermal analytical studies gave the same results as in the case of [Pd(NH$_3$)$_2$]$^{2+}$ complexes, namely palladium ions cannot be indicated in the interlayer space, consequently they must be present on the deprotonated silanol sites.

Conclusions

The sorption of palladium(II) ion on sodium-bentonite was studied. In order to avoid the hydrolysis of Pd(II) and the acidic destruction of clay Pd(II) was applied as positively charged [Pd(NH$_3$)$_2$]$^{2+}$ and [Pd(en)$_2$]$^{2+}$ complexes. The X-ray diffraction and thermal analytical studies show that palladium(II) ions practically do not enter into the interlayer space of montmorillonite. They are mainly sorbed on the deprotonated silanol sites of the clay mineral. The sorbed quantity of the palladium(II) ions is in a fairly good agreement with the concentration of the surface silanol sites. The thermal analytical results show that the palladium(II) sorbed on the surface of the clay can be reduced to Pd(0). By this method applying complex forming agents, palladium catalysts with 2 or 0 oxidation state can be produced. However, the thermal treatment increases the concentration of the amorphous phase in bentonite, more desirable from catalytic points of view. The catalyst will be applied in organic synthesis later.

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