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## PILLARED MONTMORILLONITES DOPED WITH CATALYTICALLY ACTIVE TRANSITION METAL IONS

### PART 1. SYNTHESIS AND PHYSICO-CHEMICAL CHARACTERIZATION

**Abstract.** The paper summarizes authors' experience in designing, preparation and characterization of Al, Ti-, and Zr-pillared montmorillonites doped with transition metal elements such as copper and vanadium. Various doping procedures are described and the resulting materials characterized with XRD, nitrogen adsorption studies, chemical analysis, CEC measurements, thermal analysis and ESR. Structural models of the Cu- or V-containing pillared clays are proposed, presenting the textural properties of the samples and location of transition metal dopants within the pillared clay structure.

**Key-words:** pillared montmorillonites, doping of PILC with Cu and V

## INTRODUCTION

Heterogeneous catalysis is associated with adsorption of reagents at the surface of the catalyst, where a specific chemical reaction takes place and from where products of this reaction are released. Depending on the type of the catalysed process, the catalyst surface should possess active sites of acid-base or redox nature. The catalyst not only accelerates the chemical reaction but also, in case of many possible reaction products, helps to direct the process along the desired pathway. Bearing in mind that over 90% of industrial chemical processes used all over the world is of catalytic nature, it is understandable that an immense effort is put into investigation of novel catalytic materials. This is how the concept of pillared clays (PILCs), which are a result of search for large pore catalysts capable of heavy oil cracking, emerged in the seventies (Vaughan 1988).

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Clay minerals used for pillaring, mainly smectites, belong to the family of phyllosilicates characterized by layered structure in which the main building units are negatively charged layers composed of Si-O tetrahedral and octahedral sheets in which metal centres are most frequently Al or Mg. The negative charge of the layers stems from the partial substitution of the structure-forming cations by cations of lower valency (e.g.  $\text{Mg}^{2+}$  for  $\text{Al}^{3+}$ ,  $\text{Li}^+$  for  $\text{Mg}^{2+}$ , or  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$ ) and is neutralized by the presence of compensating cations in the interlayer space. These crystallochemical properties cause that smectites, already in their natural state, possess appreciable specific surface area, cation exchange properties as well as active sites such as acid centres of Brønsted type. These features led to the application of smectites as mineral sorbents and bleaching earths (e.g. Bolewski, Skawina 1972; Kłapyta et al. 1977; Stoch et al. 1977; Rutkowski et al. 1977; Stoch et al. 1979; Bahranowski 1980; Bahranowski, Wilgat 1982; Żabiński 1991) and made them interesting objects of catalytic studies. Conversion of layered clay minerals into highly porous PILC structures is possible by exchanging the interlayer cations with oligomeric oxo/hydroxy cationic species which, after calcination, produce oxide pillars propping open the silicate layers (e.g. Brindley, Sempels 1977; Yamanaka, Brindley 1978; Yamanaka, Brindley 1979; Lahav et al. 1978; Vaughan et al. 1979; Vaughan et al. 1981; Fijał, Olkiewicz 1982; Occelli, Tindwa 1983; Pinnavaia 1983; Kikuchi et al. 1984; Tokarz, Shabtai 1985; Bartley, Burch 1985; Fijał, Żyła 1985; Plee et al. 1985; Burch, Warburton 1986; Sterte 1986; Bahranowski, Gawel 1986; Bahranowski 1989; Figueras et al. 1990; Fijał 1991; Bahranowski, Serwicka 1993a; Jones, Purnell 1993; Bahranowski et al. 1996a, b, c). The appropriate choice of the pillaring species and the conditions of preparation procedure allows to influence the chemical, surface and textural properties of the resulting solids. This makes the PILC materials extremely attractive as potential catalysts.

Part 1 of this work summarizes the results of an extensive study undertaken by the author, in cooperation with the Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences, aimed at design, preparation, and physico-chemical characterisation of pillared clays capable of performing redox catalysis (Bahranowski, Serwicka 1993a, b, 1994; Bahranowski et al. 1995a, b; Bahranowski et al. 1996a, b, c; Bahranowski et al. 1997; Bahranowski et al. 1998a, b; Bahranowski et al. 1999; Bahranowski et al. in print<sup>a</sup>; Bahranowski et al. in print<sup>b</sup>; Bahranowski et al. submitted). The pillared materials were obtained by intercalation of the montmorillonite clay with Al, Zr or Ti polycations. The redox centres were incorporated into the pillared matrices by doping with transition metal ions such as copper and vanadium. Part 2 is devoted to the description of the catalytic properties of the prepared solids in a number of catalytic processes.

## PREPARATIVE METHODS

### Starting material

The material used in this study was the <2  $\mu\text{m}$  particle-size fraction extracted by sedimentation from Milowice bentonite ("Saturn" coal mine in Sosnowiec-Milowice, Poland). This fraction contains ca. 85% of smectite, 8% of kaolinite and 7% of quartz. The smectite from Milowice bentonite is a dioctahedral montmorillonite ( $d_{060} = 1.498 \text{ \AA}$ ) with layer charge localized mainly (75%) in the octahedral sheet, containing sodium, calcium and potassium as charge compensating interlayer cations (e.g. Kulesza-Wiewióra 1976). The cation exchange capacity of the clay is 84 meq per 100 g. The starting material for pillaring procedures was the sodium form of this montmorillonite, obtained by treatment with 1N NaCl solution, followed by washing and dialysis till the negative result of reaction for the presence of  $\text{Cl}^-$ . The product, air dried at  $80^\circ\text{C}$ , is referred to as Na-mt.

### Pillaring with polycations of Al, Ti and Zr

Montmorillonites pillared with Al-polycations (abbreviated: Al-pillared) were obtained according to the procedure described by Vaughan et al. (1980). Commercial aluminium hydroxychloride manufactured by Reheis Chemical Company was added to the vigorously stirred water suspension of montmorillonite, in the amount corresponding to 6 mmol  $\text{Al}^{3+}$  per gram of clay. After 30 min. of stirring the pH of the suspension was brought down to 2 with a diluted HCl solution and the mixture heated at  $70^\circ\text{C}$  for 30 min. After washing till the removal of  $\text{Cl}^-$  and drying in air at  $80^\circ\text{C}$ , the resulting solid was referred to as Al-mt, and after additional calcination in air at  $400^\circ\text{C}$  as Al-PILC.

Montmorillonites pillared with titanium polycations (abbreviated: Ti-pillared) were prepared following the procedure described by Sterte (1986). Titanium polycations were obtained by partial hydrolysis of  $\text{TiCl}_4$  (Fluka, pract.) with 6M HCl. The solution was further diluted to give final concentration of Ti equal 0.82 M and of HCl 0.11 M. The pillaring solution was added dropwise to the vigorously stirred aqueous suspension containing 4g/l of Na-mt in the amount corresponding to 10 mmol  $\text{Ti}^{4+}$  per gram of clay. The resulting product was stirred for 3 h at room temperature and then washed free of  $\text{Cl}^-$ . The air-dried product was described as Ti-mt, and after additional calcination in air at  $400^\circ\text{C}$  as Ti-PILC.

Montmorillonites pillared with zirconium polycations were prepared according to the procedure proposed by Yamanaka and Brindley (1979). A 0.1 M  $\text{ZrOCl}_2$  solution was added to a water suspension containing about 4g/l of Na-mt in the amount corresponding to 6 mmol  $\text{Zr}^{4+}$  per gram of clay. The mixture was allowed to age for 3 h at 313 K under continuous stirring. The resulting material, denoted Zr-mt, was centrifuged, washed free of  $\text{Cl}^-$  and dried at



353 K. After calcination in air at 773 K for 3 h the product was referred to as Zr-PILC.

#### Preparation of transition metal-doped pillared montmorillonites

Three procedures were used to incorporate copper or vanadium into Al-, Ti-, and Zr-pillared clays (Bahranowski, Serwicka 1993a, b; Bahranowski et al. 1996c; Bahranowski et al. 1997; Bahranowski et al. 1998a, b; Bahranowski et al. in print<sup>a</sup>; Bahranowski et al. submitted). The first two were based on ion-exchange and adsorptive properties of pillared montmorillonites, both prior to and after calcination. The third procedure consisted in simultaneous insertion of pillaring polycations and the cations of the dopants; the process was described as co-pillaring. Aqueous solutions of copper nitrate and vanadyl sulphate were used as sources of the relevant transition metal ions.

**Procedure 1.** The calcined Al-PILC, Ti-PILC, or Zr-PILC sample (in general: Me-PILC where Me is a pillaring cation) was subjected to exchange with 0.1 M  $\text{Cu}(\text{NO}_3)_2$  or  $\text{VOSO}_4$ , thoroughly washed, dried and calcined at 400°C. To increase the amount of the dopant, the exchange procedure was repeated. The resulting samples were referred to as  $\text{R}_x\text{-Me-PILC}$  (R — cation of dopant, x — number of exchange treatments).

**Procedure 2.** The uncalcined Al-mt, Ti-mt, or Zr-mt (in general: Me-mt) sample was subjected to a single exchange treatment with the solution of dopant, following the experimental conditions of procedure 1. The resulting samples were referred to as R-(Me)-mt, and after calcination at 400°C as R-(Me)-PILC.

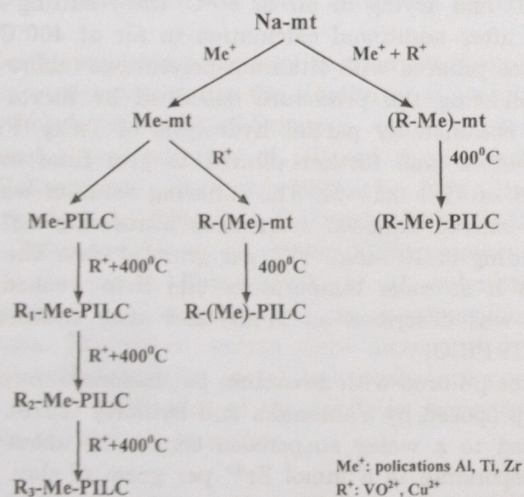


Fig. 1. Schematic description of preparation procedures

**Procedure 3.** The pillaring solution was obtained by addition of a solution of the dopant into the vigorously stirred solution of Me polycations, in the amount of ca. 10 mol%. The pillaring procedure was carried out as in the case of pure pillared forms of the relevant polycations. After washing and drying the samples are referred to as (R-Me)-mt, and after calcination in air at 400°C as (R-Me)-PILC.

The general scheme showing the preparation of transition metal ion doped pillared montmorillonites is presented in Fig. 1.

Cu<sup>2+</sup>- or VO<sup>2+</sup>-exchanged non-pillared montmorillonite, used as reference samples in ESR experiments, were obtained by stirring Na-mt with 0.1 M solutions of copper nitrate or vanadyl sulphate, followed by washing and drying. After calcination at 400°C for 1 h the products were referred to as R-mt(400).

#### PHYSICO-CHEMICAL CHARACTERIZATION

X-ray diffraction, chemical analysis and nitrogen adsorption studies

##### Al-pillared montmorillonites

Table 1 shows the  $d_{001}$  basal spacings, total specific surface areas ( $S^{\text{BET}}$ ), specific pore surface areas ( $S^{\text{t}}_{\text{mic}}$ ), specific pore volumes ( $V^{\text{t}}_{\text{mic}}$ ) and analytically determined content of Al, V and Cu (expressed as amount of the respective oxide) in Al-pillared montmorillonites. The BET specific surface areas ( $S^{\text{BET}}$ )

TABLE 1  
Basal spacings, surface area, porosity and chemical analysis data for the Cu- and V-doped Al-pillared clays

Sample	$d_{001}$ [Å]	$S^{\text{BET}}$ [m <sup>2</sup> /g]	$S^{\text{t}}$ [m <sup>2</sup> /g]	$S^{\text{t}}_{\text{mic}}$ [m <sup>2</sup> /g]	$V^{\text{t}}_{\text{mic}}$ [cm <sup>3</sup> /g]	CuO [wt.%]	V <sub>2</sub> O <sub>5</sub> [wt.%]	Al <sub>2</sub> O <sub>3</sub> [wt.%]
Al-mt	21.0	335	427	384	0.1343	—	—	25.87
Al-PILC	18.4	250	315	274	0.0939	—	—	26.94
Cu <sub>1</sub> -Al-PILC	18.2	192	223	181	0.0670	0.99	—	27.11
Cu <sub>2</sub> -Al-PILC	18.0	175	213	175	0.0621	1.89	—	26.22
Cu <sub>3</sub> -Al-PILC	18.0	168	205	167	0.0597	2.25	—	26.19
Cu-(Al)-PILC	18.2	182	231	193	0.0700	0.84	—	26.70
(Cu-Al)-PILC	18.6	274	349	315	0.1077	0.04	—	26.58
V <sub>1</sub> -Al-PILC	17.4	242	n.d.	n.d.	n.d.	—	0.98	27.96
V <sub>2</sub> -Al-PILC	17.4	235	n.d.	n.d.	n.d.	—	1.60	27.30
V <sub>3</sub> -Al-PILC	17.4	230	n.d.	n.d.	n.d.	—	1.67	27.20
V-(Al)-PILC	18.4	161	n.d.	n.d.	n.d.	—	1.21	28.48
(V-Al)-PILC	20.1	14	n.d.	n.d.	n.d.	—	1.37	31.98



available for all investigated materials are used to compare the samples. Whenever available, also the specific surface areas determined by  $t$  method are given ( $S^t$ ). The latter method is more suitable for assessment of total surface areas of microporous systems (Sing et al. 1985). It also provides information on the contribution of micropores to the total surface area and total pore volume. Analysis of the data gathered in Table 1 allows to assess the efficiency of the pillaring and/or doping procedure and its influence on the structural and textural properties of the modified clays.

Insertion of Al polycations into the interlayer space of the parent montmorillonite pushes the layers apart and results in an increase of the layer-to-layer distance  $a$  ( $a = d_{001} - 9.6$  where  $9.6 \text{ \AA}$  is the layer thickness) from ca.  $3 \text{ \AA}$  for Na-mt to  $11.4 \text{ \AA}$  for Al-mt. After calcination this distance decreases, but the gallery height is still large comparing to that of Na-mt and is equal to ca.  $9 \text{ \AA}$ . Textural parameters derived from the nitrogen adsorption studies confirm that the pillaring was efficient and resulted in a high surface area porous material (Bahranowski et al. 1998b; Bahranowski et al. submitted). The specific surface area increases from ca.  $30 \text{ m}^2/\text{g}$  for Na-mt to over  $400 \text{ m}^2/\text{g}$  for Al-mt. Analysis of the data shows that the effect is due mainly to the increase of the micropore surface. Indeed, the sample possesses a significant micropore volume of ca.  $0.13 \text{ cm}^3/\text{g}$ . Calcination leads to a certain decrease of the specific surface area and microporosity. This is due to the shrinking of the pillars associated with dehydration/dehydroxylation of polycations occurring upon thermal treatment. Nevertheless, the textural parameters of the calcined material, i.e. its specific surface area over  $300 \text{ m}^2/\text{g}$ , the gallery height of  $9 \text{ \AA}$  and the dominant micropore diameter of  $6.5 \text{ \AA}$ , make the Al-PILC an interesting material for a potential catalytic application.

Insertion of copper or vanadium into Al-PILC or Al-mt matrices by means of cation exchange allows to fix up to 2.3 wt.% CuO and 1.7 wt.%  $\text{V}_2\text{O}_5$ . Consecutive cation exchange/calcination cycles increase the loading with transition metal ions and result in a decrease of the specific surface area. The analysis of microporosity carried out for the copper-doped samples shows that multiple doping tends to decrease the surface area and volume of micropores. This is a strong indication that the transition metal ions become fixed mainly in the micropore system of the pillared matrix.

The properties of materials obtained by co-pillaring depend on the nature of the co-pillared dopant. In the case of pillaring with Cu-containing solution the resulting calcined material shows the best developed texture, manifested as the highest total surface area, micropore surface area and micropore volume. It is unlikely that the effect is due to the presence of copper dopant. Its amount in the solid is very small ( $<0.1 \text{ wt.}\%$  CuO), which shows that the major part of copper present in the pillaring solution (ca.  $10 \text{ mol}\%$ ) does not enter the structure of the pillared clay. However, the XRD pattern of the co-pillared sample points to a better structural ordering in this material when compared to Al-PILC. Such an effect could contribute to a better accessibility of the

micropore system (Bahranowski et al., submitted). In the case of (V-Al)-PILC sample, the  $d_{001}$  spacing is higher than that of Al-PILC, the vanadium content significant (ca.  $2 \text{ wt.}\%$ ) but the specific surface area comparable with that of the non-pillared Na-mt. This means that although intercalation was effective, the interlayer space is not accessible for nitrogen adsorption. Analysis of the data in Table 1 shows that the amount of aluminium incorporated upon co-pillaring in the presence of vanadyl ions is much higher than in Al-PILC. Suitable calculations show that in the case of (V-Al)-PILC sample the interlayer space is completely filled with Al oligomers (Bahranowski, Serwicka 1993). It seems that in the presence of vanadyl ions the net charge on the Al oligomers decreases and, consequently, more polycations are required for compensation of the layer charge leading to the densely packed interlayer.

#### Ti-pillared montmorillonites

Table 2 shows the structural, textural and compositional data obtained for Ti-pillared montmorillonites doped with copper or vanadium.

Intercalation of Ti-polycations between the montmorillonite layers increases the  $d_{001}$  spacing to over  $27 \text{ \AA}$ . Thus, the layer-to-layer distance amounts to ca.  $18 \text{ \AA}$ , which indicates that in the Ti-pillared montmorillonite the pore sizes may lay at the micropore/mesopore border ( $20 \text{ \AA}$  according to IUPAC classification). Specific surface areas of clays modified in such a way are around  $300 \text{ m}^2/\text{g}$ . The amount of incorporated  $\text{TiO}_2$  is ca.  $40 \text{ wt.}\%$ . Similarly as in the case of Al-pillared clays, dehydration and dehydroxylation of polycations occurring upon calcination results in a slight decrease of the  $d_{001}$  spacing (to ca.  $26 \text{ \AA}$ ) and lowering of the specific surface area.

TABLE 2

Basal spacings, surface area, porosity and chemical analysis data for the Cu- and V-doped Ti-pillared clays

Sample	$d_{001}$ [ $\text{\AA}$ ]	$S^{\text{BET}}$ [ $\text{m}^2/\text{g}$ ]	$S^t$ [ $\text{m}^2/\text{g}$ ]	$S^{\text{mic}}$ [ $\text{m}^2/\text{g}$ ]	$V^{\text{mic}}$ [ $\text{cm}^3/\text{g}$ ]	CuO [wt.%]	$\text{V}_2\text{O}_5$ [wt.%]	$\text{TiO}_2$ [wt.%]
Ti-mt	27.6	264	268	236	0.0804	—	—	n.d.
Ti-PILC	26.0	276	267	231	0.0800	—	—	43.20
$\text{Cu}_1$ -Ti-PILC	26.0	283	278	231	0.0835	1.42	—	41.20
$\text{Cu}_2$ -Ti-PILC	25.0	274	268	215	0.0804	1.82	—	39.33
$\text{Cu}_3$ -Ti-PILC	25.0	264	263	214	0.0804	2.05	—	34.76
$\text{Cu}-(\text{Ti})$ -PILC	23.0	283	278	234	0.0835	1.49	—	41.61
$(\text{Cu-Ti})$ -PILC	26.0	313	308	254	0.0924	0.09	—	49.89
$\text{V}_1$ -Ti-PILC	26.0	271	n.d.	n.d.	n.d.	—	1.62	42.10
$\text{V}_2$ -Ti-PILC	26.0	250	n.d.	n.d.	n.d.	—	3.29	41.00
$\text{V}_3$ -Ti-PILC	25.0	248	n.d.	n.d.	n.d.	—	4.28	41.50
$\text{V}-(\text{Ti})$ -PILC	25.0	362	n.d.	n.d.	n.d.	—	2.29	n.d.
$(\text{V-Ti})$ -PILC	25.9	225	n.d.	n.d.	n.d.	—	0.10	n.d.



Doping procedure based on cation exchange with Ti-PILC or Ti-mt allows to incorporate up to 4.3 wt.% of V<sub>2</sub>O<sub>5</sub> and 2 wt.% of CuO (Bahranowski et al. 1997; Bahranowski et al. submitted). Consecutive exchange/calcination procedures result in an increase of the amount of dopant. Insertion of copper affects the textural parameters to a minor degree, although a slight decreasing trend in specific surface areas and micropore volumes is observed for the Cu<sub>x</sub>-(Ti-PILC) series. The decrease of the specific surface area is more pronounced upon doping with vanadium. These observations are consistent with the picture of dopant entering the micropore system.

Only small amounts of dopants can be incorporated into the clay lattice by means of co-pillaring (ca. 0.1 wt.%). Nevertheless, the textural properties of the doped samples differ from their undoped counterparts. In the case of (V-Ti)-PILC material, the specific surface area is lower than that of Ti-PILC. The slightly lower d<sub>001</sub> spacing observed in the co-pillared sample indicates that this may be due to a slightly smaller size of Ti polycations formed in the presence of vanadyl ions. On the contrary, the specific surface area of (Cu-Ti)-PILC sample is the highest of all Ti-pillared materials. Bearing in mind that a similar effect was observed for the (Cu-Al)-PILC sample, it is suggested that also here a better distribution of pillars in the interlayer spaces may be responsible for the improved textural properties of (Cu-Ti)-PILC.

#### Zr-pillared montmorillonites

The results of XRD, nitrogen adsorption and chemical analysis of the copper or vanadium- doped Zr-pillared montmorillonites are presented in Table 3.

TABLE 3

Basal spacings, surface area, porosity and chemical analysis data for the Cu- and V-doped Zr-pillared clays

Sample	d <sub>001</sub> [Å]	S <sup>BET</sup> [m <sup>2</sup> /g]	S <sup>t</sup> [m <sup>2</sup> /g]	S <sup>t</sup> <sub>mic</sub> [m <sup>2</sup> /g]	V <sup>t</sup> <sub>mic</sub> [cm <sup>3</sup> /g]	CuO [wt.%]	V <sub>2</sub> O <sub>5</sub> [wt.%]	ZrO <sub>2</sub> [wt.%]
Zr-mt	20.1	242	320	280	0.0948	—	—	14.74
Zr-PILC(Cu)	17.7	193	239	197	0.0715	—	—	14.48
Zr-PILC(V)	17.7	213	276	234	0.0800	—	—	16.40
Cu <sub>1</sub> -Zr-PILC	18.0	182	232	191	0.0670	0.74	—	13.01
Cu <sub>2</sub> -Zr-PILC	17.9	180	229	188	0.0664	1.36	—	12.88
Cu <sub>3</sub> -Zr-PILC	17.9	180	248	208	0.0719	1.81	—	12.44
Cu-(Zr)-PILC	17.5	206	266	229	0.0807	0.77	—	14.25
(Cu-Zr)-PILC	18.4	202	271	239	0.0812	0.04	—	15.39
V <sub>1</sub> -Zr-PILC	17.2	227	282	240	0.0840	—	0.6	15.90
V <sub>2</sub> -Zr-PILC	17.0	201	n.d.	n.d.	n.d.	—	1.1	15.70
V <sub>3</sub> -Zr-PILC	17.0	200	n.d.	n.d.	n.d.	—	1.2	15.13
V-(Zr)-PILC	11.6	92	99	61	0.0260	—	2.8	7.60
(V-Zr)-PILC	17.4	188	232	195	0.0690	—	0.1	18.90

Insertion of Zr polycations into the interlayer spaces of montmorillonite results in an increase of the d<sub>001</sub> basal spacing to ca. 20 Å. The specific surface area increases to over 300 m<sup>2</sup>/g and the amount of incorporated zirconium corresponds to ca. 15 wt.% of ZrO<sub>2</sub>. Dehydration and dehydroxylation of intercalated polycations during calcination leads to a decrease of the d<sub>001</sub> to ca. 18 Å and lowering of the surface area to ca. 240 m<sup>2</sup>/g.

The results of doping with vanadium by means of cation exchange differ depending on whether the Zr-pillared matrix is calcined or non-calcined (Bahranowski et al. in print<sup>a</sup>). In the first case ca. 1 wt.% of V<sub>2</sub>O<sub>5</sub> can be loaded into the Zr-PILC matrix. The consecutive doping, similarly as in the case of Al-PILC and Ti-PILC supports, results in a slight decrease of surface area which is consistent with the concept of dopant entering the interlayer spaces of pillared clay. In the case of non-calcined Zr-mt support, the amount of incorporated vanadium is almost three times higher but the content of zirconium decreases by half. The V-(Zr)-PILC sample possesses also a distinctly lower specific surface area and its XRD patterns shows a broad asymmetric peak with the maximum around 11.6 Å. The effect is due to the fact that the exchange treatment of the uncalcined Zr-mt clay with VO<sup>2+</sup> solution results in a partial expulsion of Zr polycations from the interlayer space and their replacement by the vanadyl cations. As a result the sample contains more vanadium, less zirconium and the layered structure suffers a partial collapse due to the insufficient amount of propping pillars. When the sample is subjected to treatment with ethylene glycol, the structure swells up and the 11.6 Å low angle reflection splits into two peaks appearing at 18.2 and 9.2 Å. This indicates that the sagging of the layers in the areas with no pillars is reversible and after filling the interlayer space with ethylene glycol the pattern characteristic of a typical Zr-pillared clay emerges.

Insertion of copper by means of cation exchange allows to introduce ca. 2 wt.% of CuO and successive dopings lead to a small decrease of surface area and micropore volumes indicating that the dopant is fixed within the micropore system. The Cu-(Zr)-PILC sample obtained by doping of uncalcined Zr-pillared matrix shows an increase of specific surface area with respect to Zr-PILC. The possible reason for this could be the expulsion of some of Zr polycations by copper ions. The effect, if present, is much less pronounced than in the case of V-(Zr)-PILC sample. The zirconia content is only slightly lower than in the undoped matrix. Nevertheless, the removal of a small amount of pillars, while not sufficient for causing any collapse of the layers, would increase the accessibility of the micropore system for nitrogen adsorption and result in a higher value of the micropore surface area and volume.

The effect of co-pillaring depends on the nature of the co-pillared cation. The use of the copper-containing pillaring solution produces the sample of the highest specific surface area among the calcined Zr-pillared materials. Again, the small amount of incorporated copper shows that the dopant cannot be directly responsible for the improved texture. The data in Table 3 indicate that the



basal spacing of the co-pillared sample and its Zr content are slightly higher than in undoped Zr-PILC material. Both facts point to some changes in the nature of the pillaring species formed in the presence of copper salt solution, possibly involving a higher degree of polymerization. In the case of (V-Zr)-PILC sample the amount of incorporated dopant is also at the level of 0.1 wt.% but the amount of incorporated zirconia is by 4% higher and the specific surface area lower than that of undoped Zr-PILC. Since no important change of the  $d_{001}$  is observed, these data indicate that in the  $VO^{2+}$ -containing pillaring solution a lowering of the charge on the polycation occurs leading to a more dense packing of pillars and reduction of the surface area available for nitrogen adsorption.

An important practical observation, valid for all V- or Cu-doped pillared clays and based on a number of synthesis experiments, is that the experimental procedures are reasonably reproducible as far as the textural and compositional properties of the samples are concerned.

### Cation exchange capacity

The results of cation exchange capacity (CEC) measurement of Al-, Ti-, and Zr-pillared montmorillonites doped with copper or vanadium are gathered in Table 4. The data were obtained using the manganese method of CEC determination which consists in introduction of  $Mn^{2+}$  ions on cation exchange positions, reexchange with sodium and determination of the amount of manganese ions released to the solution by AES ICP technique. The CEC of the sodium form of the parent montmorillonite is 84 meq/100g. The CEC of calcined samples

Cation exchange capacities of modified pillared clays

TABLE 4

Sample	CEC [meq/100g]	Sample	CEC [meq/100g]	Sample	CEC [meq/100g]
Al-PILC	19	Ti-PILC	19	Zr-PILC	22
Cu <sub>1</sub> -Al-PILC	32	Cu <sub>1</sub> -Ti-PILC	38	Cu <sub>1</sub> -Zr-PILC	22
Cu <sub>2</sub> -Al-PILC	27	Cu <sub>2</sub> -Ti-PILC	37	Cu <sub>2</sub> -Zr-PILC	20
Cu <sub>3</sub> -Al-PILC	26	Cu <sub>3</sub> -Ti-PILC	35	Cu <sub>3</sub> -Zr-PILC	19
Cu-(Al)-PILC	27	Cu-(Ti)-PILC	32	Cu-(Zr)-PILC	20
(Cu-Al)-PILC	27	(Cu-Ti)-PILC	20	(Cu-Zr)-PILC	26
		V <sub>1</sub> -Ti-PILC	42	V <sub>1</sub> -Zr-PILC	23
		V <sub>2</sub> -Ti-PILC	49	V-(Zr)-PILC	35
				(V-Zr)-PILC	31

decreases to ca 20 meq/100g. It shows that formally only ca. 1/4 of protons formed during dehydroxylation of pillaring polycations, which in the calcined materials act as charge-compensating species, are available for cation exchange experiment. In the case of Al-PILC and Ti-PILC supports doping with copper and vanadium results in an increase of the CEC, while no change is observed upon doping of the Zr-PILC matrix. Bearing in mind that the R<sub>x</sub>-Me-PILC samples were calcined after each doping procedure, the result means that in the doped Al- and Ti-pillared clays the binding of compensating protons to the pillared clay lattice becomes weaker. The CEC of the co-pillared clays tends to be slightly higher than that of undoped Me-PILC materials.

Summarizing, the data in Table 4 show that the clay samples subjected to any of the modification procedures used in this work retain 20—35% of the original CEC. In particular, multiple exchange/calcination cycles do not affect the CEC in a significant way, which leaves possibilities open for further modifications.

### Thermal analysis

Thermal analysis was performed in order to check on the influence of applied modification methods on the thermal stability of transition metal-doped pillared clays.

### Na-montmorillonite

Na-montmorillonite was taken as a reference for thermal characteristics of pillared montmorillonites. The DTA profile obtained for this sample is typical of such materials (Stoch 1974) and shows an endothermic effect with maximum around 150°C and weight loss of 9%, corresponding to the dehydration of interlayer sodium cations, an endothermic effect with maximum at 700°C and weight loss of 4%, associated with dehydroxylation of the clay layers, an endothermic effect at 880°C due to the collapse of the montmorillonite structure and an exothermic effect at 920°C reflecting the formation of new solid phases.

### Al-pillared montmorillonites

The DTA diagrams of Al-mt differs substantially from that of Na-mt (Fig. 2). The low temperature endothermic effect at 160°C due to the dehydration of Al polycations is more pronounced (ca. 15% weight loss) and shows an asymmetry towards higher temperatures. The endothermic effects at 400 and 500°C are associated with the dehydroxylation of polycations which results also in 4.5% weight loss. The final stages of polycations dehydroxylation overlap with the effect characteristic of dehydroxylation of clay layers which is observed at temperature lower by 20°C than in Na-mt.



The non-swelling Al-PILC sample obtained by calcination of Al-mt at 400°C shows a strong endothermic peak at 150°C associated with the release of water physisorbed in the pore system of the sample (ca. 12% weight loss). The broad endothermic peak at 460°C is due to the removal of the remnants of hydroxyls attached to Al pillars. Dehydroxylation of the octahedral sheet gives an endothermic peak with maximum around 670°C.

Successive doping with vanadium (samples V<sub>x</sub>-Al-PILC) has no significant influence on the DTA profile of Al-PILC support.

The DTA profile of the co-pillared (V-Al)-mt sample, which from the structural and chemical analyses is known to have interlayers fully loaded with Al polycations, looks quite different (Fig. 2). The release of hydration water gives a strong, broad, endothermic peak at 150°C, tailing off towards high temperatures. The high weight loss of 22% associated with this effect is consistent with the

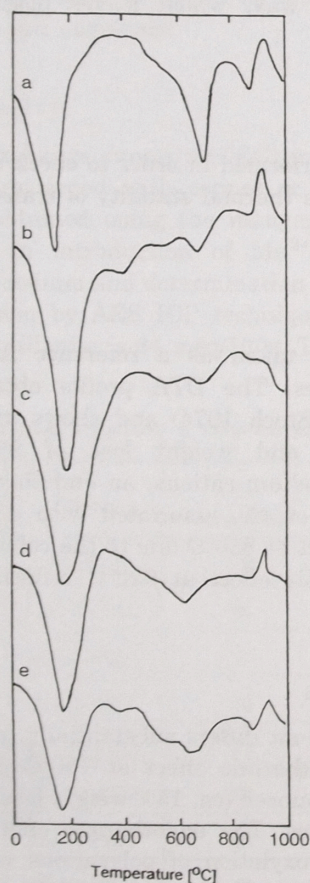


Fig. 2. DTA profiles of modified clays: a — Na-mt, b — Al-mt, c — (V-Al)-mt, d — Ti-mt, e — Zr-mt

exceptionally high amount of pillaring species present in this sample. The dehydroxylation of the layer occurs around 680°C. The relatively large quantities of Al and V in the interlayer spaces cause that the temperature at which crystallisation of new phases occurs (820°C) is by 100°C lower than in the case of Al-mt.

The diagram obtained for the co-pillared (Cu-Al)-mt sample is similar to that of Al-mt, which is understandable in view of the small amount of incorporated Cu and similar content of Al pillars.

#### Ti-pillared montmorillonites

Thermal analysis of Ti-mt montmorillonite containing Ti-polycations in the interlayer shows that the removal of hydration water (14.5 wt.%) is associated with an endothermic effect at 150°C, while dehydroxylation of pillars occurs gradually and gives diffuse endothermic peaks at 370 and 500°C (weight loss 2.5%) (Fig. 2). The latter overlaps with the effect of dehydroxylation of the octahedral sheets in montmorillonite with maximum at 670°C. In the presence of Ti polycations the temperature of montmorillonite decomposition increases to 930°C and the temperature of crystallisation of new phases to 950°C.

The endothermic effect at 120°C present in the DTA profile of the Ti-PILC sample obtained by calcination of Ti-mt at 400°C is due to the removal of water physisorbed within the pore system of the clay sample. The release of the rest of the hydroxyls remaining at the surface of Ti pillars after calcination is responsible for weak endothermic effects at 390 and 500°C.

In the case of V<sub>x</sub>-Ti-PILC samples containing higher quantities of V (>2 wt.% V<sub>2</sub>O<sub>5</sub>), beside the weak endothermic effects attributed to removal of hydroxyls attached to Ti pillars (maxima at 400 and 500°C) additional weak peaks, probably due to OH groups attached to vanadium centres are seen (250 and 350°C). The dominant effect is the dehydration with maximum around 120°C resulting from the high porosity of the material.

The co-pillared (V-Ti)-mt and (Cu-Ti)-mt forms of montmorillonite, containing less than 0.1 wt.% of dopants, give DTA profiles similar to that of undoped Ti-mt.

#### Zr-pillared montmorillonites

In the case of Zr-mt sample the strong maximum of the effect associated with the evolution of water of hydration appears at 150°C (weight loss 15%) (Fig. 2). The endothermic peaks at 400 and 580°C are attributed to dehydroxylation of Zr polycations. The latter overlaps with the thermal effect of dehydroxylation of the layers. Similarly as in the case of Ti-mt, the presence of zirconium polycations retards the processes of the montmorillonite destruction (920°C) and recrystallisation of new phases (960°C).



The diagrams obtained for the co-pillared samples (V-Zr)-mt and (Cu-Zr)-mt, both containing very little dopants, show no important differences with respect to the undoped Zr-mt sample.

Summarizing, while the pillaring slightly reduces the thermal stability of the layers, decreasing by 20–30°C the temperature of the dehydroxylation of the octahedral sheet due to the corrosive action of protons released upon dehydration/dehydroxylation of pillars, doping with transition metal ions has no deteriorating effect on the stability of hydroxyls in the octahedral sheet. As a result, the Cu- or V-doped pillared clays may be considered thermally stable up to ca. 650°C.

### ESR analysis

ESR, owing to its sensitivity to the minor changes in the nearest coordination sphere of a paramagnetic ion, represents an excellent tool for determination of the location and the electronic structure of paramagnetic centres. The ions of dopants used in this work, i.e.  $\text{Cu}^{2+}$  and  $\text{VO}^{2+}$ , possess unpaired electrons and give ESR spectra. Moreover, both ions possess non zero nuclear spins ( $I = 7/2$  for  $^{51}\text{V}$  and  $I = 3/2$  for  $^{63,65}\text{Cu}$ ). In the case of dispersed centres, interaction of the unpaired electron with the nuclear spin results in an appearance of a characteristic hyperfine structure which splits the spectrum components into  $2I + 1$  lines. The appearance of the hyperfine structure facilitates the identification of the paramagnetic species and broadens the interpretation possibilities. In all cases the ESR parameters, i.e. the values of  $g$  tensor components and the values of hyperfine splittings were determined by the best fit computer simulations. Fig. 3 shows an example of fits considered satisfactory.

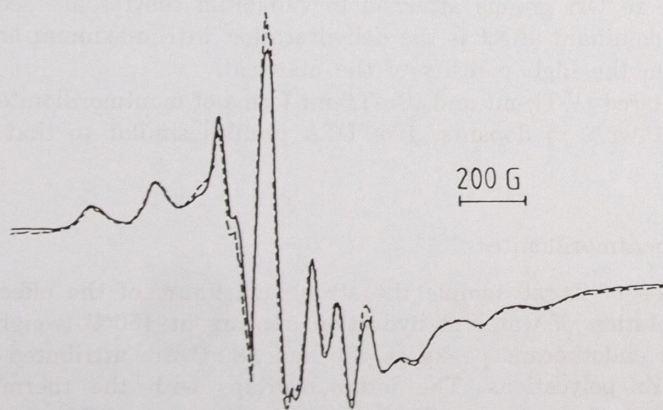


Fig. 3. Example of fitting between the experimental (solid line) and calculated (dashed line) ESR spectrum of  $\text{V}_1\text{-Ti-PILC}$

Analysis of the ESR spectra of V-doped pillared clays allowed to conclude that the location of V centres within the montmorillonite structure depends on the method of doping and on the nature of pillars (Bahranowski, Serwicka 1993b; Bahranowski et al. 1996b). In the case of co-pillared samples, the V centres are always associated with the pillars. Insertion of vanadium by the post-pillaring exchange treatment into Al- or Ti-pillared clays results in V centres bound to the pillars. In Zr-pillared samples, beside the V centres attached to the pillars, also V species associated with the interlayer surface of Si-O tetrahedral sheet play an important role. The electronic structure of V centres produced by co-pillaring differs somewhat from that of other V centres. The difference consists in the higher degree of the covalency within the V-O bonds perpendicular to the vanadyl  $\text{V}=\text{O}$  bond. It turns out that this difference is important in determining the catalytic properties of the V centres concerned (Bahranowski et al. 1995b; Bahranowski et al. 1997; Bahranowski et al. in print<sup>a</sup>; Bahranowski et al. in print<sup>b</sup>).

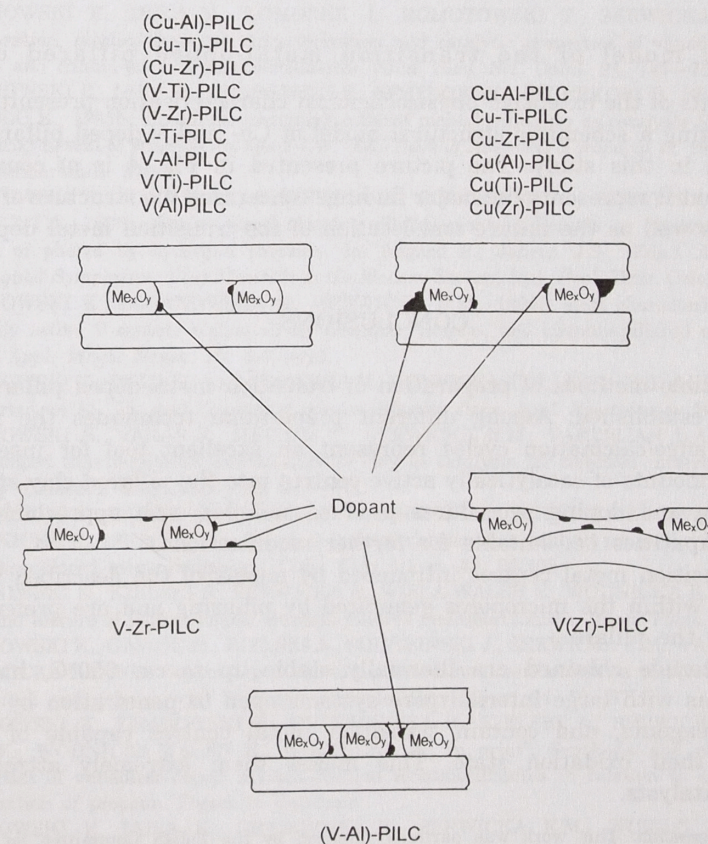


Fig. 4. Schematic structural model of clays modified by pillaring and transition metal ion



ESR analysis of Cu-doped Al-, Ti-, and Zr-pillared montmorillonites (Bahranowski et al. 1996c) showed that before calcination the major species present in pillared clays exchanged with copper at low pH are physisorbed square planar tetraaquo-complexes  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ . Only at the surface of uncalcined Al pillars a chemisorption of copper ions occurs, giving an inner-sphere square planar complex  $[\text{Cu}(\text{AlO})_n(\text{H}_2\text{O})_{4-n}]^x$ . Calcination of the exchanged samples at 400°C brings about a significant change of the  $\text{Cu}^{2+}$  environment reflected in the change of ESR parameters. The most characteristic feature is the increased covalency of the Cu–O in-plane bonding due to the attachment of copper to lattice oxygens as a result of dehydration/dehydroxylation accompanying thermal treatment. Analysis of the ESR parameters shows that in the thermally treated samples the cupric ions are attached to the pillars. The ESR spectra of all calcined materials show, besides the signal of isolated  $\text{Cu}^{2+}$  ions responsible for the signals with resolved hyperfine structure, a structureless component characteristic of clustered copper ions.

#### Structural model of the transition metal-doped pillared clays

The results of the extensive physicochemical characterisation presented above allow proposing a schematic structural model of Cu- and V-doped pillared clays investigated in this study. The picture presented in Fig. 4 is of course very simplified, but it represents the major findings concerning the structure of pillared materials as well as the nature and location of the transition metal dopants.

### CONCLUSIONS

Reproducible methods of preparation of transition metal-doped pillared clays have been established. Among different preparation techniques the multiple cation exchange/calcination cycles represent an excellent tool for insertion of controlled amounts of catalytically active centres into the pillared clay structure. All pillaring and doping procedures produce samples with appreciable cation exchange capacities i.e. suitable for further modifications.

The transition metal centres introduced by means of the described methods are located within the micropores generated by pillaring and are preferentially attached to the pillars.

The materials obtained are thermally stable up to ca. 650°C, have high surface areas with large internal pore systems open to penetration by gaseous or liquid reagents, and contain transition metal centres capable of a swift change of their oxidation state. This makes them extremely attractive as potential catalysts.

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# PODPIERANE MONTMORILLONITY DOTOWANE KATALITYCZNIE AKTYWNYMI METALAMI PRZEJŚCIOWYMI CZĘŚĆ 1. SYNTEZA I CHARAKTERYSTYKA FIZYKOCHEMICZNA

## Streszczenie

Praca podsumowuje dorobek autora w zakresie projektowania, preparatyki i charakteryzowania montmorillonitów podpieranych glinem, tytanem i cyrkonem oraz dotowanych miedzią lub wanadem. Opisane zostały różnorodne procedury dotowania, a do charakterystyki fizykochemicznej preparatów wykorzystano metodę dyfrakcji rentgenowskiej, adsorpcję azotu, analizę chemiczną, pomiar pojemności wymiany kationów, analizę termiczną i spektroskopię EPR. Zaproponowano strukturalne modele podpieranego montmorillonitu dotowanego miedzią lub wanadem uwzględniające zarówno właściwości teksturalne próbek, jak i lokalizację centrów Cu i V w strukturze podpieranego minerału.