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PREPARATION AND PHYSICO-CHEMICAL CHARACTERIZATION OF VANADIUM-DOPED PILLARED MONTMORILLONITES

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Abstract: Procedures leading to preparation of vanadium-doped alumina-pillared montmorillonites are described and physico-chemical characterization (chemical analysis, XRD, BET, DTA and ESR) of the products is provided. Results show that introduction of vanadium into the pillared montmorillonites leads to a rigid association of the dopant with pillars, irrespective of the mode of preparation. The XRD and DTA data indicate that oligocationic species formed during "co-pillaring" differ structurally from the standard Al_{13} ions. It is argued that blocking of the interlayer may occur on "co-pillaring" due to the more dense packing of oligocations, brought about by a decrease in their average charge.

Key words: pillared clays, vanadium catalysts, ESR.

Introduction

Vanadium oxides deposited on various oxidic supports (Al_2O_3, TiO_2, SiO_2) have been since long widely used as catalysts in many important oxidation processes (Bond & Konig 1982; Gasior et al. 1094; Grzybowska-Swierkosz & Haber 1984; Miyata et al. 1987). More recently, due to increased pressure on environmental protection, their application, instead of costly noble metals, for removal of nitrogen oxides from flue gases, has become particularly important (Bosch & Jansen 1988; Handy et al. 1992).

It is well known that catalytic performance is very sensitive to the composition of the suport, its crystallinity, and even crystallographic phase. Therefore modification of the physico-chemical properties of the supporting oxidic particles is one of the ways to improve the catalyst quality.

Pillared clays (PILC) are characterized by high surface area, good thermal stability and accessibility of the interlayer space for gases and vapours. These qualities, together with advantageous acid-base properties have prompted numerous attempts of their application in catalysis (Vaughan 1988).

The intention of the present authors was to use pillared montmorillonites to design a new class of supported vanadia catalysts, with the pillaring procedure serving as a means to produce alumina particles of unique properties. Thus, the smectite can be regarded as a carrier for the actual oxide support. Small size of pillars provides support particles of advantageous high surface to bulk ratio, while their separation together with firm bonding to the PILC lattice should improve resistance against sintering as compared to conventional alumina carrier of similar crystallinity. In addition, one may also expect the montmorillonite-transition metal oxide systems to display both the acid-base and the redox catalytic functions, a desirable feature for many catalytic processes.

This paper presents the physico-chemical characterization of a series of vanadium-doped alumina-pillared montmorillonite catalysts obtained by various preparative procedures.

Methods of study

X-ray diffraction: XRD analyses were performed on oriented samples prepared by spreading about 0.5 ml of a water suspension of the sample on a glass slide, followed by drying at room temperature. The XRD patterns were obtained with a DRON-2 diffractometer using Ni-filtered CuKα radiation.

BET measurement: the BET surface area of the samples was determined from argon adsorption at 77 K, after outgassing at 473 for 2 h.

Chemical analysis: the chemical analysis was carried out on a Philips PU9100 Atomic Absorption Data Station.

Electron spin resonance: the ESR spectra were recorded at room temperature and at 77 K with an X-band SE/X (Technical University Wroclaw) spectrometer. DPPH and NMR field marker were used for determination of g factors. Prior to ESR measurement and further pre-treatment, the quartz tubes containing clay samples were stored over saturated NaCl solution (p_{H2O}= 26.8 Torr at 293 K) to assure constant hydration conditions.

Thermal analysis: DTA curves were recorded by a Derivatograph thermal analyser, at standard conditions.

Experimental data

Starting material: the smectite used in this study was <2μm particle size fraction of Milowice bentonite from Saturn deposits in Silesia, Poland, of the crystallochemical formula $Ca_{0.10}Na_{0.24}K_{0.28}(Al_{2.94}Fe_{0.40}Mg_{0.70})[(Si_{7.82}Al_{0.18})](OH)_4$ The cation-exchange capacity (CEC) of the clay is 76 mEq/100 g. Na-exchanged form, referred to as Na-mt was used as substrate for pillaring.

Al-pillared clay: aluminium-pillared clay was prepared according to the procedure described by Vaughan (1980) using commercial aluminium chlorhydroxide known as "chlorhydrol" (Reheis Chemical Co.). The product is referred to as Al-mt, and after calcination in air at 673 K for 20 hours as Al-PILC.

V-Al-pillared clay: three different procedures were used to introduce vanadium, two of which took advantage of cationic exchange capacities of Al-PILC and/or Al-mt, one, referred to as "co-pillaring", involved vanadium-containing pillaring solution.

a - Al-PILC clay was treated with 1N $VOSO_4$ (Merck, pure) solution, centrifuged and washed with distilled water till the supernatant was free of SO_4^{2-} as indicated by reaction with barium chloride. This product is further referred to as V-(Al-PILC).

b - Al-mt was treated with 1N $VOSO_4$ solution, centrifuged and washed with distilled water till the supernatant was free of SO_4^{2-}. This product is further referred to as (V-Al)-mt, and after calcination in air at 673 K for 20 hours as V(Al)-PILC.

c - V-Al pillaring agent was prepared by adding 0.04M $VOSO_4$ solution acidified to ph 3.5, to chlorhydrol diluted in water acidified with HCl to pH 4.0, in an amount slightly less than that causing permanent cloudiness of the solution. The clear liquid was allowed to age for 1 hour at room temperature. Then the water suspension of Na-mt was added dropwise to the pillaring solution. Further treatment was the same as in the case of Al-mt preparation, except that the final product was washed till negative reactions were obtained for presence of both the Cl^- and the SO_4^{2-}. Final concentrations employed were 10 g Na-mt/l suspension, 1 ml chlorhydrol/1 g Na-mt, 0.013 M $VOSO_4$. The product thus obtained is referred to as (V-Al)-mt, and after calcination in air at 673 K for 20 hour as (V-Al)-PILC.

Table 1: Basal spacing (d_{oo1}), specific surface area (S) and V content of the investigated clay samples.

Catalyst	d_{001}(Å)	S(m^2g^{-1})	wt%V_2O_5
Na-mt	12.5	21.8	-
Na-mt, 673 K, 20 h	10.0	17.8	-
V-mt	15.8	27.3	2.8
V-mt, 673 K, 20 h	10.1	19.8	2.8
Al-mt	21.0	361.4	-
Al-PILC	18.4	320.7	-
V-(Al-PILC)	18.4	280.8	1.4
V-(Al-mt)	19.2	191.9	0.7
V(Al)-PILC	18.4	160.5	0.7
(V-Al)-mt	23.3	15.8	2.2
(V-Al)-PILC	21.1	13.7	2.2

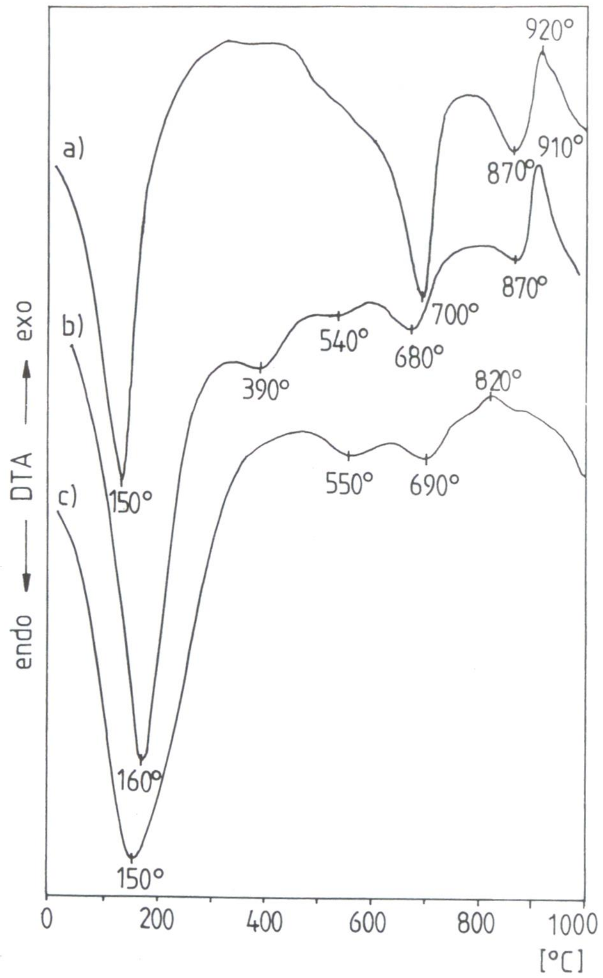

Fig. 1. DTA curves for: **a** - Na-mt, **b** - Al-mt and **c** - (V-Al)-mt.

VO^{2+}- exchanged montmorillonite: vanadyl-exchanged form of the montmorillonite was obtained by repeated treatment of the Na-mt with 1N solution of $VOSO_4$, followed by washing with distilled water till the supernatant was free of SO_4^{2-}. The product is further referred to as V-mt.

Reference V-Al sample: for the sake of providing reference material the solid produced by hydrolysis of vanadium-containing chlorhydrol solution was also obtained.

Results and discussion

XRD and BET analyses

XRD patterns and surface area measurements provide the basic test of the efficiency of pillaring process. The results obtained for the investigated clay catalysts, together with V-content, are presented in Tab. 1.

Table 2: Parameters characterizing the ESR spectra of V-doped pillared clays.

Catalyst	$g_\parallel$	$g_\perp$	$\Delta g/\Delta g_\perp$	$A_\parallel$ [G]	$A_\perp$ [G]	β_2^2
V-mt	1.931	1.980	3.2	202.4	75.8	1.01
V-(Al-PILC)	1.942	1.983	3.1	190.5	68.3	0.98
(V-Al)-mt	1.983	1.984	3.5	193.1	68.3	1.00
(V-Al)-PILC	1.943	1.983	3.1	188.7	68.2	0.97
V-(Al-mt)	1.983	1.984	3.5	188.3	69.1	0.97
V(Al)-PILC	1.939	1.984	3.5	190.9	70.2	0.97

In all but two pillared samples the increase in the d_{001} basal spacing is accompanied by increase in the surface area which confirms that the preparative procedures employed were effective. An interesting exception is samples (V-Al)-mt and (V-Al)-PILC obtained by pillaring of the montmorillonite with mixed V-Al solution. Although d_{001} basal spacing indicates that the alumosilicate layers are widely apart, the specific surface is low.

XRD data in Tab. 1 show also that the "co-pillared" species present in (V-Al)-mt and (V-Al)-PILC push the clay layers slightly more apart than pure Al_{13} oligocation, which suggests that a structural modification of the latter might have occurred.

Chemical analysis

Chemical analysis shows that while in the montmorillonite treated with pure chlorhydrol solution the amount of aluminium incorporated on pillaring equals 2.5 Al per Si_8 unit, in the samples exchanged with vanadium-containing pillaring agent the corresponding value is much larger and amounts to 6.7 Al per Si_8 unit. Assuming homogeneous distribution within the interlamellar space, the pillar density corresponds in the Al-mt sample to ca. 1 Al_{13} cation (of average charge + 3.6) per 5.2 Si_8 units, and in the co-pillared (V-Al)-mt sample to about 1 Al_{13} cation (of average charge + 1.4) per 2 Si_8 units. In view of the fact that the maximum filling of the inter-lamellar space with closely packed Keggin Al_{13} oligocations would correspond to ca. 1 pillar per 1.7 Si_8 unit (assuming Keggin oligocation diameter to be 10 Å), the pillar density calculated for (V-Al)-mt sample points to the space filling close to maximum. It seems that addition of vanadium to the chlorhydrol solution brings about a decrease in the average charge of the pillaring oligomer which in turn results in the dense packing of the pillaring species in the interlayer region and causes its blockage reflected in the low values of the respective specific surfaces. Analysis of the V content allows to estimate its distribution to be about 1 V atom per 1.5 pillar in the V-(Al-PILC) sample and 1 V atom per 2.3 pillars in the co-pillared samples.

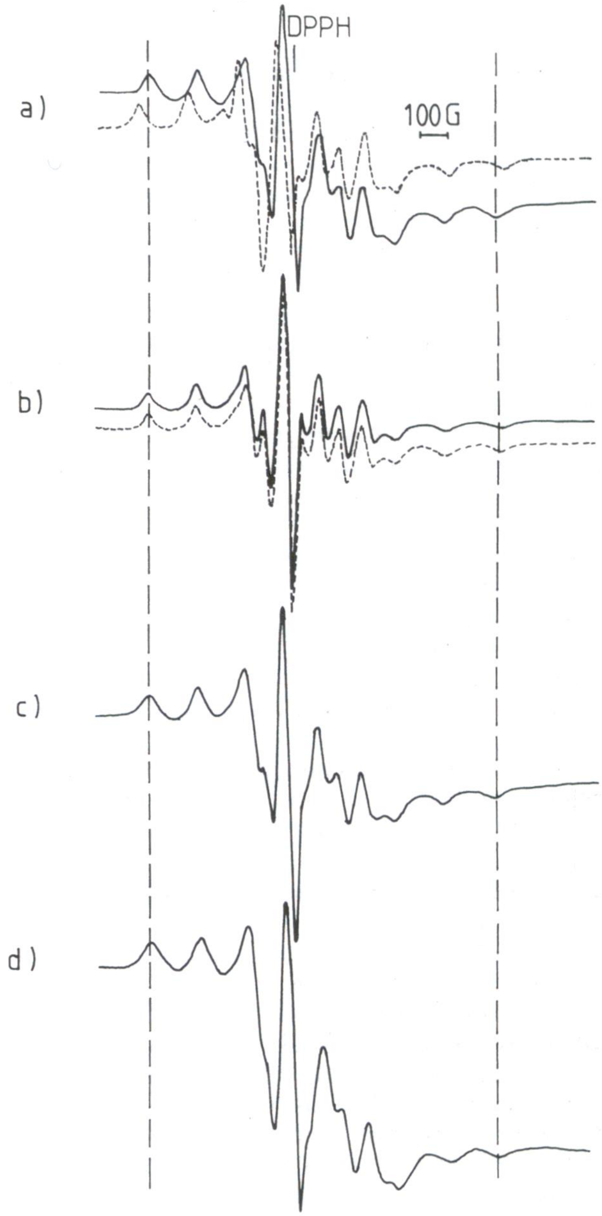

Fig. 2. ESR spectra of: **a** - V-(Al-PILC) (solid line) and V-mt (dashed line), **b** - (V-Al)-mt (solid line) and precipitate obtained by hydrolysis of V-Al pillaring solution (dashed line), **c** - V-(Al-mt), **d** - V(Al)-PILC. All spectra recorded at 77 K.

Thermal analysis

Results of thermal analysis (Fig. 1) also show that pillars resulting from the V-containing chlorhydrol solution behave differently from the usual Al_{13} species. The first endothermic peak associated with the release of water of hydration is particularly broad for the "co-pillared" sample, tailing up to 400 °C. While in the DTA profile of Al-mt sample the dehydroxylation of the Al_{13} oligocation appears as a stronger endothermic peak around 400 °C, and a weaker one around 540 °C, in the (V-Al)-mt sample the former is not visible (possibly smeared over a broader temperature range and partly hidden in the tail of preceeding peak) and the peak around 550 °C becomes more significant. There is no substantial change in the position of the endothermic peak around 680 °C signifying dehydroxylation of the clay octahedral layer, but it seems that the presence of vanadium brings about an exothermic reactive decomposition of clay already around 820 °C.

ESR analysis

The question of crucial importance for characterization of vanadium-doped pillared clays concerns location of introduced vanadium within the clay structure. Although the preparative procedures were designed with intention to deposit vanadium onto the pillars, it is by no means obvious that some other distribution has not occurred, including such possibilities as attachment to the external surfaces of the clay crystallites or presence in the interlayer spaces of vanadium species not associated with the pillars. Results of the ESR study, presented in detail elsewhere (Bahranowski & Serwicka 1993), are helpful in elucidation of this problem.

The ESR spectrum of the initial clay consists of the line at $g = 4.3$ due to the high spin ($S = 5/2$) ferric ion in the distorted octahedral sites, and also a line with $H_{p\text{-}p} = 1000$ G near $g = 2$, possibly due to some iron oxide impurity (Hall 1980). All vanadium-containing samples show characteristic eight-line hyperfine patterns due to the interaction of the unpaired electron with ^{51}V nucleus ($I = 7/2$), Fig. 2. The ESR parameters determined from the spectra are presented in Tab. 2. Experimentally observed values of $g_{\parallel} < g_{\perp}$ and $A_{\parallel} < A_{\perp}$ indicate a tetragonal distortion of the paramagnetic complex and point to the vanadyl character of the responsible vanadium species. Parameter $\Delta g_{\parallel}/\Delta g_{\perp}$, sensitive to the changes in the vanadium-oxygen distance in the $(VO)^{+2}$ ion shows no significant change, indicating similar vanadyl bond strength in all samples. The β_2^2 bonding coefficient informing about the degree of localization of the unpaired electron is almost constant and close to unity, which indicates that the ground state orbital is essentialy non-bonding, as predicted by Ballhausen & Gray (1962). The ESR parameters for signals of V-mt and vanadium-doped Al-pillared clays prepared in the present study agree well with the data reported in earlier works (Pinnavaia et al. 1974; McBride 1979; Braddel et al. 1990). However, in contrast to the findings of Braddel et al. (1990), who observed mobile, fully hydrated vanadyl species at, what they called, high vanadium loadings, all the present spectra, with exception of the V-mt sample, are characteristic of rigid species, even for samples stored over saturated NaCl solution. Noteworthy, vanadium loading in the present study exceeded maximum doping levels applied by Braddel et al. (1990). We believe that the apparent discrepancy is caused by different ways of preparing the samples for the ESR examination, leading to a different water content in the examined clays. In the present study the maximum sample hydration was determined by water vapour pressure over saturated NaCl solution, while Braddel et al. (1990) investigated water-soaked samples.

The unequivocal determination of V location on the basis of ESR parameters requires additional experiments. Usually, suitably chosen model spectra can be of great help. In the present study the ESR spectrum of VO^{2+}-exchanged V-mt sample served as characteristic of vanadyl between the aluminosilicate sheets unbound to the pillars. The spectra of hydrolyzed vanadium-containing chlorhydrol precipitate was taken as reference for vanadium associated with alumina. The model spectra are marked with dashed lines in Fig. 2. Lack of any traces of the unbound vanadyl ions in the spectra of V-doped pillared clays (marked with dashed line in Fig. 2a), irrespective of the mode of preparation, together with their similarity with the spectrum of the V-chlorhydrol hydrolysed precipitate (marked with dashed line in Fig. 2b), are taken as evidence that the vanadium species in the V-containing Al-pillared montmorillonites are indeed attached to the pillars.

Conclusion

The ESR results presented show that introduction of vanadium into the pillared montmorillonites results in rigid association of the dopant with pillars, irrespective of the mode of preparation. The XRD and DTA data suggest that oligocationic species formed during "co-pillaring" differ structurally from the usual Al_{13} ions. It is argued that blocking of the interlayer may occur on "co-pillaring" due to the dense packing of oligocations, brought about by a decrease in their average charge.

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