INTERCALATION OF ANHYDROUS VANADYL PHOSPHATE WITH ALIPHATIC ALCOHOL MIXTURES

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The intercalation of $VOPO_4$ with the mixtures of alcohols (ethanol and 1-butanol, methanol and ethanol, methanol and 1-propanol, methanol and 1-butanol) have been studied. The dependence of alcohols content and interlayer distance of the intercalates formed on composition of the starting mixtures of alcohols has been found. The ability of $VOPO_4$ to form mixed intercalates with alcohols is discussed.

Layered compounds with general formula $MOAO_4$ (M = V, Nb and A = S, P, or As) are able to insert (intercalate) various molecules into space between layers (van der Waals gap). As an example, the intercalation of α-$VOPO_4$ or isostructural $VOSO_4$ with organic molecules (alcohols[1,2], amines[3,4], carboxylic acids[5], pyridine and its derivatives[6,7]) may serve.

In the case of $VOAO_4 . 2\ C_nH_{2n+1}OH$ (A = P or S, $n = 2 - 8$), it was found recently that alcohols are arranged in van der Waals gap of hosts ($VOAO_4$) in the form of bimolecular layers. Their carbon chains are tilted to the plane of the host layer under angle 55° as was deduced from the dependence of the distance of the $VOAO_4$ layers (basal spacing) on a number of carbon atoms of intercalated alcohol[1]. On the contrary, methanol forms only monomolecular layer in interlayer space of $VOAO_4 . 1.33\ CH_3OH$.

Vanadyl sulfate is able to form mixed intercalates with alcohols. Binary mixtures of alcohols $C_nH_{2n+1}OH$ with $n = 2 - 7$ were studied[2]. Basal spacing of intercalate formed depends on the composition of the starting alcohol mixture. When alcohols differ from each other only in one carbon atom, basal spacing increases gradually with decreasing content of alcohol (y) in $VOSO_4 . y\ ROH . (2 - y)\ R'OH$ (where R and R′ are alkyl groups with higher and lower number of carbon atoms, respectively). A characteristic shape of the dependence of basal spacing on the weight ratio of alcohols in starting mixture was observed for alcohols with a difference in the number of the carbon atoms greater than one.

The aim of this work was to prove whether vanadyl phosphate behaves in the same manner in reactions with EtOH–BuOH mixture as vanadyl sulfate and to study co-intercalation of a mixture of methanol (MeOH) with longer alcohols (ethanol – EtOH, 1-propanol – PrOH and 1-butanol – BuOH) to vanadyl phosphate.

EXPERIMENTAL

Vanadyl phosphate dihydrate was prepared by reaction of vanadium pentoxide with phosphoric acid[8]. Alpha vanadyl phosphate was obtained from dihydrate by heating at 573 K in vacuum for 4 h. The reactions of $VOPO_4$ with a molar excess (1 : 20) of alcohol mixtures (MeOH–EtOH, MeOH–PrOH, MeOH–BuOH and EtOH–BuOH) were carried out in glass ampullae by shaking at 298 K for 5 days. Dried alcohols were distilled immediately before using.

The powder data of the intercalates were obtained with an X-ray diffractometer HZG-4 (Freiberger Präzisionsmechanik, Germany) using CuKα radiation (λ = 0.15418 nm for the angles $2\theta < 35°$) and CuKα_1 (λ = 0.15405 nm for $2\theta > 35°$) with discrimination of the CuKβ radiation by a Ni filter. Silicium (a = 0.543055 nm) was used as an internal standard. Diffraction angles were measured from 4° to 90° (2θ). The samples for X-ray powder diffraction analysis were neither washed nor dried. Basal spacings of the layered lattice of the intercalates were calculated from the most intensive reflections (00l). A relative content of phases (w_i) in case of co-existence of more phases was calculated from the equation

$$w_i = I_i(001)/\sum I_i(001) \ , \qquad (1)$$

where $I_i(001)$ is intensity of the diffraction line (001) of the i-th phase.

The molar ratio of the intercalated alcohols in the layered complexes was determined by gas chromatography. Before analysis the solid samples were washed with pentane, filtered in dry inert atmosphere and then the known amount was hydrolyzed. The obtained extract was analyzed by Fractovap GV 200 apparatus (Carlo Erba, Italy) with a flame ionization detector (Embacel AW, 10% diethylene glycol succinate; 423 K, column 353 K, carrier gas N_2).

RESULTS AND DISCUSSION

The dependences of basal spacing of the solid intercalate on composition of the starting mixture for EtOH–BuOH, MeOH–EtOH and MeOH–PrOH systems are given in Fig. 1.

The intercalation of the EtOH–BuOH mixture into $VOPO_4$ has practically the same course as the intercalation of this mixture into $VOSO_4$ (see ref.[2]). Basal spacing of the product obtained by the intercalation of the starting mixture of these alcohols with content of BuOH less then 60 wt.% corresponds to basal spacing (c = 1.32 nm) of $VOPO_4 \cdot 2$ EtOH. The content of BuOH in this intercalate is negligible. When the content of BuOH in the starting mixture lies between 70 and 95%, the intercalate with basal spacing c = 1.56 nm is formed. As it follows from gas chromatography, the composition of the intercalate is $VOPO_4$. BuOH . EtOH. This composition corresponds to basal spacing observed, which is close to mean value (1.556 nm) of basal spacings of

$VOPO_4$. 2 EtOH and $VOPO_4$. 2 BuOH (ref.[1]). The pure $VOPO_4$. 2 BuOH is formed when the content of BuOH in the mixture is near 100%.

The intercalate $VOPO_4$. 1.33 MeOH with constant basal spacing (c = 0.785 nm) is formed at content of EtOH less than 30% in the MeOH–EtOH system. The content of ethanol in the solid product is negligible. When the content of EtOH is higher than 30%, a compound with formula $VOPO_4$. y EtOH . (2 – y) MeOH (y varies from 1.6 to 2) is formed. Its basal spacing slightly increases in this region (Fig. 1). The formation of $VOPO_4$. EtOH . MeOH mixed intercalate was not observed.

The similar behaviour occurs in the system MeOH–PrOH (Fig. 1). The $VOPO_4$. 1.33 MeOH intercalate is formed up to 70% content of propanol in the starting mixture. At the higher content of propanol an intercalate with formula $VOPO_4$. y PrOH . (2 – y) MeOH is formed (y varies from 1.8 to 2).

The different behaviour was observed in the MeOH–BuOH system (Fig. 2). The $VOPO_4$. 1.33 MeOH was found to be a product of intercalation of the starting mixture of alcohols with content of butanol up to 91%. The simultaneous existence of two phases ($VOPO_4$. 1.33 MeOH and $VOPO_4$. BuOH . MeOH) was observed in the region of BuOH concentration 85 – 91%. The relative content of these phases is shown in the lower part of Fig. 2. The $VOPO_4$. BuOH . MeOH mixed intercalate is present as a product up to 98% of BuOH in the starting mixture of alcohols and $VOPO_4$. 2 BuOH is formed only in pure butanol. Basal spacing of $VOPO_4$. BuOH . MeOH (c = 1.55 nm)

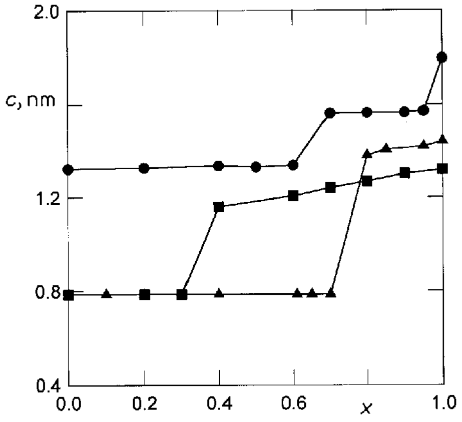

FIG. 1

Dependence of basal spacing c of solid products on the composition of starting mixture of alcohols, where x is weight fraction of alcohol with longer chain. ▲ MeOH–PrOH, ■ MeOH–EtOH, ● EtOH–BuOH

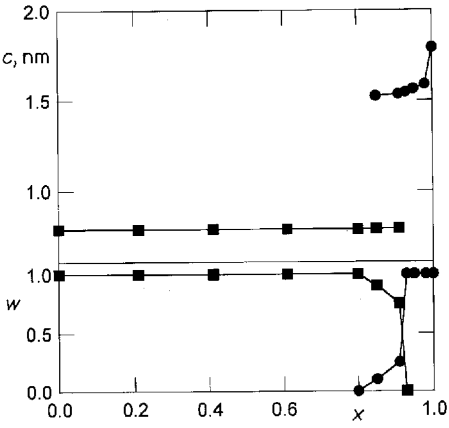

FIG. 2

Dependence of basal spacing c and content of phases w in solid reaction product on weight fraction x of 1-butanol in starting mixture of methanol and butanol. ■ $VOPO_4$. 1.33 MeOH, ● $VOPO_4$. y BuOH . (2 – y) MeOH is very close to the value (c = 1.48 nm) calculated from increments of basal spacings of monomolecular layer of MeOH (Δc = 0.374 nm) and BuOH (Δc = 0.692 nm) to anhydrous $VOPO_4$ (c = 0.411 nm)[1].

The intercalation of the alcohol mixtures into solid $VOPO_4$ is reversible reaction. The composition of the intercalate is in equilibrium with alcohol mixture from which it is formed. The change of the ratio of the alcohols in the mixture shifts composition and basal spacing of the formed solid product in agreement with the results described above.

It follows from the results obtained that the ability of alcohols to penetrate into methanolic $VOPO_4$ intercalate decreases in a series: EtOH > PrOH > BuOH (i.e. to replace methanol in the intercalate, the less concentration of ethanol in the mixture with methanol is needed than propanol or butanol). On the contrary, the mixed intercalate with higher content of methanol is formed from the starting mixture of EtOH–MeOH than in the case PrOH–MeOH, but the mixed equimolar intercalate $VOPO_4$. ROH . MeOH (R = Et or Pr) is not formed. A possible explanation consists in an existence of more spacious and energetically less advantageous cavities[2] in bilayer structure of alcohol molecules in $VOPO_4$. y PrOH . (2 – y) MeOH intercalate. The existence of these cavities in $VOPO_4$. y BuOH . (2 – y) MeOH is so disadvantageous for $y \neq 1$ that only $VOPO_4$. BuOH . MeOH is formed in this system.

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