Brief Communications

Chemical modification of alumina and silica with alkylphosphonic acids and their esters

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Alumina and silica were modified with alkylphosphonic acids and diethyl butylphosphonate. The boundaries of hydrolytic stability of the obtained surface-modified materials were determined.

Key words: alumina, silica, alkylphosphonic acids, modification, hydrolysis.

Chemical modification of the surface of oxide materials is a widespread technique for synthesis of heterogeneous metallocomplex catalysts and efficient and selective sorbents.[1,2] Porous silica is the most widely used for modification, and alumina is used more rarely. Organosilicon compounds are used most often as modifiers. However, they do not provide, in many cases, a high surface density of grafted functional groups. Therefore, it is of interest to test other classes of organoelement compounds as modifiers. The main criteria of selection of new types of modifiers are selectivity of the reaction between active groups of the support surface and modifier and the hydrolytic, thermal stability of the bond between them, and availability of the modifier.

It has recently[3—5] been shown that alkylphosphonic acids can be used as modifiers of the alumina surface.

In this work, we studied the hydrolytic stability of alkylphosphonic layers of the surface of modified alumina and silica.

Experimental

tert-Butylphosphonic and isopropylphosphonic acids were prepared by the reaction of the corresponding alkyl chlorides with phosphorus trichloride followed by the hydrolysis of the products.[6] Diethyl ester of *n*-butylphosphonic acid was synthesized by the alkylation of sodium diethyl phosphite with *n*-butyl bromide. The ester obtained was hydrolyzed to *n*-butylphosphonic acid by boiling with 10% HCl until a homogeneous liquid was obtained.

Alumina (specific surface area 210 $m^2 g^{-1}$, average pore diameter 10—12 nm) was modified from a boiling toluene solution of the corresponding phosphonic acid with azeotropic distillation off of water. The amount of the modifier was large enough to ensure a grafting density of 10 groups per nm^2 (for all acids used and diethyl ester of *n*-butylphosphonic acid) and 4 groups per nm ^{2} (for all acids used). The reaction was performed for 2 days. The samples obtained were successively washed with toluene, 1,4-dioxane, a 1,4-dioxane—water (1 : 1) mixture, and distilled water and then once more with the aqueous-dioxane mixture, dioxane, and hexane. Then the samples were dried on a glass filter at ~20 °C. Silica was modified (Silochrom C-120, specific surface area 110 $m^2 g^{-1}$, average pore diameter 40 nm) using a similar procedure, and the amount of the modifier was large enough to provide a grafting density of 4 groups per nm^2.

The hydrolytic stability of the samples obtained were studied using solutions of H_2SO_4 or NaOH in an aqueous-dioxane (2 : 1) mixture with different pH values (2, 3, 4, 5.5 (distilled water), and 12). A weighted sample (0.05 g) was placed into a solution (10 mL) and left for 48 h at ~20 °C with periodical

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Table 1. Data on hydrolytic stability of alumina modified with isopropylphosphonic acid

Modifier	pH	C (%)	ρ /number of groups per 1 nm^2
$Bu^tPO(OH)_2$	Without hydrolysis	3.3	2.1
$Bu^tPO(OH)_2$	2	1.6	1.0
$Bu^tPO(OH)_2$	3	2.2	1.4
$Bu^tPO(OH)_2$	4	2.4	1.5
$Bu^tPO(OH)_2$	5.5	2.8	1.8
$Bu^tPO(OH)_2$	12	1.4	0.8
$Pr^iPO(OH)_2$	Without hydrolysis	3.3	2.9
$Pr^iPO(OH)_2$	2	2.4	2.0
$Pr^iPO(OH)_2$	3	2.5	2.1
$Pr^iPO(OH)_2$	4	2.6	2.2
$Pr^iPO(OH)_2$	5.5	3.0	2.6
$Pr^iPO(OH)_2$	12	2.2	1.8
$Bu^nPO(OH)_2$	Without hydrolysis	4.9	3.3
$Bu^nPO(OH)_2$	2	1.7	1.1
$Bu^nPO(OH)_2$	3	2.9	1.8
$Bu^nPO(OH)_2$	4	4.4	2.9
$Bu^nPO(OH)_2$	5.5	4.5	3.0
$Bu^nPO(OH)_2$	12	3.1	2.0

Table 2. Pore volume of samples of modified alumina

Modifier	*A* /nm^{-2}	*B* /number of groups per 1 nm^2	*V* /mL g^{-1}
$Bu^tPO_3H_2$	4	2.1	0.45
$Bu^tPO_3H_2$	10	2.7	
$Pr^iPO_3H_2$	4	2.9	0.48
$Pr^iPO_3H_2$	10	3.8	0.44
$Bu^nPO_3H_2$	4	3.3	0.35
$Bu^nPO_3H_2$	10	9.1	0.25
$Bu^nPO(OEt)_2$	10	0.9	0.56
Initial			0.58

Notes. A is the amount of the modifier large enough to ensure a high grafting density; B is the obtained grafting density.

stirring. Then the sample was washed with distilled water to the neutral reaction in washing waters and dried at ~20 °C on a glass filter.

The total volume of the pores was determined by measuring the increase in the weight of the sample after the pores were filled with benzene. The oxide samples were stored in a desiccator filled with benzene vapor until a constant weight was achieved. The results are presented in Table 1.

The grafting density ρ (nm^2) was calculated using the following formula[2]:

$$\rho = (6 \cdot 10^5 p_C)/[(1200 n_C - M' p_C)S],$$

where p_C is the mass percentage of carbon in the studied sample, n_C is the number of C atoms in the grafted part of the modifier molecule, S is the specific surface area of the support (m^2 g^{-1}), and M' is the reduced molecular weight of the modifier calculated by the formula[2]

$$M' = M - nM_x + 17n - 18F,$$

where M is the molecular weight of the modifier, n is the number of groups leaving the modifier molecule, M_x is the molecular weight of the leaving group, and F is the average number of bonds formed by the modifier molecule with the surface (in our case, we accepted $F = 1.5$[2]).

Results and Discussion

Modification of alumina with phosphonic acids. The modification reaction occurred successfully (see Table 1). All obtained alumina samples (modified by both phosphonic acids and diethyl butylphosphonate) are not wetted with water, which indicates hydrophobicity of their surface preventing water incorporation into support pores. Relatively large particles of alumina (0.2—0.3 mm) taken for modification were transformed into a fine dust (the size of most particles did not exceed 2 μ). Then, in the case of a great excess of the modifier, the obtained grafting density for isopropylphosphonic and, especially, *n*-butylphosphonic acids is very high and reaches 9 groups per nm^2 (Table 2). At the same time, the acids used (*tert*-butylphosphonic and *n*-butylphosphonic) are not prone to polymerization under the modification conditions.

These facts force us to assume that phosphonic acids react with the alumina surface to form aluminum phosphonates that are insoluble in standard solutions. However, in order to form the phosphonate polylayer, the diffusion of acid through the already formed salt layer is needed. Evidently, the more bulky radical has the acid, the more hindered is the diffusion. Therefore, the maximum grafting density decreases on going from *n*-butylphosphonic acid to isopropylphosphonic acid and further to *tert*-butylphosphonic acid. It can be assumed that, in the latter case, the highest grafting density virtually corresponds to the monolayer coating.

The destruction of the alumina surface should be accompanied by a strong decrease in the pore volume of the support. The data on the pore volume of the modified samples presented in table 2 confirm our assumption about the formation of the polylayer of Al phosphonates.

The modification of alumina with alkyl esters of phosphonic acids must not result in similar destruction. We modified alumina with an excess of diethyl *n*-butylphosphonate. The modification was successful (the obtained grafting density was 0.9 nm^{-2}), however, the granulometric composition of the support and its pore volume (see Table 1) remained almost unchanged.

Study of the hydrolytic stability of modified alumina samples. The hydrolytic stability of the materials obtained is a very important characteristic. Therefore, we studied it for the alumina samples treated with the phosphonic acids at different pH values. The results obtained for the modified alumina are presented in Tables 2 and 3. These data show that the samples obtained are stable in a neutral medium, however, their

Table 3. Data on hydrolytic stability of silica modified with *tert*-butylphosphonic acid

pH	C (%)	ρ /number of groups per 1 nm^2
Without hydrolysis	1.0	1.5
2	0.5	0.7
4	0.5	0.7
5.5	0.8	1.3
12	0.5	0.8

stability is lower in acidic and alkaline media. It can be assumed that the support is dissolved in these media. However, in media with the neutral reaction phosphonic acids can successfully be used as modifiers for alumina.

Modification of silica with *tert*-butylphosphonic acid. We attempted to modify silica with *tert*-butylphosphonic acid (see Table 3). It is seen that the modification was successful, the grafting density is reasonably high (1.5 groups per nm^2), and the grafted layer is stable in a neutral medium. The granulometric composition of silica remained unchanged after modification.

Thus, in this work, we showed a possibility of the chemical modification of alumina and silica with alkylphosphonic acids and their esters.

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