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LETTERS TO THE EDITOR

Preparation and Chemical Activity of Methoxy Groups at the Surface of γ-Al_2O_3

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Nowadays surface reactions accompanying the molecular layering synthesis (ML−ALD) are used to prepare various solid compounds of the desired composition and structure [1, 2]. One of the necessary conditions of such synthesis is the presence of the suitable functional groups on the matrix surface [3]. In the case of γ-Al_2O_3, as well as in the cases of many other inorganic matrices, hydroxy groups act as the reactive sites. As the aluminum-bound hydroxy group (=Al–OH) is thermally unstable and acts as a weak nucleophile [4], the high conversion of the OH groups is hardly possible under mild conditions of electrophilic substitution with metal halides, silanes, and other agents.

Here we present the first study of the chemical activity of methoxy groups located on the surface of γ-Al_2O_3 in some surface reactions. Preparation of the sample followed the reactions (1)–(3).

$$=Al–OH + SOCl_2 > =Al–Cl + HCl + SO_2, \quad (1)$$

$$=Al–Cl + CH_3OH > =Al–OCH_3 + HCl, \quad (2)$$

$$=Al–OH + CH_3OH > =Al–OCH_3 + H_2O. \quad (3)$$

Thionyl chloride was used for γ-Al_2O_3 surface chlorination. Surface methoxy groups were obtained via reaction (2), because the interaction according to reaction (3) did not lead to the homogeneous surface coverage with the desired groups, OH and =O groups were also present. The chlorination degree was determined by the elemental analysis for Cl as well as by IR spectroscopy.

Under the studied conditions (200–400°C) the complete substitution of the surface hydroxy groups of γ-Al_2O_3 with methoxy groups could not be achieved, however, the it was possible to regulate the ratio on the surface of OH, $–OCH_3$, and =O groups.

As the =Al–Cl bond was more reactive towards nucleophilic reagents (water, alcohol) as compared with =Al–OH, we studied the interaction of CH_3OH with chlorine functional groups at the γ-Al_2O_3 surface, the latter being prepared at 200°C in the dry argon stream; the conversion of OH groups to Cl was close to 100% (2.70 mmol/g).

Further studies revealed that the treatment of the sample containing surface Cl with CH_3OH vapor at 50°C led to almost complete conversion of the Cl groups, thus giving a surface containing solely methoxy groups (2.71 mmol/g). The substitution of Cl with OCH_3 groups according to reaction (2) was confirmed by IR spectroscopy (appearance of CH_3 stretching bands at 2855 and 2960 cm^{-1}). Due to steric hindrance, a mplete substitution of Cl using other alcohols (C_2H_5OH, C_3H_7OH, or C_6H_5OH) was impossible.

Being strong nucleophiles, surface OCH_3 groups were quantitatively converted in the reactions with $SnCl_4$ or $TiCl_4$ according to reaction (4). With hydroxy surface groups, only 37% of them were substituted in the reaction with $SnCl_4$, however, the reaction with $TiCl_4$ led to the quantitative substitution.

$$2(=Al–OCH_3) + TiCl_4 > (=Al–O)_2TiCl_2 + 2CH_3Cl, \quad (4)$$

$$(=Al–O)_2TiCl_2 + 2H_2O > (=Al–O)_2Ti(OH)_2 + 2HCl. \quad (5)$$

Reaction (4) can be followed by the stage of titanium chloride polyaluminate transformation into its widely applied hydroxylated form (5).

Additional studies of the thermal stability of OCH_3 groups under inert atmosphere found that the onset of the methoxy groups destruction started at 450–470°C.

Thus the conditions of the surface methoxylation of γ-Al_2O_3 depending on the character of the surface groups =Al–OH and =Al–Cl was investigated for the first time. It was shown that the latter in contrast to the former can be quantitatively substituted by the methoxy groups. The surface reaction s of methoxy groups with $TiCl_4$ were studied. The conditions were developed permitting a complete substitution of the methoxy groups for titanium chloride ones and the latter, fpr methoxytitanium groups.

Heterogeneous reactions were performed using the previously described gas phase installation [3] in the dry argon stream (residual moisture content of 0.5–1 mg H_2O/m^3). The surface of γ-Al_2O_3 (70 m^2/g, pores diameter of 5.7 nm), was hydrated by boiling in distilled water. The content of OH groups was determined by differential thermal analysis using the DTA-500 device. The content of methoxy groups was estimated using the procedure adopted from [5].

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