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Synthesis and characterisation of hybrid carbon-alumina support

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Abstract

Hybrid carbon-coated alumina supports have been synthesised using 4,4′-methylenebis(phenylisocyanate) as carbon precursor. The adsorption of 4,4′-methylenebis(phenylisocyanate) on the alumina support is irreversible, the resulting organic moiety can undergo pyrolysis under elevated temperature with the formation of carbon coating on the alumina support. Carbon loading in the synthesised materials and thus a degree of coverage of the alumina surface with carbon layer can be increased by repetition of 4,4′-methylenebis(phenylisocyanate) adsorption–pyrolysis cycles. The carbon coating does not substantially influence the pore structure of the initial alumina support. Upon increasing the carbon loading, the carbon coating becomes more uniform with respect to carbon localisation both on the internal and the external surface of the alumina support. The carbon coating on an alumina support can be discriminated from carbonaceous deposits due to a difference in the steady-state surface charging of the samples. Moreover, carbonaceous surface species which associated with C–O, C=O and O=C–O groups in carbon coating can also be identified.

Keywords: Alumina support; Carbon coating; Adsorption

1. Introduction

In the recent years, there is a standing interest in application of carbon-coated alumina as a catalyst support [1–7]. The coating of the alumina surface with a thin carbon layer results in the preparation of hybrid carbon-alumina supports with advanced mechanical, textural and chemical properties that is important for catalytic applications. Therefore, a number of approaches concerning the synthesis of such carbon-coated materials have been reported.

The first approach proposed by Youtsey et al. [8] is based on the ability of organic compounds to be pyrolysed on the surface of the alumina and silica-alumina supports at elevated temperatures in the range of 600–700 °C. Among the tested organic pyrolysable substances such hydrocarbons as hexane, benzene, toluene, naphthalene, anthracene, cyclohexane and cyclohehene were found to be the most promising for making carbon-alumina and carbon-silica-alumina conductive composite materials.

In this way, a carbon-coated alumina was prepared by Vissers et al. [1] via chemical vapour deposition (CVD) of cyclohexene or ethene at 600–700 °C passed over the surface of the alumina support in the flow of nitrogen. It has been observed that the textural properties of the synthesised materials were dependent on the amount of deposited carbon and on the type of the used hydrocarbon. It has been found out that the ethene-derived material had a degree of the alumina surface coating with carbon two times higher as compared to that of the cyclohexene-derived material of the same carbon loading. The highest surface coating which approached the value of 77% was achieved in the case of the carbon-alumina material with the highest carbon content reaching 27 wt.%. The carbon coating was non-uniform.

The synthesis of carbon-coated alumina supports was also done by CVD of cycloxene (Rama Rao et al. [2], Boorman et al. [3–5] and Zhang et al. [6]) at 600 °C, benzene (Boorman et al. [5]) at 600 °C, liquefied petroleum gas (Leon y Leon et al. [7]) at 800 °C and a number of fluorohydrocarbons like

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trifluoroethanol, 1-fluoropentane, 4-fluorotoluene and fluorobenzene at 600 °C (Boorman et al. [5]).

It is clear, that the degree of surface coverage of the alumina support can be increased by increasing the carbon loading. Unfortunately, increasing the carbon loading results in carbon aggregation and thus in changes of the textural properties of the support namely in decreasing of the apparent surface area and pore volume. Therefore, synthetic approaches alternative to CVD should be developed.

In order to increase the degree of surface coverage of the alumina support with carbon and to increase the uniformity of surface layer a new approach was recently proposed by Sharanda and co-workers [9,10]. In contrast to CVD of hydrocarbons [1–8], the developed approach is based on a two-step procedure. Firstly, acetylacetone reacted with the alumina support at elevated temperature that resulted in the formation of aluminium–acetylacetonate surface complexes. In this way, a monolayer of carbon precursor grafted on the alumina surface was synthesised since the removal of the excess of carbon precursor was undertaken. Secondly, grafted aluminium–acetylacetonate complexes underwent pyrolysis under vacuum that resulted in the formation of carbon layer. It has been shown that the carbon coating completely blocks the coordinatively unsaturated sites on the alumina surface. The maximum carbon loading in the synthesised samples after three-fold repetition of modification-pyrolysis cycles reached 6.3 wt.%. The carbon coating does not influence the pore structure of the initial alumina support. It has been found that at low loading carbon is preferably concentrated at the internal surface of the alumina support. On increasing the carbon loading, the external surface of the alumina support appeared to be enriched with carbon. Although the surface coverage increases with increasing carbon content, a complete shielding of the alumina surface with carbon layer was not received.

In order to increase carbon loading and thus a degree of coverage of the alumina surface with carbon application of 4,4′-methylenebis(phenylisocyanate) was proposed due to extraordinary reactivity of N=C=O groups. The formation of surface complexes should be expected due to their interaction with hydroxyl groups on the alumina surface via N=C bond opening. Upon the pyrolyses, such surface complexes are assumed to form carbon coating, which will decorate the alumina surface.

The present work addressed the following questions:

- the conditions of the adsorption of 4,4′-methylenebis(phenylisocyanate) on the alumina support and the yield of carbon upon their pyrolysis;
- the influence of carbon deposition on the porous structure of the alumina support;
- localisation and distribution of carbon coating on the surface of the alumina support.

2. Experimental

Precipitated alumina (CK 300, Ketjen, $S_{BET}(N_2) = 266$ $m^2 g^{-1}$) was used as catalyst supports. The as-received precipitated alumina support was crushed and sieved to a particle size of 0.25–0.50 mm. The support was initially calcined in air at 500 °C for 2 h in a muffle furnace in order to remove organic impurities.

4,4′-Methylenebis(phenylisocyanate) obtained from Bayer AG was dissolved in *o*-xylene preliminary dried with NaX molecular sieves. Carbon-coated alumina was synthesised by an equilibrium adsorption method. The weighted amount (15 g) of the support was contacted with 340 ml of 1% *o*-xylene solution of 4,4′-methylenebis(phenylisocyanate). A mixture was occasionally shaken at room temperature for one day. Afterwards, the mixture was filtered and the sample was washed with approximately 100 ml of pure *o*-xylene followed by drying at 60 °C for 2 h. The sample was yellow in colour.

The sample was placed into a quartz cell and evacuated at room temperature to the pressure of 1×10^{-2} Pa. Then, the temperature of the sample was slowly increased to 700 °C within a period of 10 h under continuous pumping. The sample was kept at this temperature and a pressure of 1×10^{-2} Pa for 2 h in order to complete the pyrolysis of the adsorbed 4,4′-methylenebis(phenyl isocyanate) and to remove the volatile products.

To prepare samples with an increased carbon content, the adsorption–pyrolysis cycle was repeated up to three times. The above procedure resulted in samples with the carbon content 7.7, 12.3 and 17.5 wt.%, denoted hereafter as C(7.7)/Al_2O_3, C(12.3)/Al_2O_3 and C(17.5)/Al_2O_3, respectively.

Surface area (BET) and porosity were determined by nitrogen adsorption/desorption at 77 K using a Quantachrome Autosorb-6B equipment. The samples were preliminary heated in vacuum at 150 °C for 16 h.

Thermal studies (TG/DTG-DTA) were carried out with a STA-1500 H thermobalance (PL Thermal Sciences) at a heating rate of 10 °C/min in an air flow of ~50 cm^3/min.

Carbon content in the synthesised samples was determined gravimetrically from the weight loss within temperature interval 300–650 °C.

X-ray diffraction (XRD) patterns were recorded in the range 5–80° (scanning step 0.1°) with a DRON-3M automated diffractometer using the Cu Kα (λ = 1.54178 A) radiation and Ni filter.

X-ray photoelectron spectra (XPS) were recorded on a Vacuum Generator ESCA-3 photoelectron spectrometer using Al $K\alpha_{1,2}$ radiation (1486.6 eV) from an X-ray source operating at 10 kV and 12 mA. The working pressure inside the chamber was less than 2.5×10^{-6} Pa. All spectra were recorded with a step size of 0.1 eV in the constant pass energy mode at 50 eV. Samples were mounted for the analysis by dusting their powder onto a double-sided polymer-based adhesive tape.

3. Results and discussion

The contact of the initial alumina support with 4,4′-methylenebis(phenylisocyanate) dissolved in *o*-xylene resulted in partial discoloration of the solution and the initial white colour of the alumina samples turned yellow that means the adsorption of 4,4′-methylenebis(phenylisocyanate) on the support surface. Adsorption of 4,4′-methylenebis(phenylisocyanate) on the