

EFFECT OF CARBON ON THE POROSITY TEXTURE OF ALUMINA SUPPORT ON ITS IMPREGNATION WITH AMPHIPHILIC CARBONACEOUS MATERIAL

R. N. Nickolov and D. R. Mehandjiev
Institute of General and Inorganic Chemistry
Bulgarian Academy of Sciences, Sofia 1113 (Bulgaria)

Introduction

Amphiphilic carbonaceous materials (ACM) synthesized recently [1] allow direct preparation of carbon-coated supports (CCS) using approaches not different from the existing methods for active phase deposition on porous materials. The choice of a suitable mineral matrix for the preparation of CCS is limited by the effect of deposited carbon on the initial porous texture during the impregnation.

That is why the purpose of the present paper was to investigate the carbon modifying effect on the nature of the surface and the porous texture of the γ -alumina support during its impregnation with ACM.

Experimental

ACM was prepared by functionalization of thermally treated wood tar pitch (750K) using electrophilic substitution reactions [1]. Carbon-coated samples were obtained by repeated impregnation (sample A2, 6 times; sample A3, 17 times) of commercially available γ -alumina (sample A1) with an ammoniacal solution of ACM of a constant concentration (0.1%). Upon each impregnation the samples were vacuum-dried and after the corresponding number of impregnations they were heated at 573K in vacuum. For the sake of comparison, sample A1 was impregnated 17 times with NH_4OH according to the scheme and the conditions of preparation of A3. The surface and the porous texture of the samples was characterized by nitrogen adsorption (77.4K) in a conventional volumetric apparatus. The samples were studied by IR spectroscopy (Bruker IFS 25) at 400-4000 cm^{-1} and XP spectroscopy (ESCALAB MkII, VG Scientific, 1486.6eV, AlK_α source). The total carbon content of A2 and A3 was determined according to [2].

Results and Discussion

The data in Tables 1 and 2 indicate that supported carbon is concentrated on the outer surface of samples A2 and A3.

Table 1

Composition of samples established by XPS (C, O, N, Al and S) and chemical analysis (C)

Sample	Composition					C content (wt %)
	C	O	N	Al	S	
A1	*	60.1	-	39.6	-	-
A2	7.2	57.2	0.8	34.8	*	0.13
A3	22.6	55.1	1.6	20.7	*	0.31

* Data obtained are below the sensitivity threshold of the equipment

The simultaneous decrease of the C_{BET} and r_{FHH} exponent in the Frenkel-Halsey-Hill equation [3] irrespective of the different carbon contents reveals the modifying effect of the carbon phase on the chemical nature of the surface of A2 and A3. This is also evidenced by the increase (although negligible) of S_{BET} for the same samples as compared to A1.

Table 2

Texture parameters of the initial alumina and of carbon-coated samples

Sample	S_{BET}	C_{BET}	r_p *	r_{FHH}
	(m^2/g)		(\AA)	
A1	277	68	26	2.66
A2	293	39	26	2.50
A3	285	38	28	2.44

* Mean pore radii, calculated assuming a cylindrical pore structure

Analysis of the $V_a - n$ plots [4] corresponding to the experimental isotherms of A2 and A3 shows no change in

mesoporous character of the texture of A2 and A3.

The increase of their S_{BET} is probably caused by partial dissolution (< 2%) of the support in the ammonium medium of the impregnating solution. Comparison of the pore size distribution curves of the samples indicates that the partial dissolution of the support affects mainly radius sizes ranging from 60-150Å, increases the volume of mesopores within the same range and the dissolved products are deposited in the pores of 40-60Å. On the other part the ACM phase predominates within the radius range below 40Å. Because of the larger number of impregnations (A3) and the secondary dissolution of the carbon phase, the dissolved products migrate partially to the larger pores which is accompanied by deblocking of definite regions of the porous space (15-20Å).

As a result of the migration to the outer surface of the carbon phase which has been dissolved in the repeated impregnations, the C/AI ratio becomes, according to XPS, larger than 1 (Table 1). In contrast to A3, in the case of A2, more complete carbon penetration into the pores with radii below 30Å is observed. Parallel to this a blocking of the very narrow entrances and/or constrictions is taking place mainly in the range of 20-25Å. This is probably associated with the more negligible migration of ACM after secondary dissolution.

Conclusion

Repeated deposition of ACM followed by thermal treatment in vacuum ensure uniform distribution of carbon on the outer support surface. The deposited carbon exercises a strong modifying effect on the chemical nature of the surface but does not change essentially the mesoporous character of the initial texture. The impregnation medium (NH_4OH) favours the penetration of ACM into finer pores. However, depending on the ACM concentration or on the number of impregnations at a constant solution concentration, the depth to which the carbon phase penetrates, varies. Secondary dissolution of the deposited phase and its migration to larger pores are observed along with blocking of very narrow pore entrances and/or constrictions. These factors should be taken into account when carbon-coated supports with pre-set parameters are to be obtained.

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References

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