TEMPLATE-DERIVED MESOPOROUS CARBONS WITH HIGHLY DISPERSED TRANSITION METALS AS MEDIA FOR REACTIVE ADSORPTION OF DIBENZOTHIOPHENE

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Introduction

Recently, great interest has been shown in the application of adsorption for the desulfurization of liquid fuels (Song, 2003, Jirsak et al., 1999, Ania and Bandosz, 2006). The new requirements implemented in 2006 mandate the reduction in sulfur level for gasoline and diesel fuel to 30 and 15 ppm, respectively. Besides detrimental environmental effects of sulfur compounds, they also poison both catalytic conversion automobile catalysts and fuel cell reformer catalysts.

The objective of this paper is to evaluate the role of the surface chemistry of carbons further, including the presence of metals, and their porosity in the process of DBT reactive adsorption from hexane. For this purpose, the carbons obtained from metal- containing polymer carbonized within inorganic matrices are studied. As templates, alumina, amorphous silica, and zeolite were used. The differences in the porous structure and chemistry of templates lead to unique carbons with a high volume of mesopores, a significant contribution of micropores, and a very high dispersion of metals. Their behavior as DBT adsorbents is analyzed, and the performance is linked to the surface features.

Experimental

Materials

Poly(styrene sulfonic acid-co-maleic acid) sodium salt (PS) were used as the organic precursor**.** As the template, silica gel (powder, 60-200 mesh), activated alumina (particle size > 0.425 mm), and 13X ($Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]$ xH_2O molecular sieves (particle size > 0.425 mm) were used. The carbons obtained from PS were synthesized using the modified procedure described by Hines et al., 2004. The dry inorganic sorbent was impregnated with an aqueous solution of PS polymer (18 wt %). The polymer was used as received (sodium salts) and after ion exchange with nitrates of Cu (II), Co (II), or Fe(III) (0.05M). The metals were chosen on the basis of their ability to catalyze the oxidation of sulfur compounds (Cu, Fe) (Bandosz, 2006) and their catalytic effect on HDS (Co). The samples were immersed in the polymer-water solution and stirred for 72 h. Then were they filtrated, dried, and carbonized under nitrogen at 800 $^{\circ}$C for 40 min. After carbonization, the inorganic matrices were removed using 48 % HF (in the case of silica) or HF and HCl (in the case of alumina and molecular sieves). The resulting carbons were washed with water in a Soxhlet apparatus. They are referred to as C-Si-M, C-Al-M, C-Z-M where Si, Al, and Z refer to silica, alumina or zeolite matrix, respectively, and M is either Cu, Co, or Fe.

The materials were characterized using the adsorption of nitrogen, potentiometric titration, and elemental analysis.

Methods

Adsorption of DBT from Solution

The adsorption of DBT was carried out at room temperature in a stirred batch system. Before these experiments, kinetic studies were performed to determine the equilibration time of the system. Different amounts of carbon (from 25 mg to 1 g) were weighed and added to 12 bottles containing 40 ml of the sulfur-containing solution with an initial concentration of 1000 ppmw of DBT (ca. 178 ppmw S). All of the solutions were prepared in hexane. The covered bottles were placed in a shaking bath and allowed to shake for 72 h at constant temperature. After equilibration, the concentration in the liquid was determined using a UV spectrophotometer at the corresponding wavelength (312 nm). The amount adsorbed was calculated from the equation $q_e=V(C_o-C_e)/m$, where q_e is the amount adsorbed, V is the volume of the liquid phase, C_o

is the concentration of solute in the bulk phase before it comes into contact with the adsorbent, C_e is the concentration of solute in the bulk phase at equilibrium, and m is the amount of adsorbent.

The equilibrium data was fitted to the so-called Langmuir-Freundlich single solute isotherm, which has the equation:

$$\vartheta_t = q_e \Big/ q_o = \frac{(KC)^n}{1+(KC)^n}$$

where q_e is the adsorbed amount of solute per unit gram of adsorbent, q_o is its maximum adsorption per unit weight of adsorbent, K is the Langmuir-type constant defined by the van't Hoff equation, and the exponential term n represents the heterogeneity of the site energies. The fitting range was from 0 to 250 mg of S per gram of activated carbon (recalculated from its content in DBT).

Results and discussion

Characteristics of adsorbents

Table 1. Yields of materials, ash and metal contents, ignition temperatures and surface pH.

Sample	Yield after carbonization [%]	Final yield (after HF/HCl) treatment [%]	Ash content [wt %]	Metal content [%]	T_{ign} (^{o}C)	pH
C-Si	56.3	9.8	0.0	0	590	3.67
C-Si-Cu	64.5	10.2	1.1	0.49	521	3.82
C-Si-Co	62.1	10.6	2.5	0.38	575	3.70
C-Si-Fe	63.6	11.2	3.7	0.0063	577	3.55
C-Al	54.8	11.4	0.5	0	551	3.80
C-Al-Cu	68.3	11.0	1.1	0.71	506	3.49
C-Al-Co	62.5	15.4	6.7	0.32	520	3.43
C-Al-Fe	57.2	10.7	0.7	0.013	564	3.92
C-Z	57.8	14.6	3.4	0	464	4.22
C-Z-Cu	56.4	15.1	6.5	0.055	481	4.44
C-Z-Co	55.9	14.9	5.5	0.33	520	4.97
C-Z-Fe	57.1	12.3	1.2	0.19	517	5.27

The yields of materials and their ash contents, metal contents, ignition temperatures, and surface pH values are listed in Table 1. The small yields between 10 and 15% are related to the significant contribution of an inorganic matrix to the weight of the samples after carbonization. Acid treatment, although removed most of templates, still left a few percent of an inorganic matter, especially in the case of zeolite. In fact, only small fractions of that inorganic matter can be linked to metals because their amounts are less than 1%. This should ensure a high dispersion of metal within the porous carbon matrix. It is interesting that in the case of alumina- and silica-derived samples washing with acid removed almost all of the iron with much smaller effects on copper and cobalt. This may be linked to less iron than copper and cobalt present in the initial polymers as a result of its higher oxidation state (Hines et al., 2004). It is also likely that owing to the difference in chelation, copper and cobalt are dispersed in smaller pores and thus are less accessible to acids. This is not true in the case of zeolite-derived samples where high contents of inorganic matter are left after washing and the porosity is rather secondary, formed between washed out graphene layers (Seredych and Bandosz, 2007). The ignition temperatures are about 500 ^{o}C and the addition of metal generally decreases them in the case of silica- and alumina-derived carbons, whereas in the case of zeolite-derived materials an increase is observed. Although it is difficult to establish any direct relationships at this

stage in our study, these trends can be caused by the sizes of crystallites, the content of oxygen (chemisorbed or in functional groups as pH values), and the reactivity of metals. Because the presence of copper clearly decreases the ignition temperature, this can be caused by its activation of oxygen (Hu et al., 2000). The acidic pH of the carbon surfaces is related to the presence of sulfonic groups having their origin in the carbon precursor (Ania and Bandosz, 2006) and oxygen-containing acidic groups, which are formed when the samples are exposed to air (in some cases, strong exothermic reactions were observed when samples were exposed to the atmosphere).

Table 2. Structural parameters calculated from adsorption of nitrogen.

| Sample	S_{BET} [m^2/g]	V_T [cm^3/g]	V_{meso} [cm^3/g]	V_{mic} [cm^3/g]	V_{mic}/V_t
Si	255	1.162	1.061	0.101	0.09
C-Si	958	3.166	2.773	0.393	0.12
C-Si-DBT	604	2.316	2.080	0.236	0.10
C-Si-Cu	592	1.936	1.695	0.241	0.12
C-Si-Cu-DBT	480	1.813	1.625	0.188	0.10
C-Si-Co	807	2.316	1.987	0.329	0.14
C-Si-Co-DBT	550	1.868	1.640	0.228	0.12
C-Si-Fe	717	2.097	1.792	0.305	0.14
C-Si-Fe-DBT	454	1.625	1.448	0.177	0.11
Al	318	0.376	0.258	0.118	0.31
C-Al	661	0.888	0.625	0.263	0.30
C-Al-DBT	370	0.665	0.527	0.138	0.21
C-Al-Cu	391	0.531	0.369	0.162	0.30
C-Al-Cu-DBT	218	0.422	0.341	0.081	0.19
C-Al-Co	398	0.632	0.475	0.157	0.25
C-Al-Co-DBT	237	0.451	0.365	0.086	0.19
C-Al-Fe	376	0.603	0.459	0.144	0.24
C-Al-Fe-DBT	202	0.487	0.413	0.074	0.15
Z	486	0.340	0.096	0.244	0.72
C-Z	410	0.626	0.435	0.191	0.30
C-Z-DBT	115	0.441	0.395	0.046	0.10
C-Z-Cu	551	0.681	0.418	0.263	0.39
C-Z-Cu-DBT	112	0.412	0.367	0.045	0.11
C-Z-Co	456	0.654	0.445	0.209	0.32
C-Z-Co-DBT	118	0.447	0.401	0.046	0.10
C-Z-Fe	414	0.598	0.403	0.195	0.33
C-Z-Fe-DBT	108	0.411	0.368	0.043	0.10
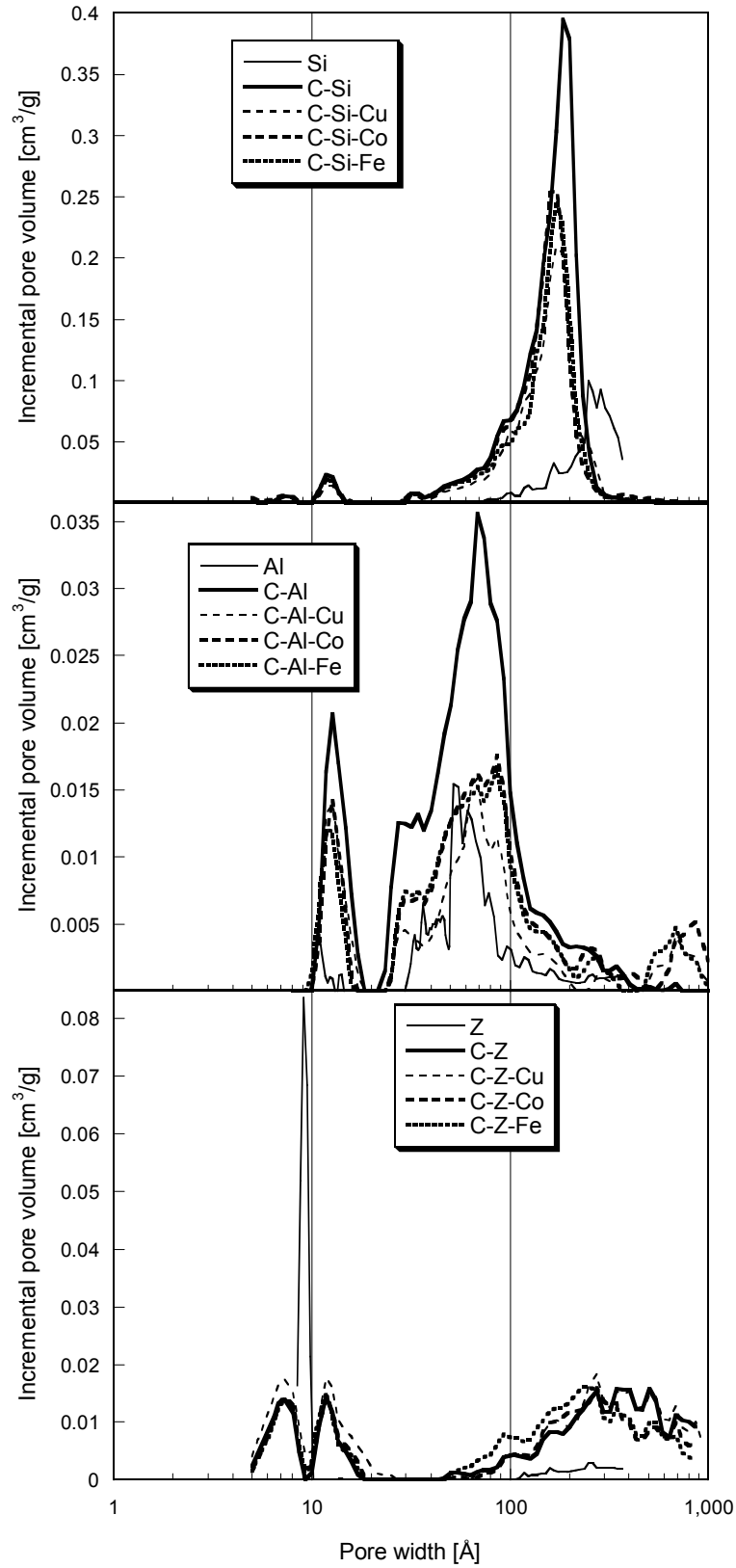
Figure 1. Comparison of pore size distributions for carbons obtained in silica, alumina, and zeolite matrices.

The decomposition of various inorganic salts during carbonization, accompanied by the release of gases and the migration of metals, must have an effect on the development of porosity in template-derived carbons (Hines et al., 2004, Seredych and Bandosz, 2007). The structural parameters calculated from the adsorption of nitrogen are collected in Table 2. Whereas the materials obtained from the sodium form of the polymer in silica or alumina matrices have the largest surface areas and pore volumes, the structural parameters of corresponding carbons obtained from transition-metal salts are much smaller, especially in the case of the alumina matrix. As mentioned previously when silica is used as a template, the high-temperature reaction of sodium with silica walls significantly increases the volume of pores, especially large mesopores (Seredych and Bandosz, 2007). It is interesting that when copper is present about a 50% decrease in the structural parameters is noticed whereas for Co- and Fe-containing samples only about a 20% decrease is found compared to that for C-Si. Similar behavior was observed for carbons obtained form bulk polymers; however, their structure was much more microporous (Hines et al., 2004). In the case of alumina templating, the presence of transition metals results in a similar, about 50% decrease in the structural parameters compared to that for the sample obtained from the initial sodium form of the polymer, C-Al. These differences in the behavior between silica- and alumina-derived materials are caused by template constrains during carbonization process which affect the mechanism of carbonization and pore formation. As hypothesized elsewhere (Hines et al., 2004), sodium as a one-valent metal should lead to the high volume of small pores formed as a result of the release of a large number of sodium atoms from the structure and their migration to the surface. An increase in the metal charge leads to fewer metal ions needed for chelation and thus a smaller contribution of pores formed as a result of metal migration. Another factor is a reduction potential that is low in the case of copper (Ania and Bandosz, 2006). Whereas other metals can form sulfates, which further decompose, resulting in pore formation. Copper, if reduced to metallic copper, is likely not involved in this process. The differences in porosity between alumina- and silica-derived samples are also caused by the fact that initially larger pores in silica enable more polymer incorporation and thicker layers of carbons, especially when the pore walls are destructed via their reaction with sodium (Ania and Bandosz, 2006, Seredych and Bandosz, 2007). In such a material, a greater volume of pores can be formed because either metals or gases have to migrate through a thick deposit of char. In the case of zeolite-derived materials, the degree of microporosity, V_{mic}/V_t, is the highest from all samples, but mesopores are still the predominant pore sizes. It is likely that the porosity of zeolite-based samples is the secondary one formed between carbon crystallites removed from small channels of zeolites (Seredych and Bandosz, 2007). In such a case, the porosities of all samples, regardless of the metal, are more or less similar. The smallest pore sizes are in those samples, although they are not replicas of the zeolite matrix.

Details of the structural parameters are presented in Figure 1 as pore size distributions (PSDs). Whereas the silica-derived samples have almost all pores with sizes between 20 and 200 Å, the alumina-derived samples are much more heterogeneous with two predominant pore ranges: between 10 and 20 Å and between 20 and 400 Å. The volume of the latter significantly depends on the metals used in the polymers and can be linked to the chelating properties (Hines et al., 2004) and the redox potential. As mentioned above, all samples derived form zeolites have similar pore structures.

Mechanism of DBT Adsorption

The carbons obtained were used as adsorbents of DBT from hexane. The isotherms along with the fit to Langmuir-Freundlich equation are presented in Figure 2. Table 3 shows the fitting parameters and the limiting capacity in mg of sulfur per gram of adsorbents. The carbons used in this study have a very high capacity for DBT removal. The lowest capacity is found for the samples obtained from the iron salt, and the highest capacity is found for the copper salt, with the exception of the samples derived in silica matrices where C-Si and C-Si-Co perform better than the sample containing copper. Knowing the significant differences in the porosity and surface chemistry of these carbons, such a comparison of the sample activity would be oversimplified. To compare the performance of the adsorbents properly, their surface features have to be taken into account.
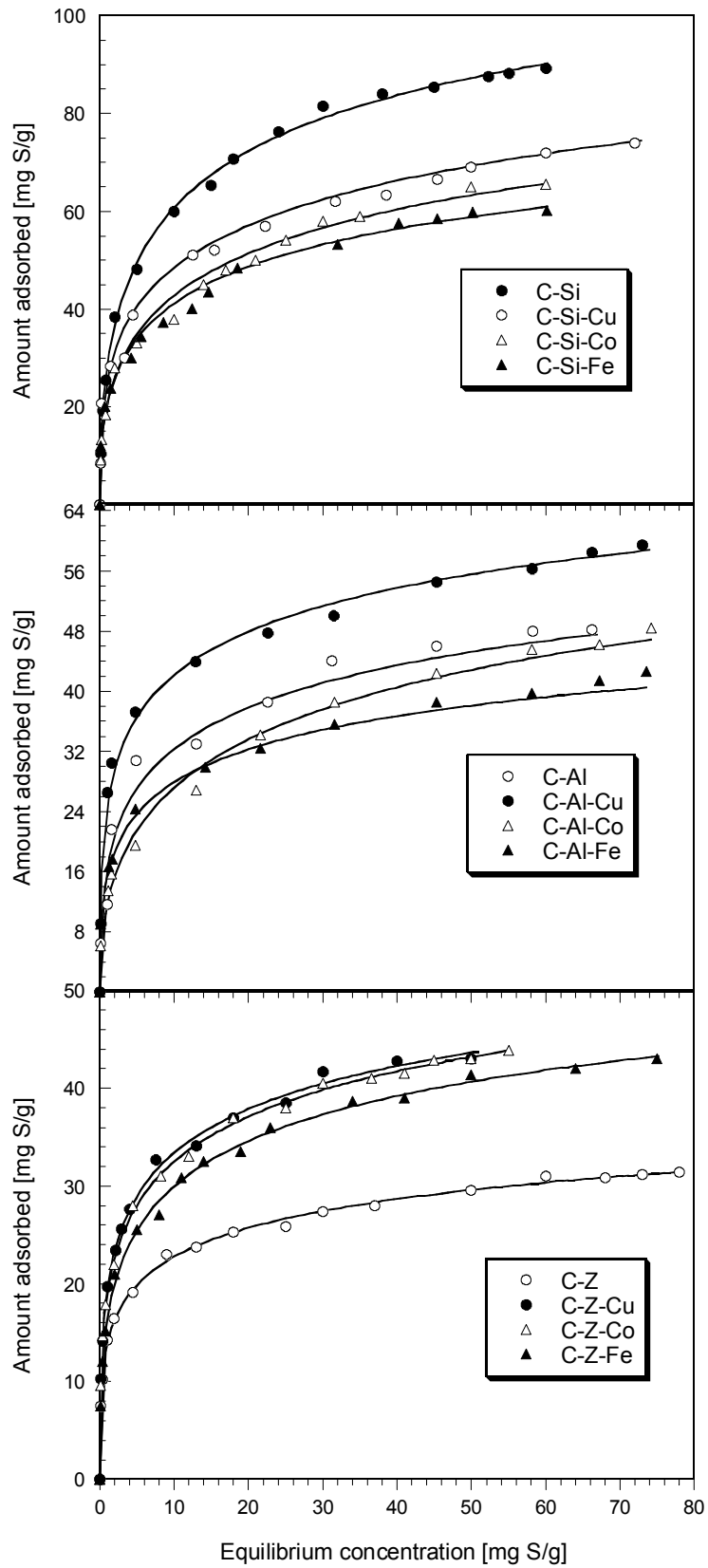
Figure 2. DBT adsorption isotherms. Solid lines indicate the fit the L-F equation.

Table 3. Fitting parameters to L-F equation.

Sample	q_m [mg S/g]	K [l/mg]	n	R^2
C-Si	138.6	0.06	0.48	0.9986
C-Si-Cu	114.3	0.05	0.44	0.9907
C-Si-Co	120.2	0.03	0.43	0.9926
C-Si-Fe	103.1	0.04	0.43	0.9902
C-Al	81.0	0.04	0.40	0.9813
C-Al-Cu	99.7	0.04	0.34	0.9963
C-Al-Co	89.4	0.02	0.46	0.9962
C-Al-Fe	66.5	0.04	0.38	0.9971
C-Z	51.4	0.05	0.33	0.9985
C-Z-Cu	69.8	0.07	0.37	0.9975
C-Z-Co	75.5	0.05	0.36	0.9991
C-Z-Fe	68.0	0.06	0.39	0.9980

Figure 3 shows the relationship between the capacity and the metal contents. Although the points are scattered, especially for low metal content, which might be related to the accuracy of the measurements of low iron content, the trend of an increasing capacity with an increasing metal content can be noticed. The correlation is especially good for copper. For zero metal content, the capacity estimated using the linear trend is about 4 mmol/m^2, which in fact is the value found for carbons without a transition metal present. This suggests that about a 90% increase in surface activity toward the retention of the DBT can be attributed to the transition-metal species highly dispersed on the surface. Because pores in our materials are rather large, the diffusion limitations are not expected to be significant, and the metals should be easily accessible to DBT molecules. Nevertheless, the certain pore sizes, especially in carbons without metals, should attract DBT molecules (Ania and Bandosz, 2006). By taking into account that the critical size of the DBT molecule is similar to that of benzene (6.8 Å), the strongest adsorption should occur in pores smaller than 7 Å. Contrary to the results reported for "classical" activated carbons (Ania and Bandosz, 2005), no dependence of capacity on the volume of pores was found in the case of template derived carbons.

Whereas in the case of carbons without or with a low content of metals, small pores (micropores and small mesopores) are very active in the adsorption, and their entrances can be blocked by DBT interacting with acidic groups. In the case of metal-containing samples, the metals located in the pores can be the active centers, and the DBT molecule can position itself parallel or perpendicular to the surface depending on the type of sulfur-metal interaction. The former geometry should result in a smaller decrease in the pore volume than the latter one. It is well known that thiophenic species can interact with metal either via donation of a lone pare of electrons, which is considered to be a direct S-M σ-bond, or via delocalized electrons of the aromatic ring, where a π-type complex with the metals is formed (Song 2003, Yang et al., 2006). The latter arrangement should lead to a parallel location of DBT on the surface, provided that the pore geometry and size allow it. Because the smallest changes in the structural parameters are noticed for the copper-containing samples, the possibility of π-type interaction is a plausible option here. Because copper has a low reduction potential, the copper species that are likely to exist are Cu^0 and Cu^{+1} or Cu^{+2} with the majority being Cu^0. The reduced copper metal possibly binds to the π system of dibenzothiophene and thus causes strong adsorption of DBT on the surface (Yang et al., 2006). In the case of cobalt, where a greater decrease in the pore volume is found, the S-M σ−bond is more likely to form. It has to be mentioned here that these hypothesized scenarios occur at low surface coverage. With an increase in

surface coverage, the surface acidic groups and dispersive interactions in the pore system become important.
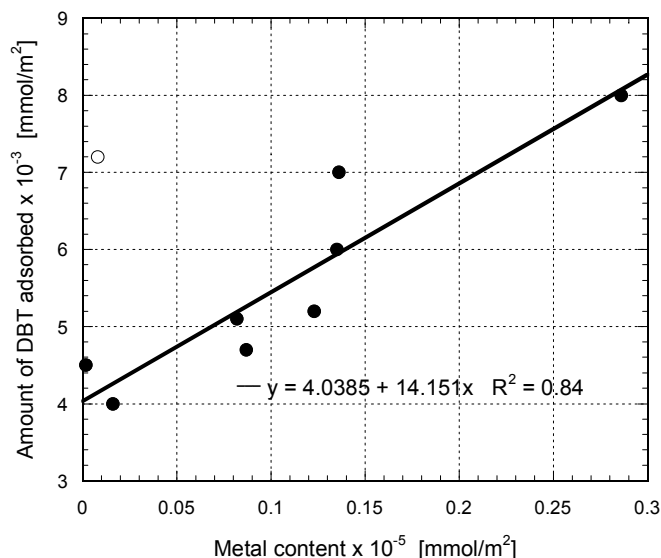

Figure 3. Dependence of the normalized limiting DBT adsorption capacity on the normalized content of metals.

The adsorption of DBT looks differently in the case of alumina-derived materials. In these, micropores are the most active in the process of DBT adsorption, and 45-50% decrease in their volume is found for all samples. In fact, the sample derived from the sodium forms of the polymer, C-Al, was indicated as the most acidic on the basis of our surface chemistry analyses. It is possible that acids present on the surface (oxygen and sulfur based) interact in the same way as metals, via a sulfur active-site bond. The small decrease in the volume of mesopores for copper-containing sample, with the high amount adsorbed on this sample, once again may suggest π complexation of DBT aromatic ring electrons with metallic copper present on the walls of mesopores.

In the case of samples obtained in zeolite templates, regardless of their metal content and the kind of metal, the same changes in the structural parameters are found after DBT adsorption: about an 80% decrease in the volume of micropores and about a 10% decrease in the volume of mesopores. As indicated previously, this is the result of a similar porous structure. With the relatively high volume of small pores, the apparent adsorption seems to have the same mechanism on all zeolite-derived carbons.

Conclusions

The results described in this article present template-derived carbons with highly dispersed metals as efficient media for DBT removal. A combination of surface acidity and the high dispersion of metals and their specific properties along with the high volume of mesopores enhance the physical adsorption via reactive adsorption on surface active centers. That reactive adsorption is based on sulfur-oxygen, sulfur-sulfur, sulfur-metal interactions. In the case of copper, the π-complexation of DBT electrons with reduced metals is possible, and it significantly enhances the amount adsorbed. The exceptionally high volume of mesopores in the carbons studied (up to 2.7 cm^3/g) is a result of the combined effects of chemistry of the carbonaceous precursor and the porous structure and chemistry of the templates.

Acknowledgement

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