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Sorption, Acid, and Catalytic Properties of a Sulfonic Cation Exchanger Supported on the Carbon Fiber

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Abstract—Distribution in strength of the acid centers in sulfonic cation in the form of exchanger granules and fibers was studied by the novel modification of the thermal desorption method.

Previously [1–3], we studied the activity of sulfonic cation exchanger granules and fibers in the synthesis of methyl *tert*-alkyl ethers and found that FIBAN K-1 surpasses in the activity KU2-8 (gel structure) in the synthesis of methyl *tert*-butyl ether (MTBE) and Dowex msm 31 (macroporous structure) in the synthesis of methyl *tert*-amyl ether (MTAE).

The main advantage of fibrous sulfonic cation exchanger FIBAN K-1 is that the fiber diameter is by approximately an order of magnitude smaller than the diameter of KU-2-8 and Dowex msm 31 granules. This decreases intradiffusion inhibition and intensifies mass exchange.

The diameter of the Carbopon fiber can be estimated as 5–10 μm, which is substantially smaller than FIBAN K-1 fiber diameter. Hence, sulfonic cation exchanger supported on Carbopon, when used as a catalyst of acid–base reactions, can provide more intense mass exchange than FIBAN K-1.

The performance of sulfonic cation exchanger substantially depends on its acidity, i.e., concentration and strength of acid centers. The literature survey [4–6] shows that the most adequate method of its determination is ammonia thermal desorption. However, for organic ion exchangers with a low thermal stability, ammonia is acceptable only for determination of weak acid centers. To determine strong acid centers, another thermal desorption method is required.

In this work, we studied sorption and acid properties and catalytic activity (by an example of MTAE synthesis) of two samples of sulfonic cation exchanger supported on Carbopon (sample I with gel structure and sample II with macroporous structure) in comparison with their structural analogs, fibrous (FIBAN K-1) and granular (Dowex msm 31) sulfonic cation exchangers.

EXPERIMENTAL

The sorption of various liquids with the initial Carbopon, synthesized samples of the supported sulfonic cation exchanger, FIBAN K-1 fibrous sulfonic cation exchanger with gel structure, and Dowex msm 31 granular sulfonic cation exchanger with macroporous structure was evaluated gravimetrically. A cation exchanger sample (~0.5 g) dried to the constant weight at 90°C was introduced into a test tube, 10 ml of a liquid was added, and the mixture was stored for 3 h. The sample was centrifuged (4000 rpm) for 15 min, weighed, and dried to the constant weight at 90°C. The sorption value, G_l (g_l g^{-1}), was calculated as the ratio of the liquid weight to the weight of dry sample:

$$G = \frac{m_1 - m_2}{m_2},$$

where m_1 is the sample weight after centrifuging and m_2, sample weight after drying at 90°C.

The average value of three parallel experiments was used in calculations. Along with G_l, the volume sorption V_l (cm_l^3 g^{-1}) was also calculated.

As seen from Table 1, sorption of water with Carbopon is 0.64 g_l g^{-1}, which is substantially larger than sorption of methanol and the other components of the reaction mixture of the MTAE synthesis, and of *n*-octane taken as a nonpolar liquid. The V_l values show a clear correlation with the molecular size of liquids [i.e., molecular-sieve effect characteristic for

Table 1. Sorption of liquids of various types with Carbopon and sulfonic cation exchangers

Liquid	Initial Carbopon	Sample I	Sample II	FIBAN K-1	Dowex msm 31
	G_l, g_l g^{-1}/V_l, cm_l^3 g^{-1}				
Water	0.64/0.64	0.95/0.95	0.44/0.44	1.04/1.04	0.96/0.96
Methanol	0.34/0.44	0.47/0.60	0.20/0.25	0.67/0.85	0.59/0.75
Methylbutenes	0.19/0.29	0.22/0.34	0.14/0.21	0.26/0.40	0.23/0.35
Methanol : methylbutenes (1 : 1)	0.23/0.33	0.33/0.48	0.16/0.22	0.70/0.97	0.62/0.86
MTAE	0.19/0.24	0.27/0.34	0.14/0.18	0.42/0.53	0.41/0.52
n-Octane	0.19/0.27	0.16/0.23	0.15/0.21	0.14/0.20	0.08/0.11

finely porous sorbents (activated carbons, zeolites, silica gels) appears].

The effect of molecular size of liquid is preserved in samples of the sulfonic cation exchanger supported on Carbopon, and, in addition, the effect of the structure of the grafted copolymer can be observed.

Sample 1 (2% DVB, gel structure) sorbs more water (0.95 g_l g^{-1}) and the other polar components than does Carbopon. However, as expected, sample I sorbs nonpolar *n*-octane more weakly than does Carbopon. The fact that sample I is a weaker sorbent than its structural analog, fibrous FIBAN K-1, can be explained by lower exchange capacity (EC).

As compared to sample I and Carbopon, sample II (25% DVB, macroporous structure) sorbs water (0.44 g_l g^{-1}) and the other liquids substantially more weakly, probably due to a rigid cellular structure of the cation exchanger caused by the high degree of cross-linking of the polymer chains. The difference between the sorption properties of this sample and Dowex msm 31 can also be explained by differences in their EC (1.3 and 4.4 mg-equiv g^{-1}, respectively).

The novelty of the suggested method of the thermal desorption of bases consists in using a weak base, diethyl ether, as a desorbate to determine the concentration of strong acid centers. It is desorbed from the strongest acid centers of the dehydrated sulfonic cation exchangers at 120°C, i.e., under conditions of their thermal stability. In addition, diethyl ether is characterized by low adsorption power, due to small size of its molecule and low boiling point. Therefore, the sorbed ether is readily eliminated from the cation exchanger, which is important for obtaining correct results.

The concentration of weak acid centers is determined performed as follows. A cation exchanger (approximately 0.2 g) is charged into a glass reactor (70 mm long, 8 mm in diameter), and the reactor is attached to a carrier gas line in a chromatograph thermostat. Then the thermostat heating is switched on, and a sample is conditioned in a helium flow (30 ml min^{-1}) at 120°C for 2 h, cooled, and saturated with ammonia for 30 min at room temperature. Physically adsorbed ammonia is eliminated from the cation exchanger at room temperature in the helium flow. The course of desorption and its completion were monitored with a recorder. Then the stage of the thermal desorption of the chemisorbed ammonia begins. The temperature of the reactor is increased to 120°C, and the sample is kept for 1 h in a helium flow. The desorbed ammonia is trapped in a U-shaped glass condenser cooled with liquid nitrogen and, after heating at 90–95°C with hot water, is transported with helium flow to the katharometer, where it is monitored as a chromatographic peak. Using a calibration plot ammonia content–peak area, we determined the amount of ammonia desorbed and calculated from the weight of the ion exchanger sample and its EC the concentration (mmol g^{-1}) and percentage of weak acid centers in the sample.

To determine the concentration of strong acid centers, a cation exchanger sample is charged into a reactor arranged in the thermostat of a chromatograph, and the reactor is attached to an empty column functioning as a preheater of the carrier gas. After sample training in a dried helium flow (30 ml mim^{-1}) at 120°C for 2 h, the reactor is cooled to room temperature and detached from the column, and diethyl ether is added. After 1-h storage, excess ether is poured off, the reactor is attached to the column and flame-ionization detector, and the thermostat temperature is set at 75°C; the sample is kept in a helium flow until the recorder pen returns to the zero level, which indicates completion of ether desorption at this temperature. Then the temperature is sharply elevated to 100°C, and the peak of desorbed ether is recorded. After stabilization of the baseline, the temperature of the thermostat is elevated to 120°C, and the second desorption peak

Table 2. Acid properties of sulfonic cation exchangers

Sulfonic cation exchanger			Concentration and strength of acid centers							
sample	DVB, %	EC, mg-equiv g^{-1}	weak		medium		strong		very strong	
			mmol g^{-1}	%	mmol g^{-1}	%	mmol g^{-1}	%	mmol g^{-1}	%
I	2	1.7	0.27	16.3	1.16	69.2	0.16	9.4	0.09	5.1
II	25	1.3	0.17	13.3	0.97	74.8	0.10	7.9	0.05	4.0
FIBAN K-1	2	3.1	0.40	12.9	2.35	75.6	0.27	8.8	0.08	2.7
Dowex msm 31	25	4.4	0.86	19.5	3.32	75.4	0.18	4.1	0.04	1.0

is recorded. Then, using a calibration plot ether content–peak area, the amount of ether desorbed within the 75–100°C range is determined and the concentration and percentage of the strong acid centers in the sample are calculated from the sample weight and ion exchanger EC. Similarly, the amount of ether desorbed within the 100–120°C range is determined and the concentration of the very strong acid centers is calculated.

In accordance with the conventional classification, centers characterized by NH_3 desorption at temperatures of up to 120°C are weak acid centers, those characterized by diethyl ether desorption within the 75–100 and 100–120°C ranges are strong and very strong acid centers, respectively. The concentration of medium-strength acid centers was determined as the difference between the total amount the acid centers in the sulfonic cation exchanger (numerically equal to EC) and the sum of weak, strong, and very strong centers. It follows from Table 2 that the sum of the strong and very strong acid centers (strongly acidic centers) in sample I amounts to 0.25 and in sample II, to 0.15 mmol g^{-1}. In sulfonic cation exchangers FIBAN K-1 (gel structure) and Dowex msm 31 (macroporous structure), which are structural analogs of samples I and II, the concentration of strongly acidic centers responsible for the catalytic activity of the cation exchanger in the etherification reactions amounts to 0.35 and 0.22 mmol g^{-1}, respectively. Thus, the concentration of strong acid centers in samples with gel structure is higher than in macroporous samples. The content of strongly acidic centers in the cation exchangers considered decreases in the order FIBAN K-1 > sample I > Dowex msm 31 > sample II.

It is interesting to compare the acid characteristics of the sulfonic cation exchanger samples prepared with their catalytic activity. The experiments on MTAE synthesis were performed on a laboratory device of the flow type. The reaction unit of the device consisted of a catalytic reactor placed in a thermostat, a vessel for the starting compounds, a cooling system, and a product collector [2]. 1 g of fibrous sulfonic cation exchanger was loaded into the reactor, and the synthesis was performed under a pressure of 0.8 MPa to ensure the liquid state of the reaction system. In the case of granular sulfonic cation exchanger, the resin sample was mixed with ground glass of the same grain size to reach the volume of the compacted fibrous sample (1.4 ml). In the experiments, the process temperature was varied at a constant rate of raw material feeding, 4 g g_{ce}^{-1} h^{-1}, and $CH_3OH : i\text{-}C_5H_{10}$ molar ratio of 1 : 1.

Methylbutenes were prepared by dehydration of isoamyl alcohol on $\gamma\text{-}Al_2O_3$ at 330°C. The mixture of isomers contained (%) 3-methyl-1-butene 45.8, 2-methyl-1-butene 19.4, and 2-methyl-2-butene 34.8.

The data on MTAE synthesis in the presence of sulfonic cation exchangers studied are listed in Table 3. The comparison of the sulfonic cation exchangers supported on Carbopon shows that sample I is more active: the maximal content of MTAE in the catalyzate reaches 42.4% at 80°C, while sample II gives 35.4% MTAE at 100°C. These results coincide with both the sorption properties of the samples and the concentration of strongly acidic centers. The decrease in the MTAE content as a result of the higher rate of the reverse reaction relative to the direct reaction rate on sample I is observed at 90°C. For FIBAN K-1 and Dowex msm 31, this decrease is observed at 100°C, and for sample II still higher temperature is required.

When the MTAE content in the catalyzate at 80°C is taken as a measure of the sulfonic cation exchanger activity, the following activity order is observed: sample I > FIBAN K-1 > Dowex msm 31 > sample II. As seen, the position of Dowex msm 31 and sample II in the catalytic activity series coincides with that in

Table 3. Synthesis of MTAE on sulfonic cation exchangers. Rate of raw material feeding 4 g g_{ce}^{-1} h^{-1}, molar ratio $CH_3OH : i\text{-}C_5H_{10}$ = 1 : 1

Component	Content in catalyzate, wt %, at indicated *T*, °C			
	70	80	90	100
Sample I				
Methylbutenes	43.5	39.6	42.3	42.7
Methanol	19.9	18.0	19.3	19.6
MTAE	36.6	42.4	38.4	37.7
FIBAN K-1				
Methylbutenes	48.6	41.5	39.2	46.0
Methanol	22.2	19.0	17.9	21.0
MTAE	29.4	39.5	42.9	33.0
Sample II				
Methylbutenes	57.1	50.2	45.1	44.3
Methanol	26.0	22.9	20.7	20.3
MTAE	16.9	26.9	34.2	35.4
Dowex msm 31				
Methylbutenes	45.1	42.2	41.5	44.9
Methanol	20.0	18.8	18.7	19.9
MTAE	34.9	39.0	39.8	35.2

the series of acid properties. FIBAN K-1 suprasses all the other cation exchangers studied in the content of strongly acidic centers; however, it is inferior in the activity to sample I. Probably, in this case a size factor (the diameter of the Carbonpon fibers is by an order of magnitude smaller than that of FIBAN K-1 fibers), and the nature of sulfonic cation exchanger support (carbon or polypropylene fiber), which can affect the structure of the matrix formed, can contribute to the catalyst activity.

Thus, sulfonic cation exchangers supported on Carbopon show much promise, opening prospects for development of the theory and practice of the catalysis with cation exchangers.

CONCLUSIONS

(1) Sorption properties of sulfonic cation exchangers supported on carbon fiber depend on the degree of cross-linking of the styrene–divinylbenzene matrix: sample I (gel structure) substantially better sorbs polar liquids than does sample II (macroporous structure), whereas sorption of a nonpolar liquid (*n*-octane) with these sorbents is virtually the same.

(2) The study of the acid properties of samples I and II by the modified method of the thermal desorption of bases showed that the concentration of strongly acidic centers in sample I is substantially higher than in sample II.

(3) By an example of the synthesis of methyl *tert*-amyl ether, it was shown that the catalytic activity of sulfonic cation exchangers in acid–base reactions depends on both the resin acid properties and the diffusion factors affecting the intensity of the mass exchange.

REFERENCES

1. Cherches, B.Kh., Shunkevich, A.A., Belotserkovskaya, T.N., and Egiazarov, Yu.G., *Zh. Prikl. Khim.*, 1999, vol. 72, no. 4, pp. 623–627.
2. Cherches, B.Kh., Kovalenko, M.A., Shunkevich, A.A., *et al.*, *Neftekhimiya*, 2002, vol. 42, no. 1, pp. 28–31.
3. Egiazarov, Yu.G. and Soldatov, V.S., *Sorbts. Khromatogr. Prots.*, 2001, vol. 1, no. 4, pp. 591–599.
4. Tanabe, K., *Solid Acids and Bases. Their Catalytic Properties*, Tokyo: Kodansha, 1970.
5. Topchieva, K.V. and Thoang Kho Shi, *Aktivnost' i fiziko-khimicheskie svoistva vysokokremnistykh tseolitov* (Activity and Physicochemical Properties of High-Silica Zeolites), Moscow: Mosk. Gos. Univ., 1976.
6. Egiazarov, Yu.G., Savchits, M.F., and Ustilovskaya, E.Ya., *Geterogenno-kataliticheskaya izomerizatsiya uglevodorodov* (Heterogeneous Catalytic Isomerization of Hydrocarbons), Minsk: Nauka i Tekhnika, 1987.