Kinetics and Catalysis, Vol. 41, No. 4, 2000, pp. 553–556. Translated from Kinetika i Kataliz, Vol. 41, No. 4, 2000, pp. 608–611.
Original Russian Text Copyright © 2000 by Jarecka, Datka.

Physicochemical Properties of Aluminosilicate- and Zeolite-supported Sulfocationite

T. Jarecka* and J. Datka**
* *Warsaw University of Technology, Institute of Chemistry, Plock, Poland*
** *Jagiellonian University, Chemical Department, Krakow, Poland*

Received October 1, 1998

Abstract—The properties of a sulfocationite supported on the surface of the zeolite/aluminosilicate catalysts are studied by IR spectroscopy.

INTRODUCTION

It has been shown that the deposition of a sulfocationite on the surface of solid aluminosilicates is a method for preparing granulated thermally stable sulfocationites with high specific surface areas [1–4]. These sulfocationites are active in hydrocarbon transformations and selective in the synthesis of esters. The goal of this work was to study the IR spectra and acidic properties of sulfocationites supported on the surfaces of zeolite-containing and aluminosilicate catalysts.

EXPERIMENTAL

The zeolite-containing amuminosilicate catalyst TsEOKAR-3 and synthetic amorphous aluminosilicate AS-230Sh were used as supports for sulfocationites. The supports had the following characteristics:

	TsEOKAR-3	AS-230Sh
Chemical composition, wt %		
SiO_2	85.50	88.35
Al_2O_3	9.35	4.65
Fe_2O_3	0.10	0.36
Na_2O	0.05	0.05
CaO	0.01	0.02
Average pore radius, nm	2.4	4.9
Specific surface area, m^2/g	328	344
Concentration of acid sites, μmol/g	320	300

Polyphenyleneketone was supported on the catalysts according to the procedure described in [5]. The samples of the supports with immobilized polyphenyleneketone were sulfonated by concentrated sulfuric acid, washed by distilled water, and dried to a constant weight at 115°C.

The exchange capacities of initial supports and supported polyphenyleneketone and sulfonated polyphenyleneketone samples were determined using the aqueous solutions of NaOH and NaCl [6, 7]. The specific surface areas were estimated by the BET method on an ASAP-2010 m (Micromeritics) apparatus. The concentration of paramagnetic centers was determined on a Bruker ELEXIS spectrometer using $VOSO_4$ as a standard, and the swelling of samples was estimated according to the procedure described in [7].

The IR spectra of supports and polymer- and sulfopolymer–mineral catalysts in the range of 400–4000 cm^{-1} were recorded on a Bruker IFS-48PC spectrophotometer as a suspension of the catalyst powder in a liquid paraffin.

We studied the acidic properties of the catalysts upon adsorption of gaseous ammonia by IR spectroscopy. The catalyst samples (15–25 mg) were ground in an agate mortar and pressed into pellets under a pressure of 8 MPa; a pellet was introduced into an evacuated cell, heated to 170°C, and evacuated for 1 h. Then, the cell was cooled and 99.97% pure ammonia was fed at a temperature of 50°C. After that, the IR spectrum was recorded.

RESULTS AND DISCUSSION

Exchange Capacity of Catalysts

The exchange capacity of the starting samples of the aluminosilicate catalysts before and after the deposition of polyphenyleneketone and its sulfurization, as well as the number of paramagnetic centers and the swelling factor were determined. Our findings are presented in the table.

The following variations in the properties of samples are notable. The overall exchange capacity of the supported sulfonated polyphenyleneketone is significantly lower than that of sulfonated polyphenyleneketone itself because the loading of the supported sulfopolymer on the surface of the TsEOKAR-3 and AS-230Sh is ~10%. The values of the stationary exchange capacity with respect to the sulfo groups determined for sulfopolyphenyleneketone and supported sulfopolyphenyleneketone using NaCl [7] are

Physicochemical properties of the supports and catalysts with the deposited polymers

Property	Polyphenyleneketone	Sulfopolyphenyleneketone	TsEOKAR-3 support	Polyphenyleneketone/TsEOKAR-3	Sulfopolyphenyleneketone/TsEOKAR-3	AS-230Sh support	Polyphenyleneketone/AS-230Sh	Sulfopolyphenyleneketone/AS-230Sh
Static exchange capacity with respect to NaOH, mg-eq/g	1.04	4.50	0.24	0.71	1.84	0.20	0.78	1.96
Static exchange capacity with respect to NaCl, mg-eq/g	0	1.9–2.2	0.08	0.18	0.29	0.09	0.13	0.24
Specific surface area, m^2/g	1.0	3.4	328	297	237	344	286	194
Concentration of paramagnetic centers, spin/g	0.5×10^{18}	2.5×10^{21}	Signal from Fe admixture, $g = 4.28$	5.19×10^{18}	2.51×10^{18}	Signal from Fe admixture, $g = 4.28$	1.13×10^{19}	1.5×10^{18}
Swelling in water, %	–	30.7	0	10	10	0	10	10

substantially lower than those determined using NaOH. This fact confirms the presence of various acid sites on the surface of the catalysts, for instance, –SO_3H, –COOH, and –OH [8]. The number of acid SO_3H sites in both polyphenyleneketone catalysts on the supports substantially increases upon sulfonation. The concentration of the SO_3H groups determined using NaCl is somewhat higher in the TsEOKAR-3- supported sulfonated polyphenyleneketone.

The specific surface area after sulfonation of the supported polymer decreases by the factor of ~1.4 for the TsEOKAR-3 and by the factor of 1.8 for the AS-230Sh. The swelling factor of the catalysts increases by 10% (see the table).

The transformation of polyphenyleneketone to sulfonated polyphenyleneketone on the surface of the mineral supports does not result in a sharp increase in the concentration of paramagnetic centers, unlike for pure and sulfonated polyphenyleneketones without supports.

The concentrations of paramagnetic centers in the sulfonated polyphenyleneketone/TsEOKAR-3 and sulfonated polyphenyleneketone/AS-230Sh systems are more than two orders of magnitude lower than that in sulfopolyphenyleneketone. This can be due to the interaction of the sulfo groups of the supported sulfopolymer with the mineral carrier.

IR Spectra of Polymer-Containing Aluminosilicates

Figure 1a shows the spectra of polyphenyleneketone and sulfopolyphenyleneketone. The absorption bands at 680, 730, 1600, and 1700 cm^{-1} can be seen [9] in the polyphenyleneketone spectrum. The absorption bands at 680 and 730 cm^{-1} disappear on curve 2, and a broad band appears in the region 1100–1200 cm^{-1}. This band characterizes the vibrations in the SO_3H group. The band at ~1600 cm^{-1} corresponds to the vibrational frequency of a conjugated double bond. The carbonyl group is characterized by the absorption band at ~1700 cm^{-1}.

The following IR bands are present in the spectrum of the zeolite-containing aluminosilicate TsEOKAR-3 (Fig. 1b, curve *1*): a broad band at 1110 cm^{-1} due to asymmetrically stretching Si–O vibrations in the SiO_4 tetrahedra with a typical shoulder due to the vibrations of the Si–O–Si groups that join the tetrahedra; a less intense IR band at 460 cm^{-1} due to the internal bending vibrations of the SiO_4 tetrahedra, and the band at 800 cm^{-1} due to the symmetrical Si–O–Si bonds in aluminosilicate [10].

The immobilization of polyphenyleneketone and sulfonated polyphenyleneketone on the surface of the supports virtually does not change the IR spectra (Fig. 1b, curves *2*, *3*). The fact that the absorption band from the SO_3H groups at 1100 cm^{-1} present in the spectrum of the support-free sulfopolymer (Fig. 1a, curve *2*) is not observed in the spectrum of the sulfonated polyphenyleneketone/TsEOKAR-3 system (Fig. 1b, curve *3*) is explained by the superposition of this band and a very broad and intense absorption band due to the vibrations of the Si–O bond in the supports (also at 1100 cm^{-1}). Note that the polymer–inorganic catalysts contain only 10% of the polymer.

Figure 2 shows the spectra of the SiOH groups on the catalyst surface These spectra were recorded after evacuation of the samples. In the spectra of supports, the absorption band at 3740 cm^{-1} from nonacidic silanol groups [11] is pronounced (Fig. 2a, curves *1*, *4*). The deposition of the polymer decreases the intensity of this band. This can be rationalized as follows: either the polymer covers these groups or the polymer is

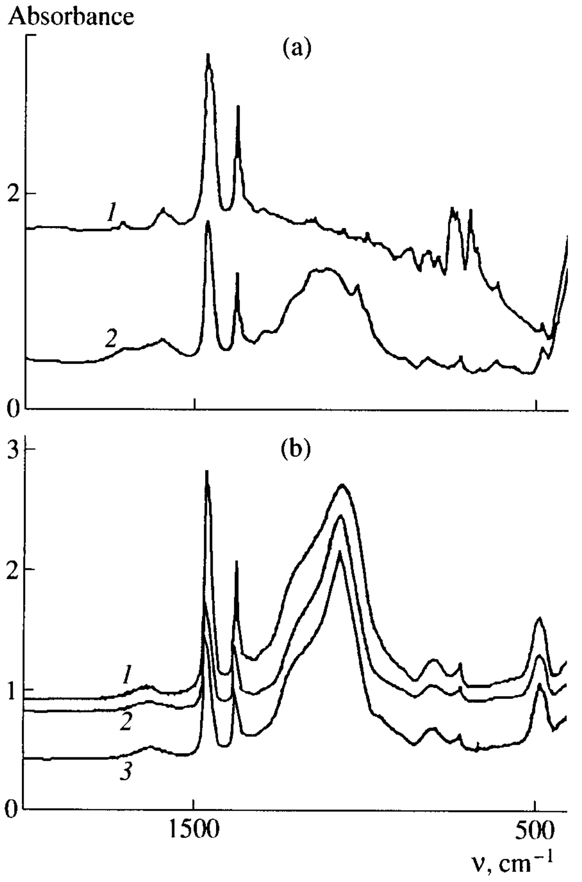

Fig. 1. IR spectra of the catalysts: (a) (*1*) polyphenyleneketone, (*2*) sulfopolyphenyleneketone; (b) (*1*) zeolite-containing aluminosilicate (TsEOKAR-3), (*2*) polyphenyleneketone on TsEOKAR-3, (*3*) sulfopolyphenyleneketone on TsEOKAR-3.

anchored to the surface of the support through these groups. This effect is more pronounced in the case of the AS-230Sh (Fig. 2a, curve *4*): the intensity of the signal decreases by ~60%, whereas in the case of the TsEOKAR-3, the intensity decreases by only 20%. This can be explained by the greater amount of the polymer on the AS-230Sh (~12% C) than on the TsEOKAR-3 (~8% C). Correspondingly, the specific surface area of the AS-230Sh decreases to a greater degree after the immobilization of polyphenyleneketone (see the table). Physical interaction between the SiOH groups and organic substances usually causes a shift of the OH band to lower frequencies by 50–200 cm^{-1}, and the band broadens. In our case, a decrease in the intensity of the absorption band at 3740 cm^{-1} after polymer deposition is accompanied by the appearance of a new broad band at 3650–3680 cm^{-1}. This may confirm the physical interaction between the polymer and the support, that is, the formation of the weak hydrogen bonds or interaction between a stable dipole and an induced dipole [11].

After sulfonation of the polymer on the supports, the intensity of the absorption bands from the SiOH groups probably decreased due to the formation of the hydrogen bond between SiOH and SO_3H.

A weak band at 1640 cm^{-1}, typical of the vibrations of the aluminosilicate framework in aluminosilicate catalysts, manifests itself in the region of 1300–1700 cm^{-1} of the IR spectrum (Fig. 2b, curves *1*, *4*). After the deposition of polyphenyleneketone on the supports, this absorption band is superimposed on the intense absorption band at 1600 cm^{-1} due to the conjugated double bonds of the polymer (Fig. 2b, curves *2*, *5*). The inten-

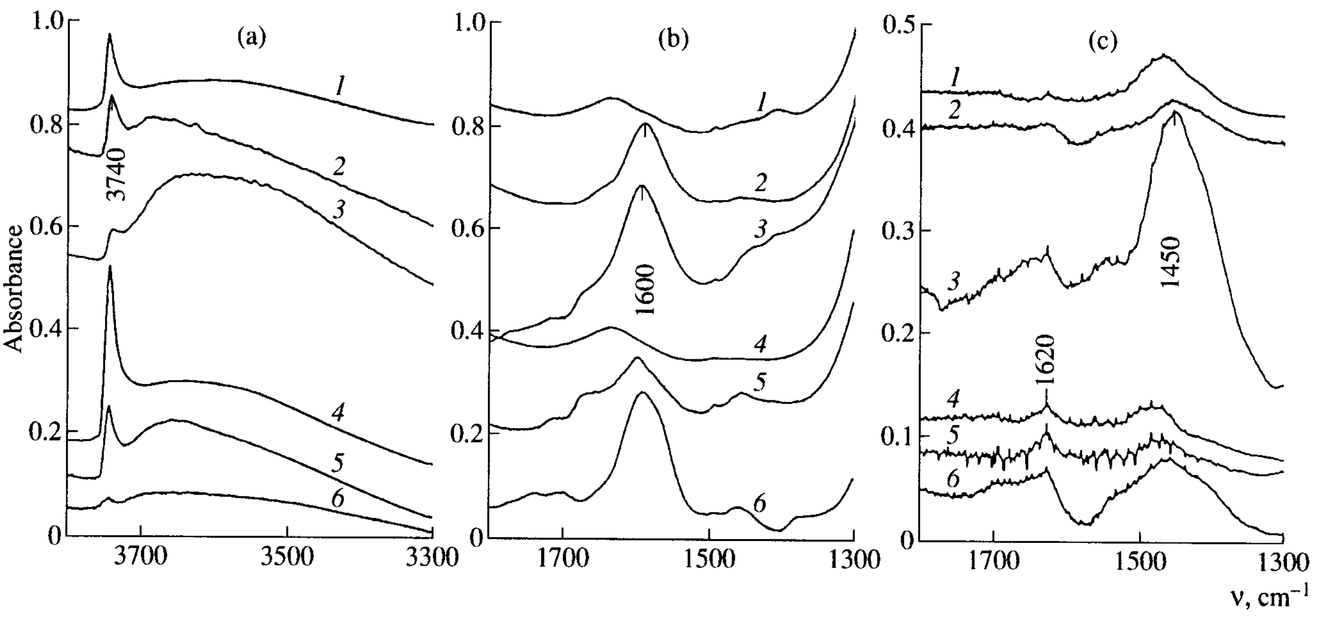

Fig. 2. IR spectra of the supports and (a) polymers immobilized on the supports; (b) sulfopolymers on the supports; (c) catalysts upon treatment with ammonia. (*1*) TsEOKAR-3, (*2*) polyphenyleneketone/TsEOKAR-3, (*3*) sulfopolyphenyleneketone/TsEOKAR-3, (*4*) AS-230Sh, (*5*) polyphenyleneketone/AS-230Sh, (*6*) sulfopolyphenyleneketone/AS-230Sh.

sities of these bands increased after sulfonation (Fig. 2b, curves *3* and *6*).

The IR spectroscopic study of the acidic properties of the catalysts by ammonia adsorption (Fig. 2c) showed that the absorption band at 1450 cm^{-1}, typical of the NH_4 ion formed by the reaction of NH_3 with the Brönsted site, appeared in the spectra of all catalysts, as well as the absorption band at 1620 cm^{-1} that characterizes ammonia bound with the Lewis acid sites (NH_3L) [11]. As mentioned before, the Brönsted sites of several types ($-SO_3H$, –COOH, and –OH) can occur on the surface of the catalysts [8]. Their concentrations were estimated from the intensity of the IR band at 1450 cm^{-1}, typical of NH_4 ion [11].

The zeolite-containing support TsEOKAR-3 is characterized by a higher concentration of the Brønsted sites than the aluminosilicate support AS-230Sh because the absorption band at 1450 cm^{-1} is more intense in the case of the TsEOKAR (Fig. 2c, curves *1* and *4*).

The deposition of polyphenyleneketone decreases the amount of the Brönsted sites as follows from a decrease in the intensity of the absorption band at 1450 cm^{-1} (Fig. 2c, curves *2* and *5*). Covering the acid sites with the polymer causes this. Note that the intensity of the absorption band at 3740 cm^{-1} also decreased (Fig. 2a, curves *2* and *5*). The sulfonation of the polymer resulted in a significant increase in the amount of the Brönsted acid sites (the intensity of the absorption band at 1450 cm^{-1} increased) due to the introduction of the SO_3H group in the polymer structure (Fig. 2c, curves *3* and *6*).

It is impossible to precisely evaluate the concentration of the Lewis acid sites because the absorption band of NH_3L (1620 cm^{-1}) is superimposed on the intense absorption band of the polymer (1600 cm^{-1}) and cannot be measured correctly.

It follows from the IR spectra of two catalysts that the surface of the sulfonated polyphenyleneketone/TsEOKAR-3 has a higher concentration of the acid sites than that of the sulfonated polyphenyleneketone/AS-230Sh.

To summarize, one can conclude that the immobilization of sulfonated polyphenyleneketone on the surface of various supports (zeolite-containing and aluminosilicate) allows variations in the number of Brönsted acid sites, the exchange and adsorption capacity of aluminosilicate and zeolite-containing catalysts and the preparation of acid catalysts with the properties of organic and inorganic cation-exchangers.

ACKNOWLEDGMENTS

We are grateful to Professor S.V. Meshcheryakov for providing us with polymer samples.

REFERENCES

1. USSR Inventor's Certificate no. 849 749.
2. USSR Inventor's Certificate no. 1070135, *Byull. Izobret.*, 1984, no. 4.
3. Jarecka, T., Żeleznaja, L., Mieszczeriakow, S., and Jasków, K., *Tezy 33 Konf. o Rope.*, Bratislava, 1988, p. 347.
4. Meshcheryakov, S.V., Evdokimov, A.Yu., Fuks, I.G., and Tyrsin, Yu.A., *Neftepererab. Neftekhim.*, 1992, no. 5, p. 40.
5. Meshcheryakov, S.V., *Doctoral (Eng.) Dissertation*, Moscow, 1992, p. 62.
6. *GOST (State Standard) 20255.1-74: Complete Exchange Capacity*, 1974.
7. Polyanskii, N.G., *Kataliz ionitami* (Catalysis by Ionites), Moscow: Nauka, 1973.
8. Lunin, A.F., Zheleznaya, L.L., Magadov, R.S., and Meshcheryakov, S.V., *Neftepererab. Neftekhim.*, 1985, no. 3, p. 26.
9. Bellamy, L.J., *The Infrared Spectra of Complex Molecules*, London: Chapman and Hall, 1980. p. 426.
10. Flanigen, E.M., *Zeolite Chemistry and Catalysis*, Rabo, J.A., Ed., Washington: American Chemical Society, 1976.
11. Kiselev, A.V. and Lygin, V.I., *Infrakrasnye spektry poverkhnostnykh soedinenii i adsorbirovannykh veshchestv* (Infrared Spectra of Surface Compounds and Adsorbed Substances), Moscow: Nauka, 1972, p. 459.