DESULFURIZATION OF CRUMB RUBBER BY MODIFIED NATURAL ZEOLITIC CATALYSTS

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ABSTRACT. The high elastomer content of the crumb rubber powder obtained from the processing of used tires increases the interest for its valorization when modifying road bitumen in order to improve its elastic characteristics. Sulfur cross-linking of elastomer chains reduces the dispersion of the crumb rubber in the road bitumen during the modification process. A novel approach was explored, involving the partial desulfurization of rubber powder using a natural zeolitic catalyst, clinoptilolite, modified in its acid form. The catalytic desulfurization of the powder was carried out in a batch system at a temperature of 280°C for 6 hours in the presence of high aromaticity solvents. The catalysts' high acidity facilitated the conversion of rubber powder effectively, reaching a more suitable form to use in improving road bitumen.

Keywords: natural zeolite, desulfurization, crumb rubber

INTRODUCTION

The utilization of crumb tire rubber resulted from the grinding of end-of-life tires as a bitumen modifier in road pavement has emerged as a viable solution for waste management challenges [1, 2].

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In contrast, the conventional methods of waste tire disposal, such as dumping or stacking, not only waste substantial land resources but also pose a risk of fire hazard. Historical approaches like land filling and incineration, once prevalent, have been largely abandoned. Incineration, though not environmentally friendly, releases pollutants like CO, CO_2, dioxins, dioxin-like compounds and volatile organic compounds (VOC) [3].

To address these challenges, pyrolysis emerges as an alternative for waste tire treatment [4,5]. This method not only minimizes waste but also produces valuable by-products such as syngas, fuel oil and char. The gaseous fraction contains C1-C4 hydrocarbons and hydrogen, the oil product is easily storable and can be further upgraded as fuel oil, and the residual char finds applications in diverse fields, including battery electrodes, super-capacitor materials and sorbents [6].

There are different kinds of zeolite structures, each with unique shapes and can be used for many processes [7]. Beyond their conventional role as adsorbents, zeolites exhibit versatility as catalysts, separation media, catalyst supports and even in animal feeding applications. The specific utilization of zeolites depends on the position of active centers, as well as the dimensions and geometric attributes of the internal cavities within the zeolite structure [8, 9]. Zeolites special catalytic abilities are being used in new applications. This is happening because environmental rules are getting stricter, requiring the use of catalysis to meet high standards. Natural zeolites stand out due to their widespread availability, cost-effectiveness and robust mechanical strength. However, their applications in adsorption studies are seldom explored, possibly due to the challenge posed by purifying them from various impurity phases present in their main structure [10,11]. The augmentation of its industrial applicability can be achieved through thermal and chemical treatments, inducing alterations in composition, structure and properties. While zeolite catalysts, in general, share essential features such as optimal acid strength, pore size and pore structure, there exists a noticeable gap in research concerning the catalytic potential of zeolite [12, 13].

Desulfurization of crumb rubber with modified natural zeolites offers numerous benefits, such as: improved mechanical properties of rubber products, reduced environmental pollution, increased reusability and recyclability of crumb rubber and sustainable and cost-effective desulfurization method [14]. The crumb rubber obtained, combined with bitumen can find application in various fields, such as road paving materials, playground surfaces, thermal insulation materials [15, 16].

This paper introduces a sustainable approach in the desulfurization process of crumb rubber, by utilizing natural zeolites, like volcano tuff, found abundantly in Romania. Incorporating modified natural zeolitic catalysts in the

desulfurization of crumb rubber not only addresses environmental and industrial challenges related to sulfur-containing compounds, but also offers a cost-effective and environmentally friendly solution. By harnessing the catalytic properties of modified zeolites, particularly in the context of road pavement applications, this process aims to enhance the performance of crumb rubber while minimizing the environmental footprint of sulfur emissions.

RESULTS AND DISCUSSION

During the experimental program, volcanic tuff sourced from Mirsid, located in the county of Mirsid, Romania, was utilized. The volcanic tuff had a grain size ranging from 0.5 to 1.5 mm and consisted of 60 to 70% clinoptilolite content. [17].

To modify the initial tuff, coded *Tuf 0*, 250 g of tuff were weighed and mixed with 2 litres of aqueous solution containing 10% ammonium nitrate and 5% nitric acid in a glass reactor while stirring at 95 °C for 3 hours. After centrifugation the ammonium form of the zeolite was washed with 8 litres of distilled water and the suspension obtained was again centrifuged. The resulting zeolite was dried at 120 °C for 12 hours, then calcined at 450 °C at a heating rate of 5° C/min for 6 hours. After grinding in a planetary ball mill it was passed through a 0.63 mm sieve, the resulting sample was coded *Tuf 1*. For obtaining the zeolite sample coded *Tuf 2* the same procedure was followed, except that the reaction time with ammonium nitrate and nitric acid solution was increased to 6 hours.

Absorption isotherms and BJH desorption curves of volcanic tuff before and after modification are shown in Figures 1-3.
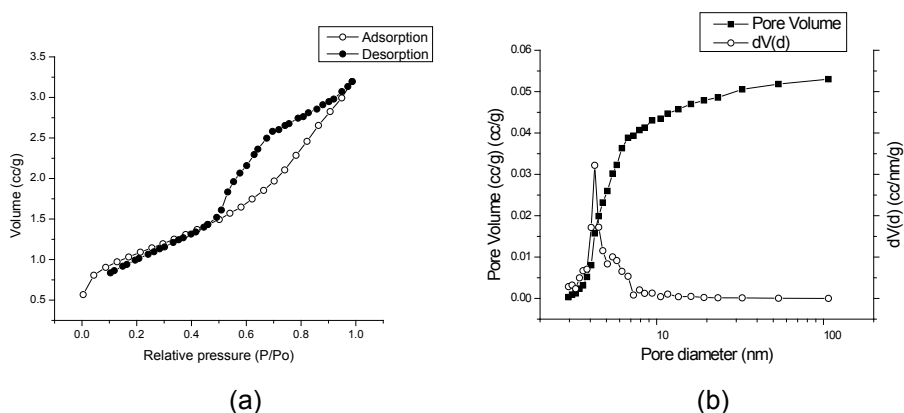

(a)   (b)

Figure 1. Isotherm (a) and BJH desorption (b) of zeolite Tuf 0

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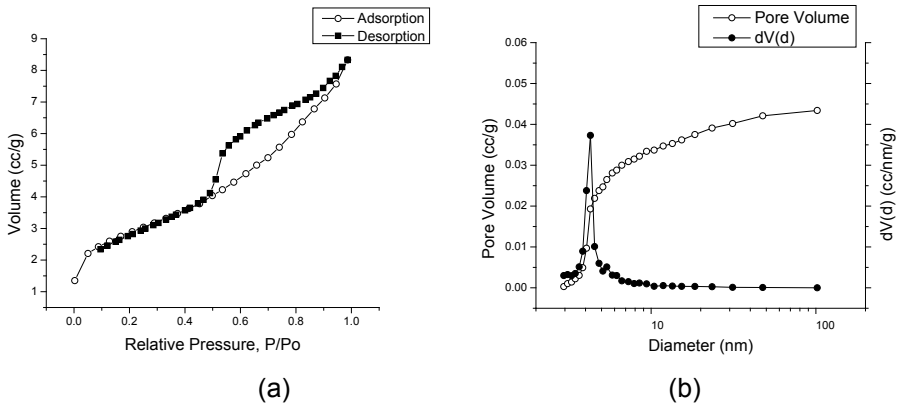(a)   (b)

Figure 2. Isotherm (a) and BJH desorption (b) of zeolite Tuf 1

Based on the conventional classification of adsorption-desorption all measured isotherms can be considered as type IV isotherms, a typical characteristic of mesoporous materials with multilayer adsorption. A type H3 hysteresis according to the IUPAC classification can be observed in all the samples, the materials analyzed being mesoporous with an average pore diameter of 4.2 nm. In this case, there is no limitation of absorption at high P/P_0 values with aggregates of plate-like particles giving rise to slit-shaped pores.

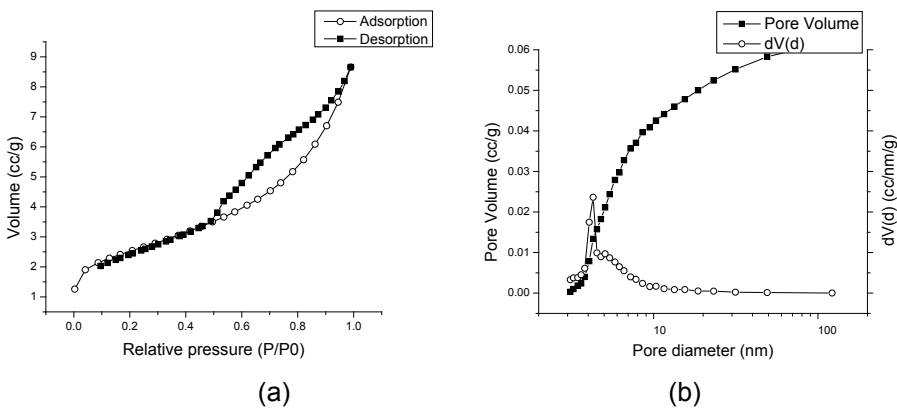

(a)   (b)

Figure 3. Isotherm (a) and BJH desorption (b) of zeolite Tuf 2

Table 1 presents the main textural characteristics of the tuff before and after modification, determined by nitrogen porosimetry.

Table 1. Porosimetry data of tuff before and after modification

Sample	Specific surface area (m²/g)	Total pore volume (cm³/g)	Average pore diameter (nm)
Tuf 0	38.41	0.043	4.254
Tuf 1	43.62	0.056	4.282
Tuf 2	46.16	0.062	4.288

The results of particle size determinations and particle size distribution of zeolites by dynamic light scattering (DLS) are shown in Figures 4 and 5 and Table 2. The Tuf 1 and Tuf 2 samples show a bimodal distribution, showing two particle populations.

Table 2. DLS analysis of modified zeolite particles

Sample	Average diameter (nm)	Peak (Intensity) (nm)
Tuf1	726	$P_1 = 655$; $P_2 = 151$
Tuf2	1611	$P_1 = 715$; $P_2 = 170$
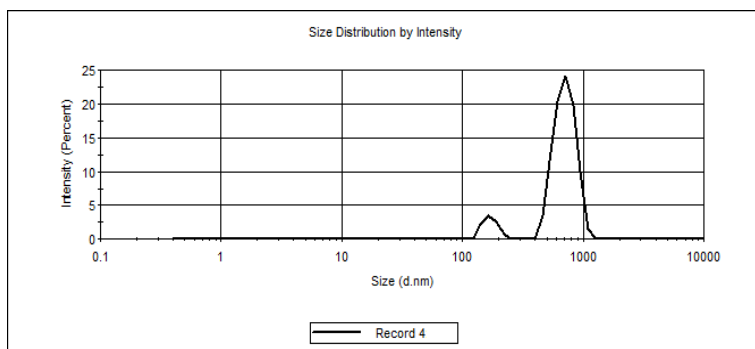
Figure 4. DLS distribution of particle sizes of Tuf 1
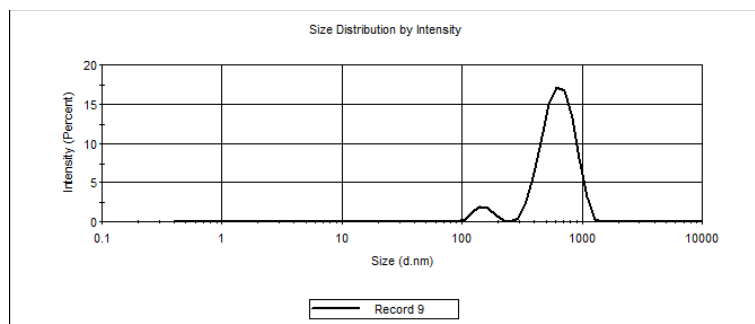
Figure 5. DLS distribution of particle sizes of Tuf 2

It can be observed that the particles of the Tuf 2 sample are relatively larger and more polydisperse than those of the Tuf 1 sample. For both samples the presence of large aggregates/particles is observed. Table 3 shows the results of acid strength determination grouped by weak, medium and strong centers obtained by diethylamine thermodesorption. A higher acid strength is observed over the whole range for the zeolite Tuf 2, with a significant increase for the medium acid centers.

Table 3. Results of acid strength determination of modified zeolites.

Sample	Acid strength mEq/ g sample		
	weak	**medium**	**strong**
Tuf 1	0.0899	0.0466	0.3065
Tuf 2	0.1005	0.1081	0.3107

The XRF analysis (Table 4) shows that the volcanic tuff has an initial Si/Al ratio of 11.8, and the modification of the tuff increases the Si/Al ratio for samples Tuf 1 and Tuf 2 to 14.23 and 16.09 respectively.

Table 4. Main elements as determined by the XRF method.

Element	Conc., %		
	Tuf 0	**Tuf 1**	**Tuf 2**
Al	2.020	1.670	1.51
Si	23.840	23.76	24.31
K	1.806	1.790	1.735
Fe	1.059	1.039	1.026

Crumb rubber powder devulcanization experiments were carried out in the presence of zeolite catalysts dispersed in xylene aromatic solvent and catalytic cracking oil (CCS) at 280°C for 6 hours. It is observed that on the Tuf 2 zeolite catalyst, 4.0% higher conversions are obtained in the presence of xylene and 2.8% in the presence of CCS, values due to the higher acidity of the Tuf 2 catalyst (Table 5).

Table 5. Performance of the zeolite on the crumb rubber devulcanization process

Catalyst	Tuf 1		Tuf 2	
Solvent	xylene	CCS	xylene	CCS
Conversion, %	50.5	45.2	52.4	46.6

CONCLUSIONS

The desulfurization of crumb rubber was achieved using a modified clinoptilolite natural zeolitic catalyst, obtained through ion exchange with ammonium ions, the catalyst being dispersed in two types of solvents. Superior results were observed with a more acidic type of zeolite Tuf 2, due to its enhanced catalytic activity, which facilitated the desulfurization process by promoting stronger interactions between the catalyst and sulfur-containing compounds in the crumb rubber. The modification of the natural zeolite was achieved by ion exchange of alkali ions with ammonium ion followed by calcination to proton form. The modification resulted in nanostructured catalysts with an acidity distribution favorable to hydrogenolysis processes and a high concentration of strong acid centers. Total acidity also increased with the duration of the ion exchange step. The textural characteristics and size distribution of the zeolite particles changed following ion exchange.

Catalytic desulfurization of rubber powder dispersion in catalytic cracking oil and xylene in batch system at 280ºC for 6 h in the presence of modified zeolite catalysts proceeded at conversion values of application interest, being favored by higher acidity catalyst and solvent aromaticity. The applicability of this research lies in its ability to offer a sustainable solution for the desulfurization of crumb rubber using readily available natural zeolites, therefore addressing environmental concerns and enhancing the performance of road pavement materials.

EXPERIMENTAL SECTION

Materials

In the experimental program a natural zeolite was used, specifically volcanic tuff from the Mirsid area, Salaj county, Romania, with a grain size of 0.5...1.5 mm, with a clinoptilolite content of 60-70% [11]. Crumb rubber powder 30Mesh from waste tires with average particle size 0.595 mm, density 459 kg/m3, with a sulfur content of 2.16% (Grote combustion method) was used.

Catalytic cracking oil, coded *CCS* (Rompetrol) and a mixture of o,m,p-xylene, referred to as xylene (Chimreactiv SRL), was used for catalyst dispersion. Chemical reagents of analytical purity ammonium nitrate, nitric acid 55% (Chimopar SRL) were used to modify the natural zeolite.

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Characterization Methods

Textural characteristics of catalysts - specific surface area, pore volume and pore size distribution were determined by nitrogen porosimetry with a NOVA 2200e apparatus (Quantachrome). From the nitrogen adsorption/ desorption isotherm recorded at 77.35 K in the relative pressure range p/po 0.005-1.0 the porosimetry data were obtained and processed with a NovaWin software. Samples were degassed for 4 h at 180°C in vacuum before adsorption measurements were performed. The specific surface area was determined from the standard BET (Brunauer-Emmett-Teller) equation, and the total pore volume was estimated from the adsorbed volume at relative pressure P/P_0 close to unity. By applying the Barrett-Joyner-Halenda (BJH) model from the desorption branch of the isotherm, the mesopore volume and pore size distribution were calculated.

The particle sizes and particle size distribution of the zeolite catalysts were determined by dynamic light scattering (DLS) with a NanoZS Zetasizer, Malvern Instruments UK. For the determinations the samples were dispersed in water, approximately 0.005g zeolite in 25 mL distilled water, prior to each determination the samples were ultrasonicated in an ultrasonic bath.

The acid strength and acid strength distribution of the modified zeolites was carried out with a DuPont Instruments apparatus by diethylamine thermodesorption [18]. Samples were maintained in a vacuum oven for 12 hours at 120ºC prior to analysis for moisture removal.

The elemental composition of samples of zeolites was determined by X-ray fluorescence spectrometry (XRF) using a portable Olympus Vanta C XRF Analyzer in GeoChem mode, an X-ray tube with rhodium anode at 40 kV and a silicon drift detector.

Modification of zeolites

For the modification of the tuff, the following procedure was used: the zeolite in powder form was mixed with an aqueous solution of nitric acid and ammonium nitrate in a glass stirred reactor with a thermostated heating jacket. A laboratory centrifuge Rotina 420R was used for separation. After centrifugation the resulting zeolite was washed with distilled water and the obtained suspension was centrifuged again. The resulting zeolite was dried in an air circulation oven and then calcined in a temperature programmed furnace. After grinding in a Fritch Pulverisette planetary ball mill, it was passed through a 0.63 mm sieve.

Desulfurization experiments

The devulcanization experiments were carried out in a stainless steel autoclave, with stirring at a speed of 180 rpm, at a temperature of 280ºC at a mass ratio of crumb rubber to aromatic solvent of 1/2 for 6 hours in an inert gas atmosphere (nitrogen). The solvents used for the experimental tests were aromatic catalytic cracking oil (CCS) and xylene. The desulfurization conversion of rubber powder in the presence of modified zeolites was calculated with equation (1), based on the total sulfur content of rubber powder before and after the experiments.

$$Conversion, \% = \frac{TSCi - TSCf}{TSCi} \cdot 100$$

(1)

TSCi = initial total sulfur content of the crumb rubber sample;
TSCf = final total sulfur content of the crumb rubber sample after the desulfurization with zeolites.

ACKNOWLEDGMENTS

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