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General Characteristics Of Methods For Obtaining Nanomaterials In HSZ-Cationites During Ethyltertbutyl Synthesis

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Abstract: In this work, the preparation, modification, and application of mesoporous zeolitic cationites with high sorption and catalytic properties for the synthesis of ethyl tert-butyl ether (ETBE) from an ethanol–isobutene mixture are presented. The acidity distribution (pKa = 0.8–6.4) and isothermal heat of ethanol adsorption were evaluated for sulfonic cation exchangers. Catalytic tests conducted in a continuous fixed-bed reactor (333–373 K; 0.6–1.2 MPa) showed that mesostructured resins such as Amberlite IR-120, Tulsion T-52H, and KU-2-8 exhibit high activity and selectivity, achieving up to 97–99% selectivity toward ETBE. In contrast, Amberlyst 15Dry/36Dry demonstrated lower efficiency due to their smaller mesopores. It was proven that transition pores with diameters greater than 100 Å, which facilitate mass transfer, along with a high concentration of strong Brønsted acid sites, are the decisive factors that increase conversion and selectivity.

Keywords: Nanomaterials, mesoporous zeolitic cationites, decationization, modification, acid sites, pKa distribution, ethyl tert-butyl ether, isobutylene, tert-butanol, conversion rate, selectivity, space velocity.

INTRODUCTION:

Environmental monitoring results show that MTBE (methyl tert-butyl ether) is one of the most frequently detected volatile organic compounds in groundwater [1–2]. For example, it often ranks second among organic pollutants found in underground water sources [3–5]. This is explained by the high solubility of MTBE in water and its weak adsorption capacity on soil particles [6–9]. As a result, it can spread rapidly through groundwater, contaminating large areas.

The impact of MTBE on human health is also a serious concern. High concentrations of MTBE have been found to irritate the eyes and skin [10–11]. Moreover, scientific sources report that MTBE exhibits genotoxic effects and can suppress the central nervous system [12]. These hazardous factors highlight the urgent need to effectively eliminate MTBE-related contamination sources.

Various technologies have been used for the removal of MTBE from water and soil environments [13–18], including adsorption, air stripping, advanced oxidation processes, and biological degradation. However, each of these methods has certain limitations. The adsorption method faces difficulties in the disposal or regeneration of used sorbents [19–20]. Air stripping, due to MTBE's low Henry's law constant, is inefficient and costly [21–22]. Although advanced oxidation processes are effective in degrading MTBE, they often produce new, more toxic compounds, becoming secondary sources of pollution [23–29].

From this perspective, biological degradation is considered a promising technology for the remediation of MTBE contamination [30–31]. Its main advantages are low cost, environmental friendliness, absence of additional toxic by-products, and ease of control [32–34]. It has been established that under aerobic conditions, MTBE can be decomposed by microorganisms into carbon dioxide, water, and harmless organic metabolites [35–37]. Therefore, biodegradation is increasingly recognized by the scientific community as the most efficient and environmentally sustainable solution for eliminating MTBE-related pollution [38–39].

METHODS

The IR spectra of the synthesized mesoporous zeolitic cationites with high sorption and catalytic properties were recorded using a UR-20 spectrophotometer in the range of 450–2000 cm^{-1}, as this region corresponds to the main absorption bands of AlO_4 and SiO_4 tetrahedral vibrations in the structure. For this purpose, 1–2 mg of the sample and 400 mg of KBr were pressed into a special ring-shaped mold. The prepared ring was then placed into the sample holder and positioned inside the spectrophotometer.

The observed spectra may correspond to two types of vibrations.

The first type of vibrations, found in all spectra of mesoporous zeolitic cationites with high sorption and catalytic activity, show the most intense peaks at 1120 cm^{-1}, 820 cm^{-1}, and 470 cm^{-1}. The strong absorption band at 1120 cm^{-1} is associated with the antisymmetric stretching vibrations of TO_4 tetrahedra. The band at 820 cm^{-1} corresponds to stretching vibrations mainly involving SiO_4 tetrahedra. The position of this peak is influenced by the Si/Al ratio in the framework of mesoporous zeolitic cationites with high sorption and catalytic properties.

1. The presence of intense absorption zones in the regions 1300–900, 820, and 400–600 cm^{-1} confirms that all samples belong to mesoporous zeolitic cationites with high sorption and catalytic activity.
2. The similarity of the absorption bands around 560 cm^{-1} in all obtained IR spectra indicates that all studied samples correspond to the high-silica zeolite (HSZ) structural type.

RESULTS AND DISCUSSION

The Amberlyst 15Dry and Amberlyst 36Dry samples have the lowest concentrations of acid sites (1.65×10^{-7} and 3.2×10^{-7} mol/m^3, respectively). Differences in the number of acid sites at the same pKa value reflect the ability of sulfonated cation exchangers to form and stabilize hydroxyl groups on acidic samples. As shown in Table 1, for Amberlite IR-120 and Tulsion T-52H—which contain equal amounts of divinylbenzene but differ in the quantity of pore-forming agents—the concentration of acid sites varies accordingly: the greater the amount of stabilizing agent in the cation exchanger, the higher the concentration of acid sites. Similar trends were observed in the $(\text{-R–SO}_3\text{H–})$⍰/HSZ and Amberlyst 36Dry series.

The Tulsion T-52H and Amberlyst 15Dry catalysts are characterized by equal amounts of pore-forming components; however, the divinylbenzene content in Amberlyst 15Dry is three times higher than that in Tulsion T-52H. Consequently, the total concentration of acid sites sharply decreases in Amberlyst 15Dry, reaching only 1.65×10^{-7} mol/m^2, whereas for Tulsion T-52H it is 29.63×10^{-7} mol/m^2. The low concentration of acid sites in Amberlyst 15Dry may be associated with its high degree of cross-linking, which limits sulfonation to the outer surface of the cationite, resulting in a thinner active layer.

When these data are compared with the structural characteristics of the resins measured by benzene adsorption, it can be noted that the Amberlyst 15Dry sample, which has the largest micropore volume, also shows the highest ethanol adsorption value—1.19 mmol/g. This adsorption capacity is approximately twice as high as that of other sulfonated cation exchangers, indicating improved sorption performance.

Table 1. Limiting ethanol adsorption values on sulfonic cation exchangers at various experimental temperatures (P⍰/P = 0.02).

T,K	Adsorption of ethanol on the catalyst (a, mmol/g)	
	KU-2	KU-23-

	10	10/60	10/100	30/100	16/60	16/80
273	0,36	0,14	0,79	1,16	0,10	0,29
293	0,38	0,10	0,35	0,44	0,05	0,14

During the experiments, we investigated the effects of temperature, process pressure, space velocity, and the ethanol/n-butene ratio on the conversion rate of the reactants and the selectivity of ethyl tert-butyl ether (ETBE) formation. The temperature range of the experiments was determined by the thermal stability of the ion-exchange resins; therefore, the experiments were conducted at 333, 343, 353, 363, and 373 K.

The lowest selectivity and catalytic activity in the synthesis of ETBE were observed with Amberlyst 15Dry and Amberlyst 36Dry catalysts. For Amberlyst 36Dry, the maximum ether yield was achieved at T = 363 K. The most promising catalysts were Tulsion T-52H and Amberlite IR-120, which exhibited high concentrations of acid sites (~22.11 × 10^{-7} and 30.24 × 10^{-7} mol/m^2, respectively) and large mesopores (d > 100 Å).

Additionally, the KU-2-8 gel-type cation exchanger demonstrated excellent performance, achieving up to 99.2% selectivity toward ETBE formation. These results confirm that the combination of a high concentration of strong acid sites and the presence of wide mesopores facilitates the diffusion of reactants and products, thereby enhancing both conversion and selectivity in the synthesis of ethyl tert-butyl ether.

Table 2. Effect of pressure on the catalytic properties of sulfonic cation exchangers during ethyl tert-butyl ether synthesis (T = 353 K).

Samples	P, МПа	S, %			α,% конверсия
		Этил Тре бутилэфир	изобутилен	третбутанол	
KU-2-8	0.6	96.9	3.1	0.9	54.3
	0.8	98.7	1.4	0.9	53.4
	1.0	96.6	2.7	1.6	75.4
Amberlite IR-120	0.6	91.6	2.6	6.7	61.9
	0.8	98.9	0.5	1.6	81.7
	1.0	97.8	1.1	1.8	74.9
	1.2	91.6	0.0	9.4	73.5
Tulsion T-52H	0.6	91.2	0.1	2.1	38.8
	0.8	94.1	0.3	3.2	45.4
	1.0	92.5	0.1	4.3	40.7
	1.2	91.2	0.2	4.9	41.3
Amberlyst 15Dry	0.6	-	-	-	-
	0.8	85.9	0.2	13.8	60.1
	1.0	94.4	0.2	5.8	73.4
	1.2	99.1	0.1	2.7	85.0
KU-23 10/60	0.6	96.3	1.2	3.5	56.2
	0.8	95.4	1.2	4.4	72.0
	1.0	97.3	0.3	3.4	83.6
	1.2	94.5	1.9	4.7	77.9
	0.6	92.6	0.0	7.4	30.0

Amberlyst 36Dry	0.8	92.7	0.0	7.3	47.4
	1.0	91.3	0.0	8.7	40.4
	1.2	95.7	0.0	4.3	44.8

The influence of pressure on the conversion rate of the butane–butylene fraction and the selectivity of ethyl tert-butyl ether synthesis from ethanol and butane–butylene fraction is presented in Table 2.

At a pressure of 0.8 MPa, the samples Amberlite IR-120 (d_{max} = 17.50 > 100 Å), Tulsion T-52H (d_{max} = 25.65 > 170 Å), and the KU-2-8 gel-type sample (d_{max} = 14 > 100 Å) were investigated. Among them, Amberlite IR-120 showed the highest selectivity for ethyl tert-butyl ether, reaching 98%. Moreover, under the same pressure (P = 0.8 MPa), this sample also demonstrated the highest isobutylene conversion rate of 82%, compared with other sulfonic cation exchangers.

Thus, the efficiency of ethyl tert-butyl ether synthesis on these resins is determined by both the acidic and structural properties of the catalysts. Taking the above findings into account, we can propose the following reaction scheme for the conversion of ethanol and isobutene on sulfonic cation exchangers:

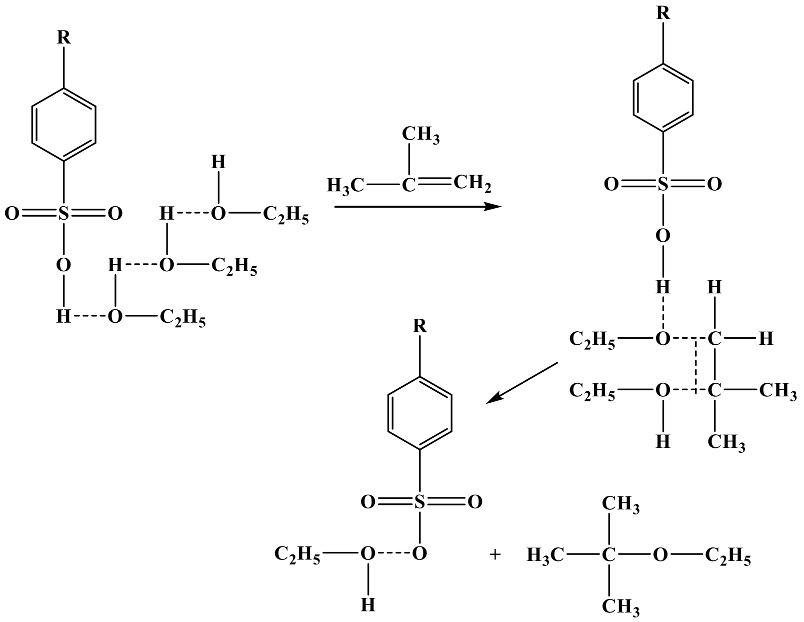

Figure 1. Reaction scheme for the formation of ethyl tert-butyl ether (ETBE).

CONCLUSIONS

1. As optimal operating conditions, a temperature range of 333–353 K and, in most cases, a pressure of approximately 0.8 MPa are recommended. In certain systems, increasing the pressure up to 1.0–1.2 MPa may positively affect selectivity; however, for catalysts with diffusion limitations, the opposite effect was observed.
2. Increasing the ethanol/isobutene molar ratio up to 2:1 slightly improved both selectivity and isobutene conversion for Amberlite IR-120. Raising the space velocity from 0.5 to 2 h^{-1} slightly reduced overall productivity, indicating that the contact time should be optimized for maximum efficiency.
3. From a mechanistic standpoint, an ethanol molecule adsorbed on a strong Brønsted acid site can form associative hydrogen bonds with adjacent ethanol molecules, promoting ETBE formation in the presence of mesopores. In contrast, within smaller pores, associative ethanol adsorption becomes hindered, leading to a higher tendency toward the formation of side products.

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