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The Use Na, Li, K cations for Modification of ZSM-5 Zeolite to Control Hydrocarbon Cold-Start Emission

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Abstract: This paper addresses the problem of controlling hydrocarbon emissions from cold-start of engines by investigating the adsorbents which could adsorb the hydrocarbons at cold temperatures and hold them to 250-300 °C. The materials, that has been studied, are based on the modification of ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3=35$) zeolite with Li, K, Na cations. It has been shown that the introduction of Li, Na and K in an amount that is equivalent to the content of Al in zeolite results in occurrence of toluene temperature desorption peaks at high-temperatures. The toluene temperature desorption curves for 5%Li-ZSM-5 and 2.3%Na-ZSM-5 zeolites are identical and have peak toluene desorption rate between 200 to 400 °C. Upon analysis of toluene adsorption isotherms for 2.3%Na-ZSM-5 and 5%Li-ZSM-5, it was concluded that the toluene diffusion inside of the modified zeolites channels is extremely slow and the sorption capacity of 2.3%Na-ZSM-5 is higher than with 5%Li-ZSM-5. The 2.3%Na-ZSM-5 didn't change toluene temperature programmed desorption (TPD) rate of curve after the treatment in environment with 10 % H₂O at 750-800 °C for about 28 h. The 2.3%Na-ZSM-5 zeolite is very promising as adsorbent to control the cold-start hydrocarbon emissions.

Keywords Adsorbents · Hydrocarbon emission control · Temperature programmed desorption · Toluene adsorption · Zeolite modification · ZSM-5 zeolite

1 Introduction

The hydrocarbons and NO_x releases during the engine cold-start contribute about 80 % of the total hydrocarbon emissions. The modern arrangement of catalytic purification of exhaust gases makes it possible to meet the requirements of the current standards, but the implementation of Super-Ultra Low Emission Vehicle (SULEV) standards requires more effective exhaust gas purification. Therefore, the question of the trapping toxic components of emissions at the cold-start until the catalytic converter in the vehicle heats up, is still open. The main reason of the catalytic adsorber inefficiency is the following: an adsorbent releases the hydrocarbons before the system reaches the temperature of the catalyst start (about 300 °C). To increase the efficiency of exhaust gas purification, one should develop the adsorbent which could hold hydrocarbons up to the temperature of 250-300 °C.

At present time different zeolites are used as adsorbents of cold-start hydrocarbons: Y zeolite [1], ZSM-5, USY, BETA [2, 3, 4], mordenite [4]. The promising adsorbent candidate materials have been intensively studied. FAU, MFI, MOR, FER zeolites where Si/Al ratio varies in the wide range from 1.23 to 150, are both initial and different metal-bearing ones [5, 6, 7, 8]. SAPO-11, SAPO-5, SAPO-36, SAPO-41 materials are considered in the reference [9]. In spite of a great number of investigations intended for searching materials for cold-start adsorbents, the material with required characteristics has been not been found.

In this work we have studied possibility to obtain adsorbents which adsorb well hydrocarbons and hold them to the temperature of 250-300 °C by modification of ZSM-5 zeolite with Li, Na and K cations.

2 Experimental Section

2.1 Adsorbents preparation

To obtain the adsorbents we have used ZSM-5 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3=35$) in H-form (HZSM-5), which refers to the narrow-porous zeolites. The pore size is determined by 10-membered ring structures; their diameters change within the range of 0.6-0.65 nm that is practically comparable with toluene molecules. Different amounts of Li, Na, K have been introduced in HZSM-5 using impregnation method based on different concentrations of the salt solutions [10]. After treatment with the salt solution, the zeolites have been dried at the temperature of 120 °C and tempered for 2 hours at the temperature of 500 °C in the flow of dry air for decomposition of metal salts.

We have shown by example of 2.3%Na-ZSM-5 zeolite and using XRD structure analysis that by modification of initial samples with Na ions, there were no changes observed in the crystal structure of zeolite.

2.2 Adsorbent Research Methods

The investigation of adsorbents has been carried out using method of temperature programmed desorption (TPD) of toluene, which is widely used as a surrogate to investigate behavior of cold-start hydrocarbons adsorbents [7-9]. The toluene TPD has been carried out in the flow facility using helium as gas-carrier. The helium from the tank has been preliminary dehydrated in zeolite trap and then arrived through the gas preparation unit into the quartz reactor with sample. The 0.1g adsorbent sample has been placed in reactor and chromel-alumel thermocouple has been installed above its surface to measure the temperature during the test. The evaporator has been installed in front of reactor with sample and toluene has been introduced inside of evaporator using chromatographic syringe. The evaporator temperature was 200 °C. The reactor output was connected with detector for toluene concentration monitoring. The gas-carrier flow rate has been controlled with gas preparation unit. Before saturation of the sample with toluene it has been activated in helium flow (40 ml/min) at temperature of 400 °C during 1 hour and cooled to 50 °C. Then the sample has been saturated with toluene by injection using syringe into evaporator. After that the sample has been blown-off with pure helium during 30-50 min. with simultaneous cooling to the room temperature. The toluene TPD has been conducted while heating with rate of 10 °C/min. to 350-450 °C, and He flow rate - 40 ml/min.

The equilibrium isotherms have been determined by the weight method using McBen balance. The 0.15–0.20 g samples have been used. Before measuring isotherms the samples have been evacuated in vacuum of 0.01 Pa and at 400 °C to the constant weight.

To examine hydrothermal stability, the adsorbent has been tested in presence of 10 % H₂O at 750-800°C for about 6 h in a stream of air with a flow rate 200 ml/min. The adsorbents have been placed into reactor which was heated using oven to 750-800 °C. During heating and after obtaining operation temperature 700 °C the adsorbents have been blown through with air containing 10 % H₂O. After the treatment the adsorbents have been tested using toluene TPD method; toluene adsorption has been fulfilled at presence of 10 % H₂O that correspond to exhaust gas composition.

To measure toluene content the gas chromatography method has been used.

3 Results and Discussion

The initial zeolite HZSM-5 as well as zeolites with 3.5 wt% K, 2.3 wt% Na and from 0.6 wt% to 5 wt% Li have been tested. The Fig. 1 presents the toluene TPD curves for initial HZSM-5 and with cations, which have been introduced in amount equivalent to Al atomic content in zeolite: 0.6%Li-ZSM-5, 2.3%Na-ZSM-5 and 3.5%K-ZSM-5. Toluene TPD curve have shown that introducing Li cations results in emergence of high-temperature peak of toluene desorption and in

decreasing toluene fraction that is desorbed at lower temperature. The introducing in zeolite a larger Na cation results in disappearance of low-temperature toluene and only high-temperature peak could be observed, the toluene starts to be desorbed only above 200 °C. The modification by a larger K cation results in that toluene appears after 150 °C on the TPD curve and is desorbed in two forms with maxima at 190°C and 280°C, at a temperature that is lower than for 2.3%Na-ZSM-5.

The effect of introduced cation amount on toluene TPD has been studied for ZSM-5 zeolite with 0.6 %, 1.5 %, 2.3 % and 5 % of Li, Fig. 2. Increasing Li content to 5 % results in shifting the high-temperature peak to the region of higher temperatures and to practical disappearance of low-temperature peak, toluene temperature desorption from 5%Li-ZSM-5 is very close to toluene desorption from 2.3%Na-ZSM-5 (Fig.1). Such toluene TPD curves for ZSM-5 zeolite are most probably connected with blocking zeolite pores while introducing univalent cations. Probably the other molecules larger than toluene, which molecules size is comparable with this zeolite pores size will be not at all adsorbed on ZSM-5 with introduced univalent cations.

Thus, obtained results showed: the univalent alkaline cations with a small ionic radius introduced in zeolites enable one to retain aromatic hydrocarbons at higher temperatures compared to proton forms and alkaline cations with a larger radius during temperature desorption. The same results were obtained using FTIR spectroscopy by Bao-Lian Su and co-workers [11]. It was demonstrated that the interaction of benzene with Na⁺ ions is stronger than that with 12-R windows of zeolites. The reason behind the strong interaction of aromatic molecules with Li⁺ and Na⁺ cations and a weaker interaction with H⁺ and K⁺ is the donor-acceptor mechanism of complex formation due to the withdrawal of π -electrons of the aromatic ring by the rather strong Lewis acidic sites (electron-accepting sites), i.e. Li⁺ and Na⁺ cations. Also, in the case of potassium forms, steric hindrances may decrease the energy of the interaction as well as destabilize the optimized geometry of the complexes. This explanation is in a good agreement with the data of [12]: the heats of hydrocarbon adsorption on cationic forms of zeolites are higher than in the case of H-forms. The choice of univalent cations is also consistent with the fact that the polycharged cationic forms usually contain Brønsted acid sites formed as a result of partial hydrolysis of the cations [13]. The presence of acidic centers may cause undesirable reactions of hydrocarbons at elevated temperatures, coke formation and the loss of the adsorption capacity. It was shown [14] that in the case of hydrocarbons capable of specific interactions with cations in zeolites, the heats of adsorption increase with decreasing radius of the univalent cation due to the increase of the polarizing action of the cation and electrostatic interactions. The difference in the heats of adsorption can reach 20 kJ/mol in the row Cs⁺ - Li⁺.

For 2.3%Na-ZSM-5 and 5%Li-ZSM-5, that showed the best toluene TPD curves, the toluene adsorption isotherms have been measured under static conditions, Fig.3. For these zeolites the adsorption temperature decrease already to 100 °C results in increasing toluene diffusion velocity inside the zeolite channels and adsorption isotherms lie higher than at 30 °C. For 2.3%Na-ZSM-5 the isotherm at 100 °C coincides with isotherm for initial H-ZSM that indicates accessibility of zeolite

pore volume for toluene. In case of 5%Li-ZSM-5-35 a part of zeolite pore volume is occupied with Li cations and corresponding anions and toluene adsorption isotherm lie lower than for H-ZSM-5-35.

The steps on isotherms indicate extremely slow toluene diffusion inside of zeolite channels. Such a slow adsorption enables obtaining the temperature desorption curves where one can see only high-temperature peaks, Fig.2. It is evident that in case of these samples fast saturation with toluene before the temperature desorption (~20 min.) the adsorption occurs only in mouths of channels on available there cations, and diffusion has no time to flow inside of channels. The sorption capacity of zeolites with univalent cations reduces as compared to initial HZSM-5. The 2.3%Na-ZSM-5-35 zeolite has higher sorption toluene capacity than that 5%Li-ZSM-5-35 zeolites.

2.5%Na-ZSM-5 zeolite durability has been tested, cycle time of adsorbents treatment at 700 °C lasted at the beginning 2 hours, then 6 hours. These were realized 8 cycle; the total time of hydrothermal treatment was 28 h. Fig 4 presents TPD toluene curves for initial adsorbent and after treatment. It was shown that 2.3%Na-ZSM-5 adsorbent didn't change toluene TPD curve after the hydrothermal treatment. Adsorbent has a strongly pronounced high temperature desorption peak from 250 to 400 °C with maximum in the point about 350 °C. It is evident that the presence of water vapor doesn't disturb the toluene adsorption in centers where it is adsorbed with high heat. These centers are cations introduced in zeolite. The water fills mainly the rest of the volume of zeolites micropores, therefore there is no toluene desorption low-temperature peak on the temperature desorption curves. With increasing the treatment time the amount of toluene desorbed decreases: for initial adsorbent the amount of desorbed toluene is 0.1 mmole/g, after 28 hours of treatment the amount of desorbed toluene decreases by two times and makes 0.03 mmole/g.

Conclusion

The investigations to obtain adsorbents for unburned hydrocarbons and NO_x, for cold-start of engines and adsorption of hydrocarbon emission when catalytic converter heats up. The modification of H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3=35$) zeolites with cations of univalent metals have shown that by introducing Li, Na and K in amount equivalent to atomic amount of Al in zeolite, results in occurrence of high-temperature peaks of toluene TPD curve. The increasing Li content in ZSM-5 to 1.5 % and to 2.3 % results in shifting the toluene TPD maximum to the low-temperature region. The further increasing Li content to 5 % results in shifting the high-temperature peak to more high -temperature region. The toluene TPD curves from 5%Li-ZSM-5 and 2.3%Na-ZSM-5 zeolites are identical. Upon analysis of toluene adsorption isotherms at 293 K for 2.3%Na-ZSM-5 and 5%Li-ZSM-5 zeolites we have concluded that the toluene diffusion inside of the modified zeolites channels is extremely slow and the sorption capacity of zeolites with univalent cations decreases as compared with initial HZSM-5. The 2.3%Na-ZSM-5-35 zeolite has higher sorption toluene capacity.

The best result for control of hydrocarbon cold-start emission has been obtained for 2.3%Na-ZSM-5. The 2.3%Na-ZSM-5 zeolite didn't change toluene TPD curve after the hydrothermal treatment in environment with 10% H₂O at 750-800 °C for about 28 h. Toluene TPD curve had high temperature desorption peak from 250 to 400 °C with maximum in the point about 350 °C. The amount of toluene desorbed at temperature from 250 to 400 °C is 0.1 (for initial zeolite) and 0.03 mmole/g (after hydrothermal treatment for about 28 h).

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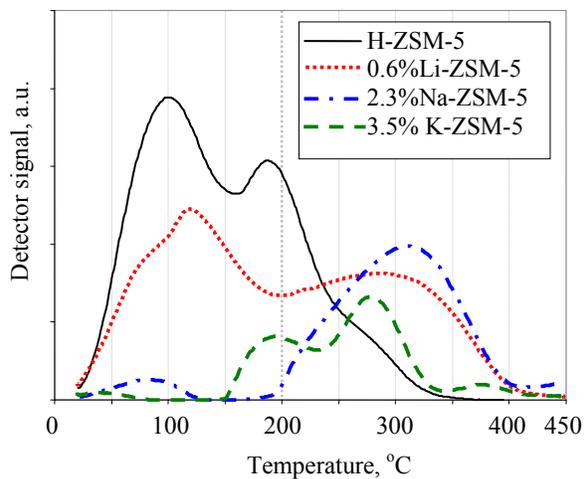


Fig. 1 Toluene TPD for initial HZSM-5 and 0.6%Li-ZSM-5; 2.3%Na-ZSM-5; 3.5%K-ZSM-5

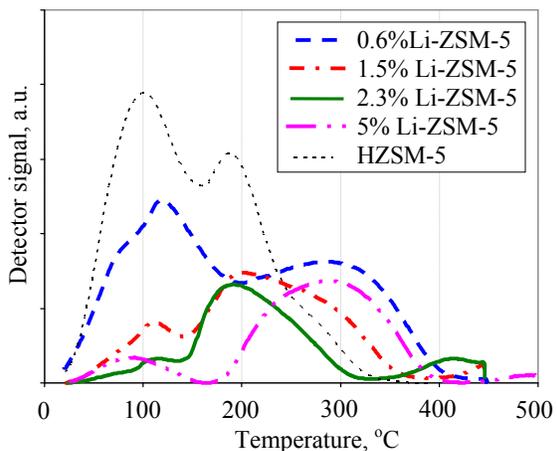


Fig. 2 Toluene TPD curves for initial HZSM-5 and 0.6%Li-ZSM-5; 1.5%Li-ZSM-5; 2.3%Li-ZSM-5; 5%Li-ZSM-5

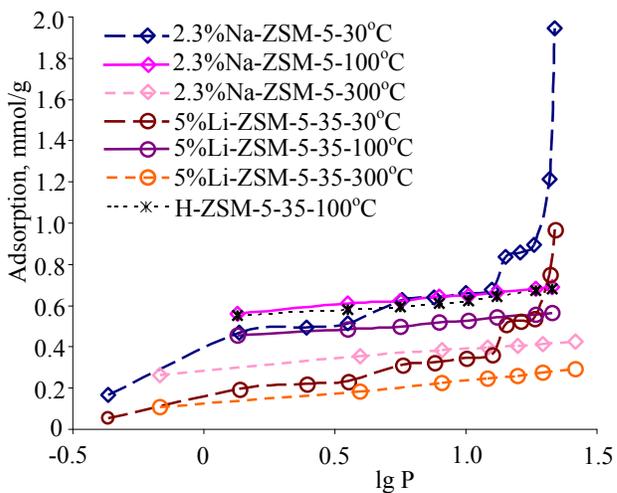


Fig. 3 Toluene adsorption isotherms at 30 °C, 100 °C and 300°C for 2.3%Na-ZSM-5 and 5%Li-ZSM-5 zeolites

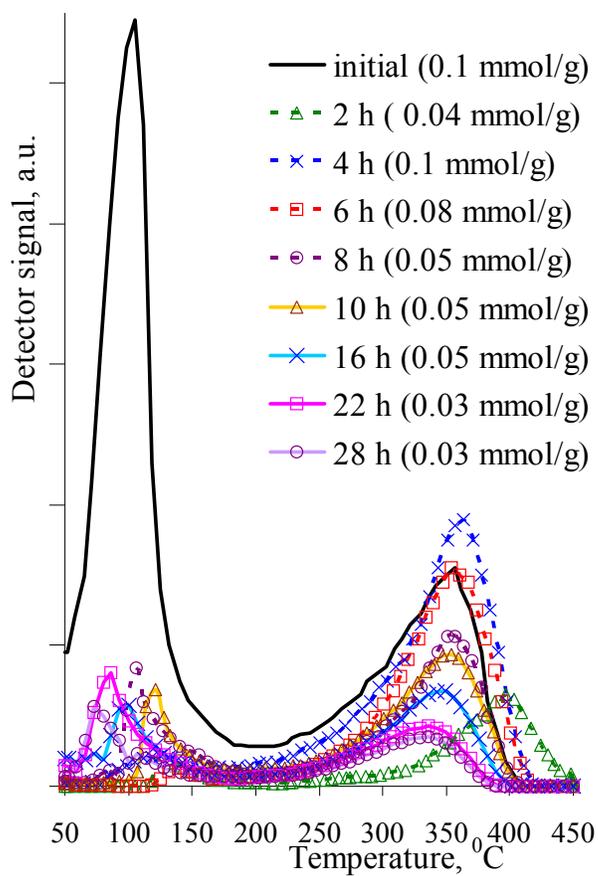


Fig. 4 Toluene TPD curve for 2.3%Na-ZSM initial zeolite and after its hydrothermal treatment at temperature 700 °C in environment 10 % H₂O (the amount of toluene desorbed at temperature from 250 to 400 °C is indicated in brackets)