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Study of Mordenite ZSM-5 and NaY Zeolites, Containing Cr, Cs, Zn, Ni, Co, Li, Mn, to Control Hydrocarbon Cold-Start Emission

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***Abstract*—**The implementation of Super-Ultra Low Emission Vehicle standards requires more efficient exhaust gas purification. To increase the efficiency of exhaust gas purification, an the adsorbent capable of holding hydrocarbons up to 250-300 ^{O}C should be developed. The possibility to design such adsorbents by modification of zeolites of mordenite type, ZSM-5 and NaY, using different metals cations has been studied.

It has been shown that introducing Cr, Cs, Zn, Ni, Co, Li, Mn in zeolites results in modification of the toluene TPD and toluene sorption capacity.

5%LiZSM-5 zeolite exhibits the most attractive TPD curve, with toluene desorption temperature ranging from 250 to 350^{O}C. The sorption capacity of 5%Li-ZSM-5 is 0.4 mmol/g. NaY zeolite has the highest sorption capacity, up to 2 mmol/g, and holds toluene up to 350^{O}C, but at 120^{O}C toluene desorption starts, which is not desirable, since the adsorbent of cold start hydrocarbons should retain them until 250-300^{O}C. Therefore 5%LiZSM-5 zeolite was found to be the most promising to control the cold-start hydrocarbon emissions among the samples studied.

***Keywords*—**Hydrocarbon emission control, adsorbents, zeolites, temperature-programmed desorption.

I. Introduction

THE emissions released during the engine cold start make 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. The implementation of Super-Ultra Low Emission Vehicle (SULEV) standards requires more efficient exhaust gas purification. Therefore the question of trapping toxic components at the cold start and vehicle heating remains still open. The main reason behind the poor catalytic adsorber efficiency is the following: an adsorbent releases the hydrocarbons before the system reaches the temperature of the catalyst start (about 300^{O}C). To increase the efficiency of exhaust gas purification, one should develop an adsorbent that could hold hydrocarbons up to the temperatures of 250-300^{O}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 are intensively studied. FAU, MFI, MOR, FER zeolites with the Si/Al ratio varying in a wide range from 1.23 to 150, both initial and different metal-bearing materials have been studied [5, 6]. The paper [7] considers SAPO-11, SAPO-5, SAPO-36, SAPO-41 materials for the title application. In spite of a great number of studies related to materials for cold start adsorbents, the material with required characteristics has not been found so far. In this work, we have studied the possibility to design adsorbents capable of adsorbing efficiently hydrocarbons and holding them to the temperatures of 250-300^{O}C by modification of mordenite, ZSM-5 and NaY zeolites with different metal cations

II. Experimental Part

A. Adsorbents preparation

To prepare the adsorbents, we used mordenite (SiO_2/Al_2O_3=16.3), ZSM-5 (SiO_2/Al_2O_3=35) and NaY (SiO_2/Al_2O_3=5.4) zeolites. X-ray diffraction patterns (XRD) of zeolites show highly crystalline structure, Fig. 1. Zeolites differ both in the size of pore entrances (windows) and in the pore accessibility. Y and ZSM-5 zeolites have the pores accessible in different directions via 12- and 10-membered windows, respectively. Mordenite and ZSM-5 have identical 10-membered windows, but the mordenite pores are one-dimensional, and ZSM-5 channels are two-dimensional.

The metals (5 wt. %) were introduced in zeolites using the impregnation method from water solutions of $Ni(NO_3)_2 \cdot 6H_2O$, $LiNO_3$, $Mn(CH_3COO)_2 \cdot 4H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, $CsNO_3$, $Co(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$. Then zeolites were dried at 120^{O}C and annealed at 500^{O}C in a dry air flow for decomposition of metal salts. The air flow velocity was 200 ml/min, the temperature raised at 0.5-1 ^{O}C/min.

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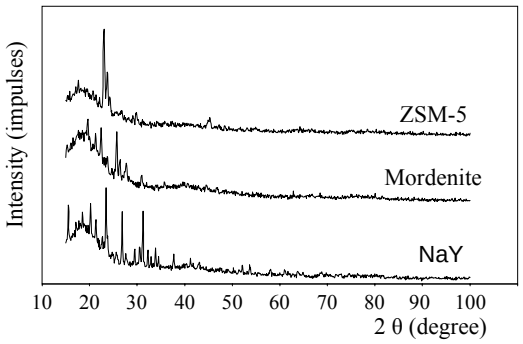

Fig.1 XRD of initial zeolites

B.Adsorbents research method

The investigation of adsorbents was performed using the toluene temperature-programmed desorption (TPD) method, which is widely used to study the behavior of cold-start hydrocarbons adsorbents [5, 6]. The TPD of toluene was studied in a flow setup using air as a gas-carrier. The air was preliminarily dehydrated in a zeolite trap and then supplied through a gas preparation unit into a quartz reactor loaded with the sample under study. The 1 g sample loading was placed in the reactor and a chromel-alumel thermocouple was installed above its surface to measure the temperature during the test. The evaporator was placed in front of the reactor with the sample and toluene was introduced inside the evaporator using a Burette. The reactor output was connected with a chromatograph for toluene concentration monitoring.

Before saturation of the sample with toluene it has been activated in the air flow (100 ml/min) at 400-450 ^{o}C during 1 hour and cooled to 50^{o}C. Then the sample has been saturated with toluene. The evaporator temperature was 110 ^{O}C, toluene dosing rate was 0,0166 ml/min., air flow rate was 100 ml/min. After that the sample has been blown-off with air during 30 min. with simultaneous cooling to the room temperature. The toluene temperature desorption has been conducted while heating with rate of 10 ^{o}C/min. to 450 ^{o}C, air flow rate was 100 ml/min. The amount of toluene adsorbed has been determined using gas chromatographic method.

III. Results and Discussion

The toluene TPD curves for initial zeolites and zeolites with supported metals are given in Fig. 2-4.TPD results show that mordenite, both in the initial form and with introduced cations, holds toluene to insufficiently high temperatures, not higher than 250^{O}C, Fig. 2. Introducing 5 wt. % of Cr, Zn, Ni, Co, Li, Mn in mordenite results in a decrease of the amount of adsorbed toluene. The maximum amount of toluene, 0.35 mmol/g, is adsorbed by the sample of the initial H-mordenite.

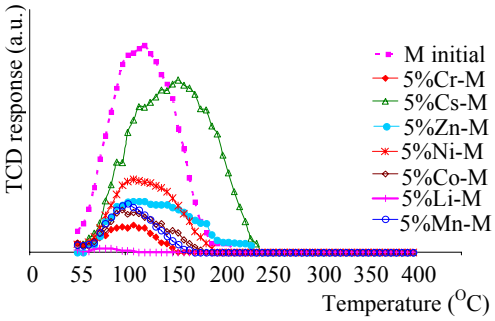

Fig.2 TPD curves for initial mordenite (SiO_2/Al_2O_3=16.3) and for mordenite with different metals

Initial ZSM-5 zeolite holds toluene to 300^{O}C, Fig. 3. Introducing 5% Li, Co, Zn in ZSM-5 results in increasing desorption temperature. The 5%Li-ZSM-5 sample exhibited the best performance: the toluene desorption occurs at temperatures from 250 ^{O}C to 350^{O}C, the desorbed toluene amount was 0.4 mmol/g. The maximum toluene amount, 1.0 mmol/g, is adsorbed by 5%Mn-ZSM and 5%Zn-ZSM samples.

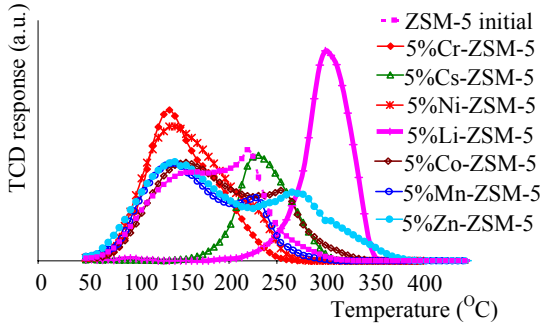

Fig. 3 Toluene TPD curves for initial ZSM-5 (SiO_2/Al_2O_3=35) and for ZSM-5 with different metals

Initial NaY zeolite desorbs toluene at temperatures from 120 ^{O}C to 350^{O}C, figure 4. Introducing cations in NaY zeolite results in decreasing desorption temperature. The amount of adsorbed toluene for initial NaY and the samples with 5% Zn, Mn, Cs, Ni, Co is from 1.5 to 2.0 mmol/g. Introducing Cr and Li in NaY results a decrease of the desorption temperature.

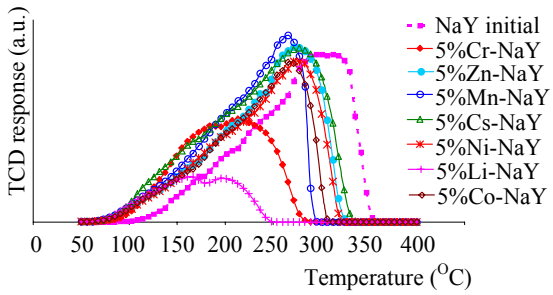

Fig. 4 Toluene TPD curves for initial NaY (SiO_2/Al_2O_3=5.4) and for NaY with different metals

IV. Conclusion

The studies focused on the design of efficient adsorbents of cold start hydrocarbon emissions using modification of mordenite, ZSM-5 and NaY zeolites with cations show that introducing Cr, Cs, Zn, Ni, Co, Li, Mn results in variation of the TPD curves and the sorption properties with respect to toluene. The 5%LiZSM-5 zeolite for which the toluene desorption temperature was from 250 to 350^{O}C manifested the most attractive TPD curve.

The sorption capacity of 5%Li-ZSM-5 is 0.4 mmol/g. NaY zeolite has the highest sorption capacity, up to 2 mmol/g, and holds toluene to 350^{O}C, but at 120^{O}C toluene starts to desorb, which is not desirable, since the cold start hydrocarbon adsorbents should hold them to the temperature of 250-300^{O}C. Therefore the 5%LiZSM-5 zeolite seems to be the most promising to control the cold start hydrocarbon emissions among all samples studied

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