

Research Article

MFI and FAU-Type Zeolites as Trapping Materials for Light Hydrocarbons Emission Control at Low Partial Pressure and High Temperature

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The adsorption of light hydrocarbons (C₂–C₅ olefins and paraffins, toluene) on HZSM-5, silicalite, and HY was studied for application in treatment of exhaust streams of the petrochemical industry and of vehicles under cold start conditions. At this aim the trapping capability was evaluated on hydrated zeolites by breakthrough curves at low hydrocarbon partial pressure (0–1 kPa), in the temperature range 298–523 K and at space velocity of 30000 h⁻¹. The basic adsorption properties of materials were also verified for three selected hydrocarbons (ethylene, isobutene, and toluene) by equilibrium isotherms on dehydrated zeolites at 298 K. The role of physicochemical characteristics of adsorbent materials was discussed in relation with their trapping capability of different types of hydrocarbons.

1. Introduction

Adsorption techniques have been studied in the past several years as methods for separation or capture of hydrocarbons (HC) in applications that require the recovery of these compounds in high purity (petrochemical industry) [1–3]. Liquefied petroleum gas and bottom contents of refinery deethanizer or depropanizer columns are the common industrial source of light hydrocarbons such as methane, ethane, propane, n-butane, and i-butane, which can be recovered and used as a fuel or petrochemical feed stocks [4, 5]. Light hydrocarbons are also the main components of natural gas and represent a significant proportion of most crude oil [6]. More recently adsorption-based processes have been also proposed for the abatement of organic pollutants at the exhaust of light-duty gasoline vehicles under cold start conditions. This last application is justified by the future legislative limits for passenger car emissions incoming all over the world, which will become more and more stringent and will require the development of new technological

solutions, including more effective after-treatment devices [7]. It is known that the largest fraction (more than 80%) of the total organic pollutants flows out from the tailpipe during the short time following the engine startup (200 seconds). During this period the air/fuel ratio is on the rich side that implies more HC emissions, while the temperature of the three-way catalyst (TWC) is lower than its light-off value (473–573 K), which requires some minutes to be reached. The worldwide diffusion of hybrid vehicles makes the problem of HC cold start emission more critical, due to the higher number of ignition times occurring in this type of vehicle with respect to the conventional ones.

The three basic technologies that have been developed for the control of the cold start HC emissions are the close-coupled catalyst, the electrically heated catalyst, and the HC traps. An extensive review of these solutions, with a description of the related patents, is reported in [8]. The combination of catalytic converters with HC traps has been proposed in several patents and appears as the most promising technology in terms of efficiency and cost [8–10].

TABLE 1: Zeolitic materials used for adsorption tests.

Sample	Form	Si/Al	Pore opening, Å	Surface area ^a , m ² /g	Pore volume ^b , cm ³ /g
HZSM-5	Powder	15	5.3 × 5.6	405	0.24
			5.1 × 5.5		
Silicalite	Powder	∞	5.3 × 5.6	400	0.24
			5.1 × 5.5		
HY	Powder	15	7.4	730	0.51

^aData provided by the manufacturer.

^bData from [11].

These traps are constituted by a bed of adsorbent material able to catch hydrocarbons until the working temperature of the catalytic converter is reached. When the temperature of the exhaust gas increases, trapped hydrocarbons are desorbed and oxidized in the TWC. Then the fundamental features required for a successful hydrocarbon trap to be used in automotive applications are the high selectivity towards light hydrocarbons at relatively low temperature range (from room temperature to about 470 K) and the low sorbate concentration levels.

The most suitable materials for HC trapping are carbon-based materials, silicoaluminophosphates and zeolites [8]. Activated carbons are effective and not expensive; however, they would be oxidized in the presence of oxygen and at the high temperature occurring in exhaust gases of an internal combustion engine. Among inorganic commercial adsorbents with high surface area zeolites are the preferred materials for the present application. They are crystalline aluminosilicates which exist in both natural and synthetic form, characterized by different Si/Al ratios and a porosity of molecular size (3–10 Å), uniquely determined by the unit structure of the crystal. As a consequence they have a high internal surface area (generally higher than 400 m²/g) available for adsorption due to channels that uniformly penetrate the entire volume of the solid [12]. These materials have been used for adsorption-based separations for several decades, finding applications in numerous fields [13–15]. Zeolites have been object of many studies related with HC trapping, since a particular zeolite can be selected as a function of the type of HC to be trapped and of the particular gaseous environment they have to be removed from. In particular experimental data regarding the HC adsorption capacity of different zeolites, such as ZSM-5, Y, beta, mordenite, ferrierite, and silicalite, are extensively reported in literature [16–21]. The properties of these materials have been evaluated with respect to main parameters that can affect the HC adsorption, that is, molecular size of HC, zeolite pore size, and Al content, but all these data refer to selected hydrocarbons studied at room temperature. A comparison between the adsorption properties of different zeolites and silicoaluminophosphates for propene adsorption is reported by López et al. [22]. The promising performance of beta and ZSM-5 zeolites and SAPO-5 under cold start conditions are evidenced in this paper for the single hydrocarbon considered.

Other investigations have been conducted in real conditions, using a zeolite based HC trap located at the exhaust of

a gasoline engine [23, 24]. These studies have provided useful indication regarding the behaviour of selected materials towards the overall gas effluent, without discerning the effect of the adsorbent material on individual HCs.

The aim of the present paper was to study the adsorption properties of various zeolitic materials towards different HCs, taking into consideration those compounds which need to be recovered in petrochemical applications, such as light paraffins, or removed from the engine exhaust of light-duty gasoline vehicles, typically C2–C5 paraffins and olefins, plus monoring aromatic compounds [25]. Because of the variety of HCs considered, zeolites with pore opening ranging from 5 to 7.4 Å (HZSM-5, silicalite and HY) were examined. Preliminary adsorption isotherms were acquired on dehydrated zeolites to obtain a basic characterization in saturation conditions at room temperature. The study of trapping capability was carried out by dynamic tests in a flow microreactor at temperature, partial pressures, and space velocity values compatible with the applications considered (298–523 K, 0.1 kPa, 30000 h⁻¹, resp.). The zeolites were not thermally treated before these tests, in order to evaluate their performance in real conditions. This approach permitted not only the acquisition of experimental data regarding adsorption equilibria but also obtaining indications regarding the adsorption rate and removal efficiency of different hydrocarbons on three zeolitic materials (both single compound and mixtures) in HC trap conditions.

2. Experimental

2.1. Materials. All adsorption measurements presented in this paper were performed on HZSM-5, silicalite, and HY in powder form (Zeolyst International). The main characteristics of these zeolitic materials are reported in Table 1. HZSM-5 is the acidic form of ZSM-5 and is a well-known material widely used as a catalyst in chemical industry. It is characterised by a MFI (Mobil Five) three-dimensional channel system with pore openings of 5–6 Å, responsible for surface area and pore volume values of 405 m²/g and 0.24 cm³/g, respectively. Silicalite has the same MFI crystalline structure of ZSM-5, therefore the same microchannel system, but no Al atoms in the framework. HY zeolite is characterised by a faujasite type structure having channels with pore opening of 7.4 Å and containing H⁺ as a counteranion. Its surface area and pore volume are 730 m²/g and 0.51 cm³/g, respectively.

TABLE 2: Composition and sources of hydrocarbon mixtures used for adsorption tests (provided by Praxair).

Mixture HC/N ₂	Composition of individual HC, ppm	Total concentration, C3 ppm
Ethylene/N ₂	1280	853
Isobutene/N ₂	643	857
Toluene/N ₂	358	835
C4-C5 alkanes ^a /N ₂	n-Butane: 123	847
	Isobutane: 128	
	n-Pentane: 105	
	Isopentane: 102	
	Neopentane: 100	
	C5: 102	
Isobutane-isobutene ^b /N ₂	Isobutane: 323	858
	Isobutene: 320	

^aEquimolar mixture (as C3) of n-butane, isobutane, n-pentane, isopentane, and neopentane.

^bEquimolar mixture (as C3) of isobutane and isobutene.

While petrochemical applications require the removal of light paraffins and olefins, the HCs present in engine exhaust gases comprise paraffins, olefins, and aromatics of various molecular weights in the range C1–C11. In Table 2 the details of used mixtures are reported, with the specifications of their composition. The adsorption measurements were firstly carried out using mixtures of individual hydrocarbons in nitrogen. In particular, three hydrocarbons were identified as a representative of the major species present in the engine exhaust during cold start (ethylene, isobutene, and toluene) [25]. The adsorption isotherms were carried out on these three selected hydrocarbons, while all the mixtures reported in Table 2 were used for the tests in flow microreactor at atmospheric pressure. A mixture of C4-C5 alkanes (n-butane, i-butane, n-pentane, i-pentane, and neopentane) was tested to study the competitive adsorption between some selected light paraffins, while a mixture of isobutane and isobutene was selected to have indications about the possible interactions between paraffins and olefins during the adsorption phenomena on zeolites. Taking into account that the adsorption capacity of zeolites is mainly due to a pore filling mechanism, the concentration of each hydrocarbon was selected in order to have mixtures with the same total concentration in terms of carbon atoms. This allowed for comparable carbon mass flow rates in different molecular structures. As propane mixtures were used for calibration of the HC analyzer (see Section 2.3), the total concentration was expressed in terms of C3 and resulted in about 850 ppm for all mixtures (corresponding to about 0.1 kPa, approximately the actual partial pressure of HCs in the engine exhaust). Within each mixture the same number of moles in terms of C3 was present for each hydrocarbon.

2.2. Adsorption Isotherms Procedure. Adsorption isotherms at room temperature were obtained by a gravimetric technique and performed with the apparatus sketched in Figure 1 [26]. This is a McBain-type adsorption balance, equipped with a quartz spring (Ruska Instrument Co., Houston, Texas), whose elongation law is known. A small quartz pan, containing the adsorbent material, hooked to the spring, enables

the evaluation of the amount of adsorbate by measuring spring elongation with the help of a cathetometer. Equilibrium gas pressure was measured through electronic devices (Edwards Datametrics 1500). A Heto thermostating unit allowed a temperature control within the range of ± 0.1 K. Before measurement samples were thermally activated at 623 K under high vacuum ($P < 10^{-6}$ kPa) by means of an Edwards turbomolecular pump for 3 hours using a toroidal furnace, after cooling to 298 K aliquots of gas were allowed from time to time to enter the balance chamber and sufficient time was awaited to attain equilibrium. Adsorption isotherms were outlined by plotting the amounts of adsorbate on dry basis versus gas partial pressures at equilibrium.

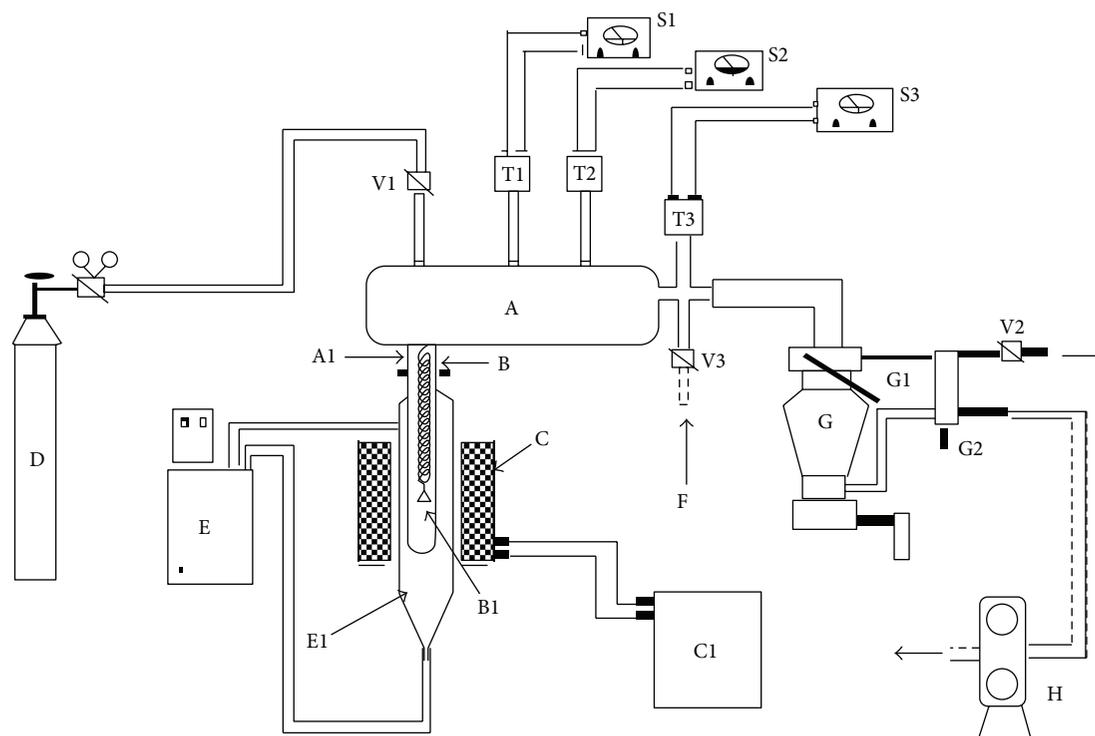
The gravimetric tests were affected at room temperature for the three selected HCs (ethylene, isobutene, and toluene) in order to obtain a basic characterization of the three zeolitic materials in terms of equilibrium adsorption capacity towards compounds representative of the main HC families that need to be captured in the applications considered.

2.3. Adsorption Kinetics Procedure. The breakthrough curves were performed by the experimental apparatus shown in Figure 2. A fixed bed microreactor, constituted by a stainless steel tube of 10 mm i.d., was inserted in a tubular electric oven equipped with a temperature controller. The reactor was loaded with zeolites in powder form (1 g, 180–350 μ m). The gas flow rate (1 l/min) was selected to realise a space velocity value (gas gravimetric flow rate/adsorbent weight) of 30000 h⁻¹ that is representative of conditions occurring at the engine exhaust on TWC during automotive start-up phase.

An online analyzer equipped with flame ionisation detector (Siemens Fidamat 5 E-AP) was used for hydrocarbon concentration analysis before and after the adsorbent bed.

These tests were effected at different temperature values (from 298 K to TWC light off values) and low hydrocarbon partial pressures (0–1 kPa), which are usually encountered in engine exhaust gases.

The breakthrough curves were constructed reporting hydrocarbon concentrations measured at the outlet of



- (A) Balance chamber
 (A1) Quartz spring zone
 (B) Quartz spring
 (B1) Pan
 (C) Toroidal oven for sample activation
 (C1) Oven programmer
 (D) Cylinder of N₂ for chamber purge
 (E) Thermostatic unit
 (E1) Water jacket
 (F) Gas inlet
 (G) Diffusion pump
 (G1) Baffle valve
 (G2) Backing/roughing valve
 (H) Rotary pump
 (S1, S2, and S3) Pressure indicators
 (T1, T2, and T3) Pressure transducers
 (V1) Purge inlet valve
 (V2) Purge outlet valve
 (V3) Needle valve

FIGURE 1: Scheme of the experimental apparatus used for measurements of equilibrium isotherms by gravimetric tests.

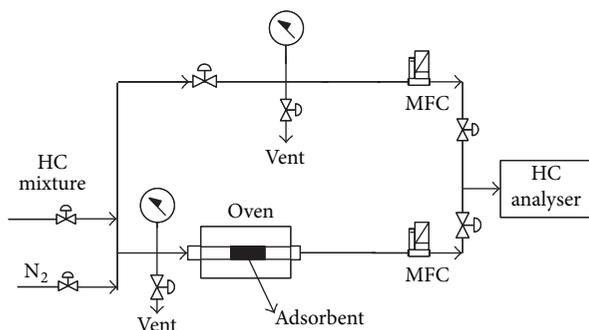


FIGURE 2: Scheme of the experimental apparatus used for measurements of adsorption properties by flow microreactor.

the adsorbent bed as function of time on stream. These concentrations were acquired in terms of C₃, since the analyzer calibration was affected by using propane mixtures (see Section 2.1). From these curves the values of hydrocarbon

cumulative adsorption were calculated as mass of adsorbed HC per 100 g of zeolite (wt%), according to the following formula:

$$\frac{g_{\text{HC}}}{100 g_{\text{zeolite}}} = \sum_{i=1}^n [(C_{\text{in}} - C_i)(t_i - t_{i-1})] Q M_{\text{C}_3\text{H}_8} 100, \quad (1)$$

where C_{in} is the HC concentration (expressed as C₃) at the reactor inlet, C_i is the HC concentration at the reactor outlet at the time t_i , n is the generic instant of concentration acquisition, Q is volumetric flow rate of the gas stream in NL/min, and $M_{\text{C}_3\text{H}_8}$ is the molecular weight of propane. These percentage cumulative values were used for presentation of experimental results relative to dynamic tests described in the next section.

The zeolitic materials were tested in all flow adsorption runs without any preliminary thermal treatment, in order to simulate the utilization conditions of a HC trap at the engine exhaust. In this way each material retained its intracrystalline water content when it was exposed to hydrocarbon gas stream.

TABLE 3: Equilibrium adsorption capacities (wt%) obtained at 298 K by gravimetric tests at saturation and 0.1 kPa for different HCs on HZSM-5, silicalite, and HY.

Zeolite	Ethylene		Isobutene		Toluene	
	Saturation	0.1 kPa	Saturation	0.1 kPa	Saturation	0.1 kPa
HZSM-5	7.2	3.8	8.1	5.7	12.8	8.0
Silicalite	6.8	2.3	11.5	8.7	13.8	7.7
HY	5.4	1.6	22.5	14.8	17.1	7.1

TABLE 4: Adsorption capacities (wt%) derived by breakthrough curves at various temperature values for different HCs on HZSM-5, silicalite, and HY. HC partial pressure: 0.1 kPa, space velocity: 30000 h⁻¹.

Zeolite	T, K	Ethylene	Isobutene	Toluene	Isobutene Isobutane	C4-C5 paraffins
HZSM-5	298	0.5	2.2	4.0	4.1	1.7
	348	—	3.7	2.9	5.4	0.8
	373	0	4.5	—	5.4	0.2
	398	—	—	1.4	—	—
	413	—	4.6	—	4.0	—
	423	—	—	1.0	—	—
	463	—	2.4	—	1.6	—
	523	—	0.6	—	—	—
Silicalite	298	0.2	1.1	5.0	—	0.3
	373	0	0.5	2.5	—	—
	423	0	0.1	1.6	—	—
HY	298	0.04	2.8	6.8	—	0.7
	348	—	—	—	—	0.2
	353	—	6.3	—	—	—
	373	0	—	5.2	—	0.1
	403	—	4.5	—	—	—
	423	0	—	2.1	—	—

3. Results and Discussion

In Table 3 the equilibrium adsorption capacities in wt% for ethylene, isobutene, and toluene as measured at room temperature in gravimetric tests are summarized for the three zeolitic materials. In Table 4 the adsorption capacities of all hydrocarbons investigated, derived by breakthrough curves and calculated by (1), are reported for temperature values ranging from 298 to 523 K, at partial pressure of 0.1 kPa and space velocity of 30000 h⁻¹.

3.1. Adsorption Measurements at Room Temperature. In Figure 3 adsorption isotherms under equilibrium conditions of ethylene, isobutene, and toluene at 298 K on HZSM-5 are compared. A magnification of the low pressure zone (0–0.1 kPa) is reported on the top right. All curves show the typical shape of the adsorption isotherms on microporous solids [27].

Increasing pressure gave rise to a sharp weight increase for toluene, because of the capillary condensation phenomena occurring when the saturation vapor pressure of toluene (3 kPa at 298 K) was approached [28]. As regards ethylene and isobutene, the saturation conditions occurred at higher pressures. At 53 kPa (out of Figure 3, but reported in Table 3)

the amounts of ethylene and isobutene adsorbed on HZSM-5 expressed in wt% resulted in 7.2 and 8.1%, respectively. Ethylene, isobutene, and toluene exhibited adsorption capacity relatively high even at low pressure; that is, more than 50% of the maximum amount at saturation was adsorbed at a pressure of 0.1 kPa (Table 3).

The breakthrough curves were used to calculate the cumulative values of adsorption capacity as a function of time (equation (1)). Figure 4 reports the results obtained with ethylene, isobutene, and toluene on HZSM-5 at 298 K and 30,000 h⁻¹. The maximum adsorption capacity was obtained with toluene (3.97%, Table 4), for which bed saturation was reached after about 50 minutes. As regards isobutene an adsorption capacity of 2.2% was obtained, with a faster decay of zeolite trapping capability. Ethylene adsorption was very poor, as the bed saturation was reached after only 4 minutes and the adsorption capacity did not exceed 0.5%. The removal efficiency of the zeolite adsorbent bed, defined as $1 - C_i/C_{in}$, was used as indicator of adsorption kinetics and was derived by slopes of the cumulative adsorption curves. In particular, the magnification shown in Figure 4 shows that slopes of about 0.18 g_{HC}/min/100 g_{ZEO} (corresponding to unitary removal efficiency) were reached for toluene and isobutene on HZSM-5 at room temperature during the first 5

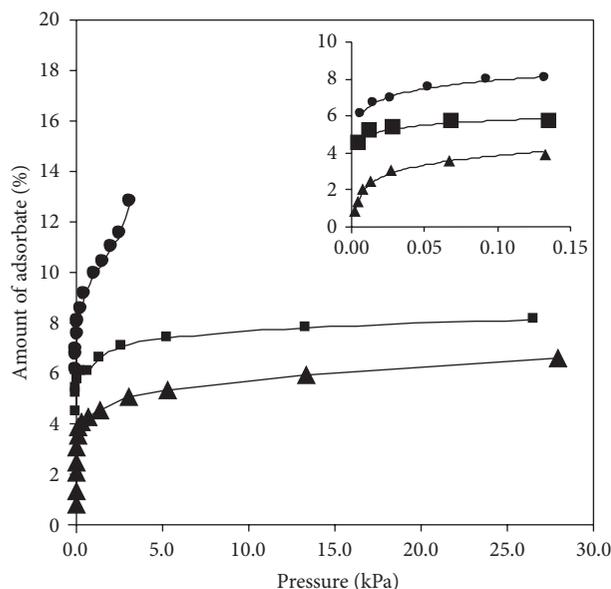


FIGURE 3: Adsorption isotherms at 298 K of ethylene (▲), isobutene (■), and toluene (●) on HZSM-5.

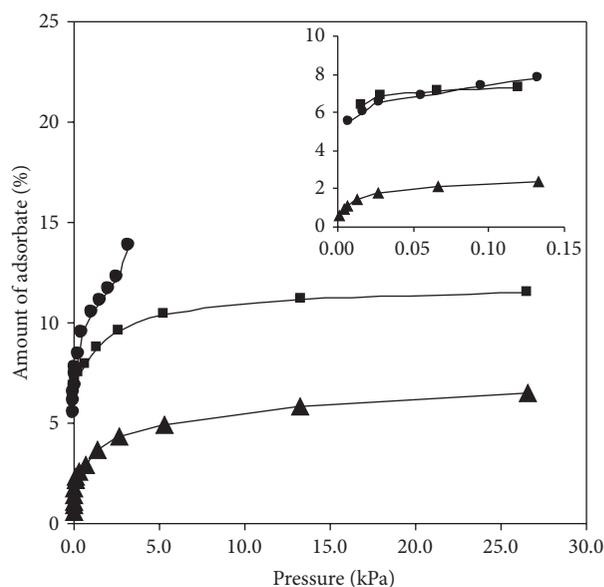


FIGURE 5: Adsorption isotherms at 298 K of ethylene (▲), isobutene (■), and toluene (●) on silicalite.

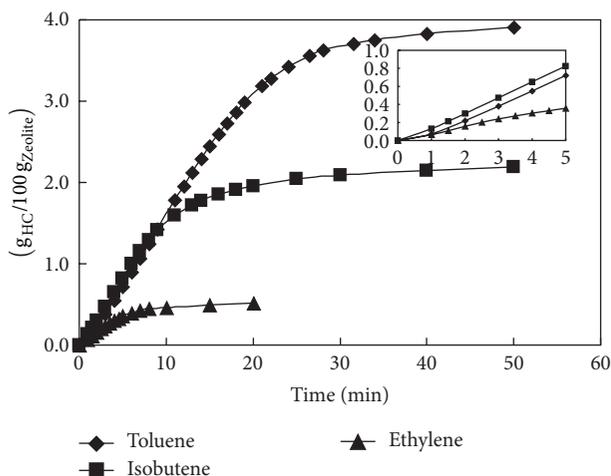


FIGURE 4: Cumulative adsorption of ethylene, isobutene, and toluene on HZSM-5 adsorbent bed versus time on stream at 298 K and $30,000 \text{ h}^{-1}$.

minutes, which normally include the time range necessary to reach the TWC light-off temperature. In the same time range the removal efficiency for ethylene resulted at least 50% less.

In the hypothesis that adsorption of the three hydrocarbons on HZSM-5 at 298 K is essentially due to physical interaction between gas molecule and solid surface (van der Waals interaction) the low adsorption capacity exhibited by HZSM-5 for ethylene can be attributed to the absence in the molecule of any permanent dipole moment that implies a weaker contribution of coulombic forces to the overall van der Waals interaction [27]. The higher trapping capability for toluene can be explained considering the larger molecular size with respect to the other two hydrocarbons. In fact, for a larger molecule the enhancement of the interaction energy,

due to the overlap of the adsorption field from neighboring walls, can be expected in very fine pores [27].

In order to investigate the influence of Si/Al ratio on adsorption capacities, measurements on silicalite, a zeolite isostructural of ZSM-5 and Al-free, were performed. The comparison between adsorption isotherms of ethylene, isobutene, and toluene at 298 K on silicalite is shown in Figure 5. In saturation conditions no significant difference was observed for ethylene and toluene adsorption (Table 3), where a strong increase was detected for isobutene with respect to HZSM-5. Considering in particular the low pressure range (0–0.1 kPa, top right figure) a slight reduction of adsorption capacities for ethylene and toluene was observed, while also in these conditions the adsorption of isobutene resulted in being higher on silicalite than on HZSM-5. The absence of Al reduces the number of adsorption sites and, as a consequence, the intensity of adsorbate-adsorbent interaction energy, responsible for adsorption phenomena. This can explain the adsorption reduction observed for ethylene and toluene on silicalite at low partial pressure. Regarding ethylene a further contribution to uptake on HZSM-5 can be caused by reactivity phenomena [18].

The lower adsorption capacity observed in gravimetric tests for isobutene on HZSM-5 with respect to silicalite (Figures 3 and 5) can be attributed to a chemical adsorption contribution resulting from the interaction of C=C double bond with the acid sites of HZSM-5 (highly active Brönsted acid sites) [29]. This implies that under conditions reached in gravimetric tests on dehydrated zeolites some oligomer species can be formed on HZSM-5, with partial blockage of micropore opening and consequent limitation of adsorption capacity.

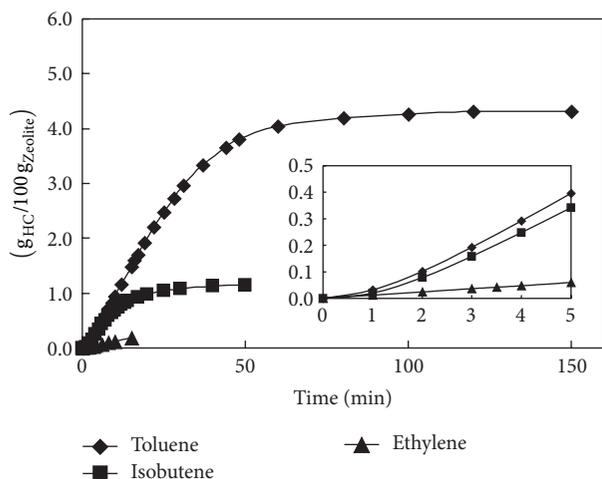


FIGURE 6: Cumulative adsorption of ethylene, isobutene, and toluene on silicalite adsorbent bed versus time on stream at 298 K and $30,000 \text{ h}^{-1}$.

In measurements affected under dynamic conditions (Figure 6 and Table 4), a global reduction of trapping capability was observed on silicalite with respect to HZSM-5. In particular, adsorption of ethylene was negligible, while a 50% decrease was observed for isobutene adsorption.

It is possible to hypothesize that the presence of water intracrystalline inside the zeolites tested by dynamic experiments hindered the oligomerization phenomena and made prevalent the effect of the adsorption sites number associated with the presence of Al in the MFI framework, determining higher adsorption capacities of isobutene on HZSM-5. Saturation uptake for toluene was comparable to that obtained on HZSM-5, but the process turned out slower, with bed saturation being reached after about 150 minutes. On the other hand, the adsorption rate during the first minutes was lower on silicalite with respect to HZSM-5 for both isobutene and toluene (the maximum slope did not exceed $0.11 \text{ g}_{\text{HC}}/\text{min}/100 \text{ g}_{\text{ZEO}}$, corresponding to a removal efficiency of about 0.6). Also this behavior can be correlated to lower number of adsorption sites in silicalite, hypothesizing that molecule diffusion through the microchannels is retarded in the absence of strength adsorption fields.

The influence of structure type on adsorption capacities was analyzed by adsorption measurements on HY, a faujasite-type zeolite, with the same Si/Al ratio of ZSM-5. Adsorption isotherms of ethylene, isobutene, and toluene at 298 K on HY are reported in Figure 7. Also in the case of HY the affinity for ethylene resulted very low. On the contrary, a very high adsorption capacity was shown on HY for isobutene (at a pressure of 0.1 kPa was already about 15%, as reported in Table 3). In particular, this zeolite adsorbed more isobutene than toluene, and the amount of adsorbed isobutene was also larger than that observed on HZSM-5 and silicalite, for all pressure values. This result can be explained considering the greater chemical reactivity of C=C double bond of isobutene with respect to ethylene [30]. As recalled before chemisorption phenomena involving acidic

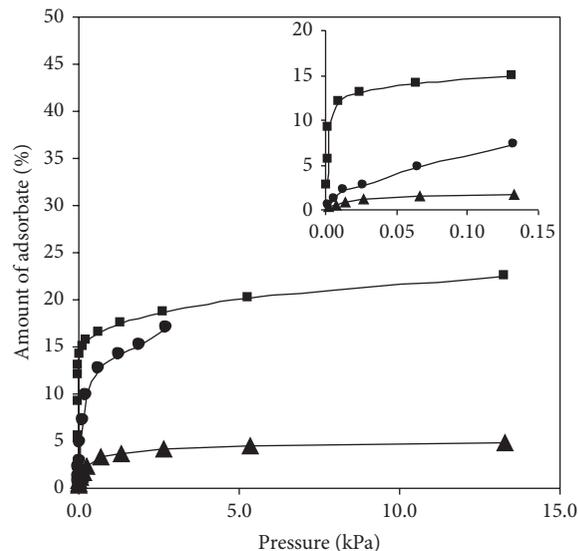


FIGURE 7: Adsorption isotherms at 298 K of ethylene (▲), isobutene (■), and toluene (●) on HY.

zeolites and unsaturated hydrocarbons are likely due to an oligomerisation process of alkenes [29]. According to this hypothesis it is possible to distinguish two cases:

- for HZSM-5, having pore opening of 5-6 Å, a pore-mouth blocking occurs because of the production of isobutene oligomerisation, with the subsequent reduction of adsorption capacity compared to silicalite, as reported above;
- in the case of HY, having a pore opening (7.4 Å) larger than HZSM-5, oligomerisation process of isobutene proceeds in parallel with the adsorption and stops only when the free volume inside the zeolite is filled with the oligomer products.

The results of flow experiments on HY at 298 K are reported in Figure 8. Adsorption of ethylene on HY zeolite was negligible, while a strong uptake was detected for isobutene and toluene. The adsorbed amount of these two hydrocarbons turned out about 1.5 times greater on HY than on HZSM-5, due to the larger micropore volume of HY. However, unlike the gravimetric test, under flow conditions the uptake of toluene was much larger than isobutene. It should be taken into account that in flow experiments the adsorbent material was tested without any preliminary thermal treatment; thus, the oligomerisation phenomena inside the microchannels could be affected by the presence of intracrystalline water molecules. The behavior of HY in flow adsorption experiments can be explained hypothesizing that the contribution of physical adsorption is predominant with respect to chemisorption.

The flow tests also evidenced that on HY the adsorption rate was lower than on HZSM-5 during the first 5 minutes and comparable to that observed on silicalite (i.e., the slope of toluene curve did not exceed $0.10 \text{ g}_{\text{HC}}/\text{min}/100 \text{ g}_{\text{ZEO}}$). The effect of minor energy of adsorption fields can be invoked to

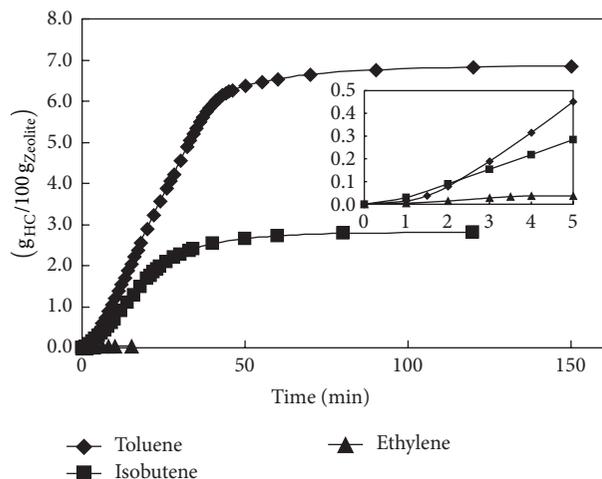


FIGURE 8: Cumulative adsorption of ethylene, isobutene and toluene on HY adsorbent bed versus time on stream at 298 K and $30,000 \text{ h}^{-1}$.

explain this phenomenon. In fact, in spite of Al presence in the framework, the larger micropore diameter of HY makes the interaction energy undergone by hydrocarbon molecules weaker [27].

The above results evidence that the adsorption capacities calculated by breakthrough curves were always lower with respect to the values obtained by gravimetric tests. Taking into account that the zeolite microchannels contained intracrystalline water molecules during flow adsorption runs (see Section 2); these lower adsorption capacities can be attributed to the competition inside the zeolite microchannels between intracrystalline water and HC adsorbate.

3.2. The Effect of Temperature on HC Trapping. The breakthrough curves were determined at various temperatures in the range 298–523 K in order to determine adsorption properties in conditions simulating the engine warm-up phase. As regards ethylene the already scarce adsorption observed at 298 K on HZSM-5 became negligible at 373 K confirming that this material is not suitable for trapping this type of hydrocarbon at low partial pressure. Further, no adsorption was detected for ethylene on HY and silicalite also at higher temperatures.

The adsorption of toluene on HZSM-5 as function of temperature is shown in Figure 9.

The trapping capability progressively decreased raising the temperature up to 423 K, but an appreciable adsorption was measured also at the highest temperature investigated (1% at 423 K). The decrease of the uptake capacity when temperature is raised is expected, being adsorption of an exothermic process, and indicates that interaction between toluene and HZSM-5 at low partial pressure is of physical nature. Similar behaviors were observed for toluene on silicalite (Figure 10) and HY (Figure 11) when temperature was raised from 298 to 423 K. In particular, at 423 K the adsorption of toluene on silicalite and HY was reduced of about 70%.

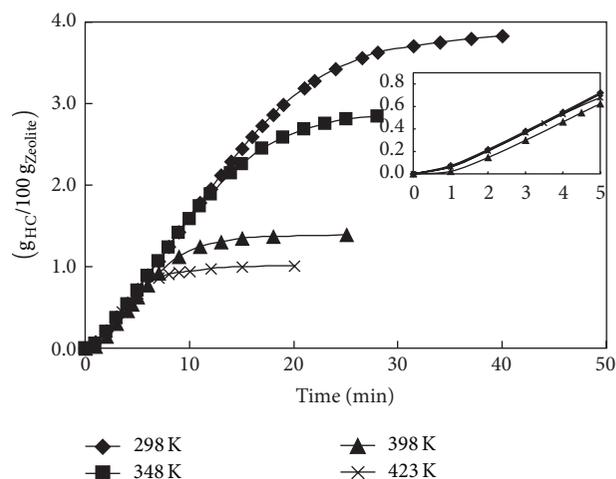


FIGURE 9: Cumulative adsorption of toluene on HZSM-5 adsorbent bed versus time on stream at $30,000 \text{ h}^{-1}$ and different temperature values.

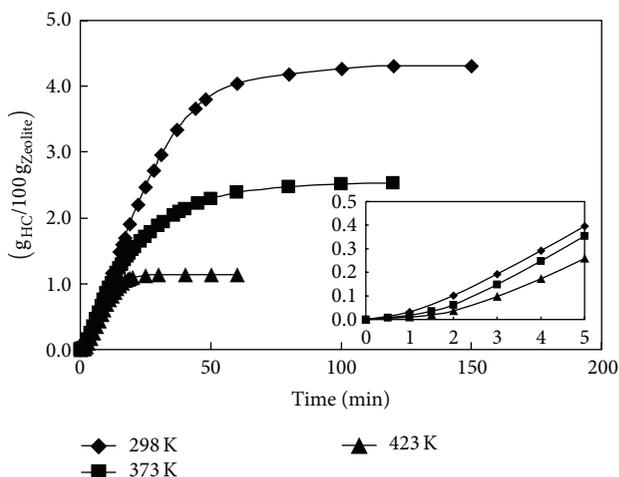


FIGURE 10: Cumulative adsorption of toluene on silicalite adsorbent bed versus time on stream at $30,000 \text{ h}^{-1}$ and different temperature values.

Regarding the adsorption rate no significant effect of temperature was detected, in particular an almost unitary efficiency (slope close to $0.18 \text{ g}_{\text{HC}}/\text{min}/100 \text{ g}_{\text{ZEO}}$) was detected on HZSM-5 at all temperatures up to 423 K during the first 5 minutes.

A particular behavior was observed for isobutene adsorption when temperature was increased. Increased uptakes were found on HZSM-5 (Figure 12) from 298 to 413 K (4.55%), with removal efficiency practically unitary, whereas a smaller amount was adsorbed for higher temperature up to 523 K (0.63%), with slower adsorption rate.

Activated physical adsorption can occur in microporous solids when the width of the pores is very close to the diameter of the adsorbate molecule, since in this case the molecule encounters an energy barrier to its passage through the constriction [27]. This effect cannot be invoked for adsorption of isobutene on HZSM-5 from 298 to 413 K,

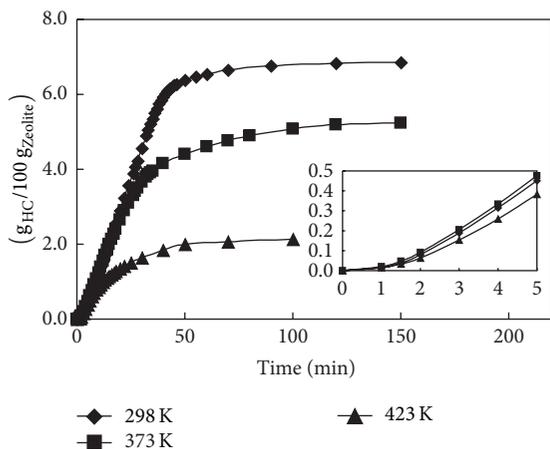


FIGURE 11: Cumulative adsorption of toluene on HY adsorbent bed versus time on stream at $30,000 \text{ h}^{-1}$ and different temperature values.

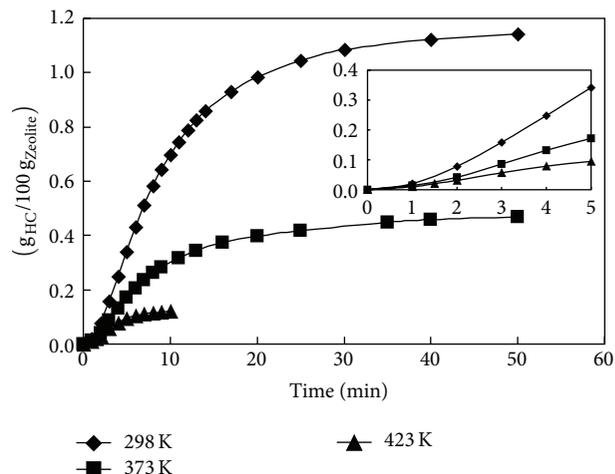


FIGURE 13: Cumulative adsorption of isobutene on silicalite adsorbent bed versus time on stream at $30,000 \text{ h}^{-1}$ and different temperature values.

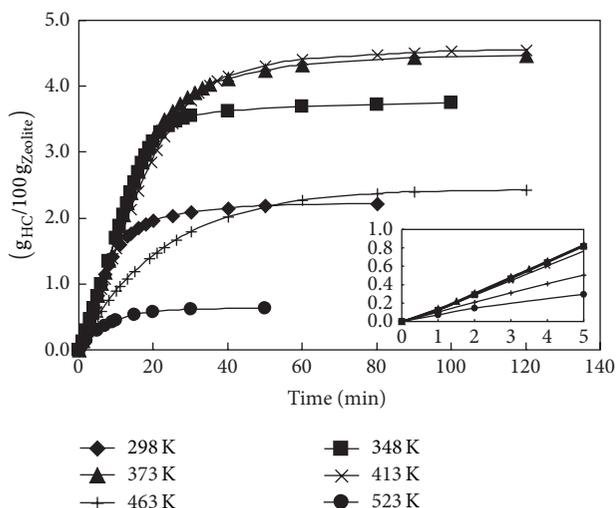


FIGURE 12: Cumulative adsorption of isobutene on HZSM-5 adsorbent bed versus time on stream at $30,000 \text{ h}^{-1}$ and different temperature values.

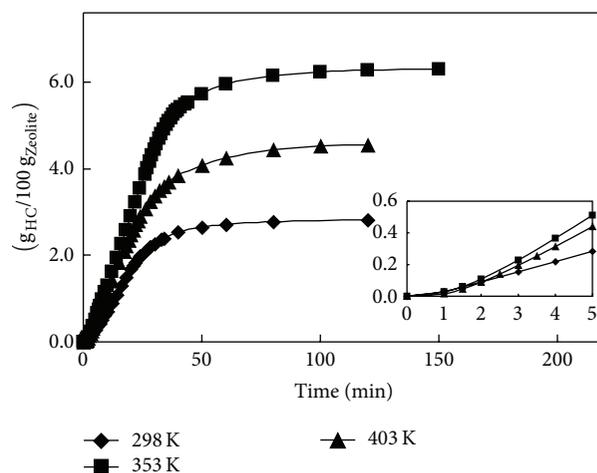


FIGURE 14: Cumulative adsorption of isobutene on HY adsorbent bed versus time on stream at $30,000 \text{ h}^{-1}$ and different temperature values.

because this molecule has a diameter inferior to that of toluene and does not involve any physical activation effect with temperature. Then a contribution of chemical adsorption can be taken into account to explain the results obtained for isobutene in flow experiments. On the other hand the greater stability of aromatic unsaturation, compared to that due to the $\text{C}=\text{C}$ double bond of isobutene, can give reason of the absence of chemical activation in the case of toluene.

As regards silicalite (Figure 13) the already scarce adsorption capacity observed for isobutene at 298 K became negligible at higher temperatures, while the adsorption rate slightly decreased, confirming the role of framework Al on the physical adsorption interaction energy. On the contrary, the effect of chemical activation made the uptake capacity of isobutene on HY (Figure 14) at 353 and 403 K about 2 and 1.5 times higher than at 298 K, respectively, while no improvement was observed regarding the removal

efficiency during the first 5 minutes. The results of Figures 12–14 confirm the hypothesis of the chemical contribution to isobutene adsorption and suggest a correlation between this contribution and the Si/Al ratio.

The adsorption affinity of HZSM-5 towards paraffins is shown by curves of Figure 15, which refer to an equimolar mixture of C_4 - C_5 paraffins (n-butane, isobutane, n-pentane, isopentane, and neopentane, total C_3 concentration of 850 ppm). Both uptake capacity and adsorption rate rapidly decreased increasing the temperature, becoming negligible already at 373 K. A very low affinity for paraffins was also observed on silicalite and HY (Table 4). The results for HY are reported in Figure 16; it can be noted that already at 298 K the adsorption capacity at bed saturation is only 0.73%.

The role of olefin double bond and the low affinity towards paraffins was confirmed by the curves shown in Figure 17, where the results of flow tests for an equimolar mixture

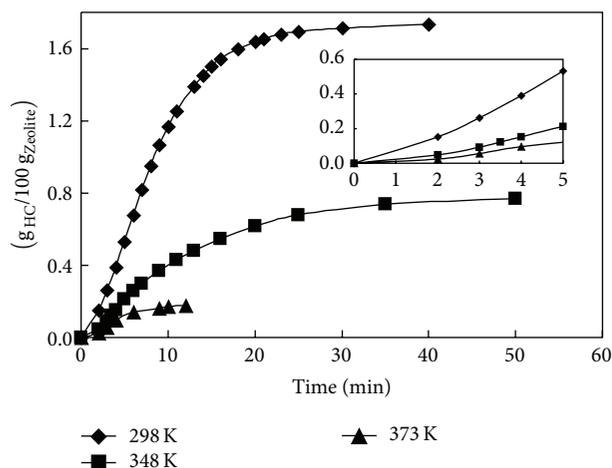


FIGURE 15: Cumulative adsorption of C_4 - C_5 paraffin mixture on HZSM-5 adsorbent bed versus time on stream at $30,000\text{ h}^{-1}$ and different temperature values. Reactor feed: n-butane, isobutane, n-pentane, isopentane, and neopentane equimolar mixture.

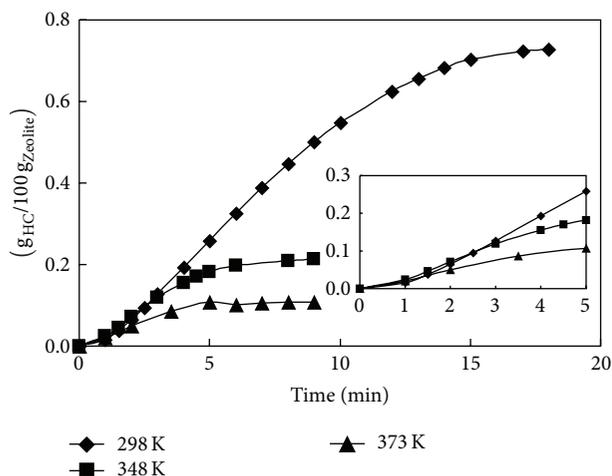


FIGURE 16: Cumulative adsorption of C_4 - C_5 paraffin mixture on HY adsorbent bed versus time on stream at $30,000\text{ h}^{-1}$ and different temperature values. Reactor feed: n-butane, isobutane, n-pentane, isopentane, and neopentane equimolar mixture.

of isobutene and isobutane on HZSM-5 are reported. The adsorption of this mixture on HZSM-5 was higher than isobutene at temperature between 298 and 373 K (Figure 12 and Table 4), probably due to a synergic effect associated with isobutane alkylation by isobutene, favored on zeolite catalysts at low temperatures [30]. A reduction of bed trapping capacity was observed increasing the temperature, when the minor affinity of ZSM-5 towards the paraffin adsorption did not favor alkylation reactions. Only at room temperature the adsorption rate permitted high removal efficiency to be reached during the first minutes.

4. Conclusions

Three zeolitic materials (HZSM-5, silicalite, and HY) were studied as adsorbents for light hydrocarbon traps. Isotherm

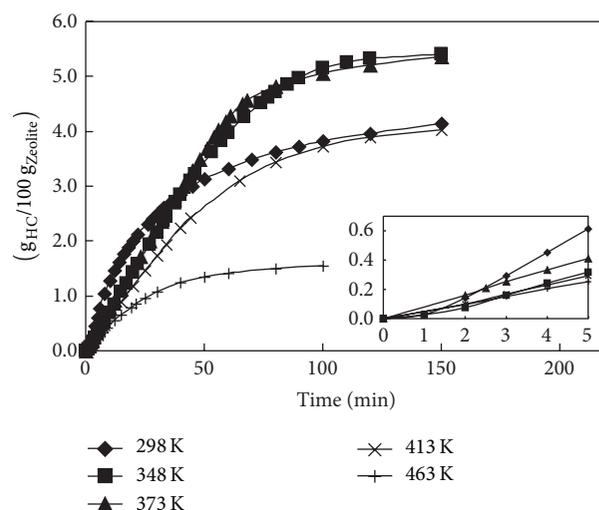


FIGURE 17: Cumulative adsorption of equimolar isobutane/isobutene mixture on HZSM-5 adsorbent bed versus time on stream at $30,000\text{ h}^{-1}$ and different temperature values.

gravimetric tests at room temperature were performed up to saturation pressure for ethylene, isobutene, and toluene, while dynamic tests in flow microreactor were carried out at low partial pressure (0.1 kPa) and different temperature values (298–523 K) on the same three hydrocarbons plus two mixtures of C_4 - C_5 paraffins and isobutane/isobutene.

The three adsorbents showed high affinity at room temperature for toluene and isobutene, but minor affinity for paraffins and ethylene. In particular the adsorption of ethylene was appreciable on HZSM-5, but resulted negligible for silicalite and HY. Equilibrium adsorption capacities obtained with breakthrough curves at 0.1 kPa resulted in being very lower with respect to values reachable by gravimetric tests at the same partial pressure, due to the presence of intracrystalline water in zeolite samples.

Gravimetric tests and breakthrough curves evidenced chemisorption phenomena as regards isobutene adsorption on Al containing materials (HZSM-5 and HY), with possible formation of oligomeric species inside zeolite microchannels.

Increasing temperature from 298 up to 423 K adsorption capacity measured by dynamic tests for toluene on the three materials decreased while it became negligible for ethylene already at 373 K also on HZSM-5. As regarding isobutene a maximum in adsorption capacity was reached for HZSM-5 at 413 K and for HY at 353 K. While the results obtained for ethylene and toluene could be interpreted in terms of physical adsorption, a chemical adsorption contribution was invoked to explain isobutene uptake increment with temperature.

Experiments affected with a C_4 - C_5 paraffin mixture evidenced the minor affinity of the three materials towards saturated hydrocarbons. Breakthrough curves performed with isobutene-isobutane equimolar mixture evidenced the role of $C=C$ double bond on adsorption capacity of HZSM-5 towards hydrocarbons and the possible occurring of alkylation reactions.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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