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Zeolite-Based Adsorbers for Reducing Light Hydrocarbon Emissions from Engine Exhaust

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ABSTRACT

Adsorption of light hydrocarbons, such as ethane, ethylene, *n*-butane, isobutane, and isobutene, on zeolites 5A [LTA] and H-Beta [BEA] was investigated, in order to evaluate the possible use of these zeolites as adsorbents for reducing cold start emissions at engine exhaust. Equilibrium isotherms at 25°C were determined and analyzed by Langmuir and virial equations to estimate adsorption capacities at saturation and adsorption affinity for single hydrocarbons at low pressure. Good affinities of zeolites 5A and H-Beta for the tested light hydrocarbons were found either at saturation or at low pressure. Flow measurements were

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also carried out with a fixed-bed microreactor using a real engine exhaust gas. Reasonable performances of zeolite H-Beta in trapping hydrocarbons present in the emission at engine exhaust were obtained. Poor performances, obtained, on the contrary, with zeolite 5A, were interpreted as due to the preferential adsorption of water vapor, compared to hydrocarbons. On the basis of the present and of previously collected data, the possibility of use of zeolite H-Beta, coupled to zeolite H-Y or zeolite H-ZSM5, to realize a hydrocarbon adsorbent trap for reducing cold start emission is, at last, envisaged.

Key Words: Cold start; Engine exhaust emission; Light hydrocarbons; Ethane; Ethylene; *n*-Butane; Isobutane; Isobutene; Hydrocarbon adsorbent trap; Zeolite 5A; Zeolite H-Beta.

INTRODUCTION

Future legal restrictions on passenger car emissions involve the development of new after-treatment systems. In particular, exhaust hydrocarbon concentration needs to be strongly reduced during cold start. It is well known, in fact, that the largest fraction (about 80%) of the total organic pollutants flows out during the short time following the engine start-up (200 sec).[1] In recent years, technologies based on electrical heated catalyst (EHC) or burner heated catalyst (BHC) systems have been explored as potential solutions for reducing cold-start emissions.[2] An alternative solution based on a hydrocarbon trap combined with catalytic converters has been proposed.[2–8] The trap is made up of adsorbent materials that allow hydrocarbon molecules to be caught until the working temperature of the catalytic converter is reached. The most attractive solution consists in combining both catalytic and adsorbent functions on the same cordierite washcoat [adsorber-coated substrate (ACS)].[2,9] This technique requires much work to be done, in order to match catalyst performance with adsorber characteristics, but it appears to be the best solution for car manufacturers.[9] The main performance characteristics required of adsorbent materials are thermal stability and a capability to trap all hydrocarbon species in a low-temperature range (25–150°C). Zeolites, due to their adsorption and catalytic properties coupled to good thermal stability, appear able to fulfill all these requirements.[4–9]

Zeolites are a class of crystalline framework aluminosilicate materials having a microporous structure characterized by interconnected channels and cavities, in which water molecules and extraframework cations are located.[10] The possibility that water molecules can be removed on heating and substituted for other molecules gives rise to the adsorption property. Differently from other commercial adsorbents (e.g., activated carbons and clays, inorganic gels, etc.), the typical structure of zeolites, characterized by uniform pore arrays of molecular size (3–10 Å), results in a "selective" adsorption, based on a "molecular sieving" effect.[10]

A study concerning these issues was funded a few years ago by the Italian Research National Council (CNR) in the frame of the Finalized Project on Special Materials for Advanced Technologies II. The objective of this investigation continues to be the realization of an adsorbent trap using zeolitic material that is able to reduce hydrocarbon emissions during the cold start phase according to the ACS technology. An original procedure to grow zeolite microcrystals on a cordierite washcoat surface has been set up.[11] Meanwhile, a systematic investigation is being carried out to select suitable zeolite terms that might be used to adsorb most hydrocarbons present at engine exhaust during the start-up.

In a previous paper[12] was found that zeolitic materials, belonging to the structural types [MFI] and [FAU],[13] display a very high selectivity for toluene and isobutene, whereas their adsorption capacity for ethylene and paraffins is negligible. In order to test suitable zeolite phases able to efficiently adsorb light hydrocarbons, zeolite 5A [LTA],[13] characterized by a three-dimensional channel system with pore openings of ~5 Å;[10] and zeolite H-Beta [BEA][13] with two different channel systems, having pore openings of 5.5 × 5.5 Å and 7.6 × 6.4 Å,[14] were chosen for the present investigation. Selected gases representative of light hydrocarbons are ethane, ethylene, *n*-butane, isobutane, and isobutene. Similar data for zeolite H-Beta are to be considered original, as adsorption data for this zeolite are lacking in the literature. On the contrary, data for zeolite A, which are absolutely not original,[10] were needed to perform an accurate data modeling and a detailed investigation of adsorption at low pressures.

MATERIALS AND METHODS

Materials

The calcium form of zeolite type A (Si/Al = 1, usually referred to as zeolite 5A) and the hydrogen form of zeolite Beta (Si/Al = 12.5, usually referred to as zeolite H-Beta)[13] were used for all the experiments. Both zeolites were commercially available powder products, supplied by Carlo Erba and Zeolyst, respectively. Zeolite powders were compacted under suitable pressure and the resulting pellets were gently ground. Upon sieving, the 180–350 μm-sized grains were collected and used for the measurements.

Ethane, ethylene, *n*-butane, isobutane, and isobutene (analytical grade, 99% purity, supplied by Società Ossigeno Napoli (SON), Italy) were chosen as representative of light hydrocarbons (olefins and paraffins) detectable at engine exhaust during the start-up.[1] Their characteristic kinetic diameters are reported in Table 1.[10]

Adsorption Runs

The adsorption properties of the zeolitic materials were investigated by determining the equilibrium isotherms of the gases. Reference isotherms also were determined for water vapor.

Adsorption isotherms were obtained using a gravimetric technique based on a McBain-type balance.[15] This device is equipped with a quartz spring (Ruska Instrument Co., Houston, Texas), whose elongation law is known (sensitivity $= 5.0\,\mathrm{mm/mg}$). 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 (resolution $= 0.05\,\mathrm{mm}$). Equilibrium gas pressure was measured through electronic devices (Edwards Datametrics 1500). A Heto thermostating unit allowed a temperature control within the range of $\pm 0.1^\circ\mathrm{C}$. Before measurement samples were thermally activated at 350°C under high vacuum ($P < 10^{-5}$ mbar) for 3 hr (Edwards Diffstak MK2 diffusion pump). After cooling to 25°C, aliquots of the selected gas were allowed to enter the balance chamber and sufficient time was allowed to attain equilibrium. Adsorption isotherms were outlined by plotting the amounts of adsorbate on dry basis vs. the partial gas pressure at equilibrium.

Flow measurements were also carried out with a fixed-bed microreactor using a real engine exhaust gas. Tests consisted of determining breakthrough curves at 40°C with zeolitic materials not previously heat treated and, therefore, retaining their intracrystalline water content. The dynamic adsorption tests were preliminarily performed at constant temperature in order to compare the adsorption properties of different materials in terms of equilibrium adsorption capacity. The temperature of 40°C was chosen as representative of the temperature range detectable during the first seconds from the engine start-up. The microreactor was created from a stainless steel tube of 10 mm i.d., inserted in a tubular electric oven (Lenton Thermal Designs Ltd.), equipped

Table 1. Kinetic diameters of tested hydrocarbons.

	Ethane	Ethylene	Butane	Isobutane	Isobutene
Kinetic diameters (Å)	3.8	3.9	4.3	5.0	4.9

with a temperature controller. The amount of 0.5 g of adsorber were loaded in the reactor as coarse powder (180–350 μm sized grains) and the exhaust gas flow rate was adjusted to realize a space velocity of 30,000 hr^{-1}. This space velocity was adopted in all dynamic adsorption tests because it represents the order of magnitude of space velocity typically realized on catalytic converters installed on medium size cars during start-up phase (low engine speed). The engine, a spark ignition four cylinder, 1350 cm^3 displacement, was installed on the test bench and coupled with an electric dynamometer (Borghi & Saveri). A portion of the exhaust gas was collected by a probe, heated at 180°C, and sent to the reactor by a pump heated at 120°C. A flame-ionization in-line analyzer (Rosemount, Model 404) was used for hydrocarbon analysis before and after the adsorbent bed.

Theoretical

Physical adsorption on an uniform surface at such a low concentration that all molecules can be considered isolated from their nearest neighbors, can be adequately described by the Henry's law:[16]

$$q = Kp \tag{1}$$

where p is the partial pressure in the fluid phase; q, the concentration of the adsorbed phase (amount of adsorbate relative to dry adsorbent, w/w); and K is the adsorption equilibrium constant (namely Henry's constant).

Generally, Eq. (1) is a good model for a very limited portion of the adsorption isotherm, in the range of low pressures. Different models have been proposed to describe the whole isotherm.

A simple theoretical model, based on the hypothesis that adsorbed molecules are distributed on a plane adsorbent surface as a monomolecular layer ("monolayer") is the Langmuir equation:[16]

$$\frac{q}{q_{\max}} = \frac{bp}{(1 + bp)} \tag{2}$$

and in its linear form

$$\frac{p}{q} = \frac{1}{bq_{\max}} + \frac{p}{q_{\max}} \tag{3}$$

where q is the actual amount of adsorbate relative to dry adsorbent (w/w); p the partial pressure; and $q_{\max}$ and b are two constants. Actually, $q_{\max}$ represents the amount of adsorbate relative to dry adsorbent (w/w), necessary to cover the whole surface of the adsorbent with a monolayer and $b = k_a/k_d$

is the adsorption equilibrium constant, namely the ratio between the kinetic constant of adsorption (k_a) and desorption (k_d) processes.[16]

Since at low pressure ($p \rightarrow 0$) Henry's law [Eq. (1)] can be considered valid, from Eq. (2), we can obtain:

$$\lim_{p\rightarrow 0}\left(\frac{q}{p}\right) = bq_{\max} = K \tag{4}$$

with $bq_{\max}$ being the inverse of limiting slope of the linear isotherm of Eq. (3).

Another relationship between the amount of adsorbate q and the partial pressure p is given by the virial equation:[16]

$$\frac{Kp}{q} = \exp(2A_1q + \frac{3}{2A_2q^2} + \cdots) \tag{5}$$

where A_n are the virial constants and K is the Henry's constant. In fact, for $q \rightarrow 0$ Eq. (5) takes the form of the Henry's law. According to Eq. (5), a plot of ln (p/q) vs. q should be linear at concentrations well above the limit of validity of Henry's law, so that extrapolation of such a plot to zero-adsorbed phase concentration (i.e., $p \rightarrow 0$) provides a simple method of determining the Henry's constant K.[16]

RESULTS AND DISCUSSION

Equilibrium Isotherms

Adsorption isotherms of ethane, ethylene, butane, isobutane, and isobutene on zeolite 5A and zeolite H-Beta, at 25°C, are reported in Figs. 1 and 2, respectively.

Inspection of the curves allows some general information on the affinity of the various gases for the two zeolites to be collected. A rough indication of the affinity sequence may be, in fact, worked out from the obtained sequence of the adsorption capacities:

5A: butane $\gg$ ethane $\approx$ ethylene $\gg$ isobutane $>$ isobutene;

H-Beta: isobutene $\gg$ isobutane $\gg$ butane $>$ ethane $>$ ethylene.

A further important observation is that zeolites 5A and H-Beta display quite higher adsorption capacities for ethylene than those obtained with the previously tested zeolites (silicalite, H-ZSM5 and H-Y).[12] In addition, both zeolites in general show reasonable affinities for paraffins, with a preference of zeolite 5A for butane and ethane and zeolite H-Beta for isobutane.

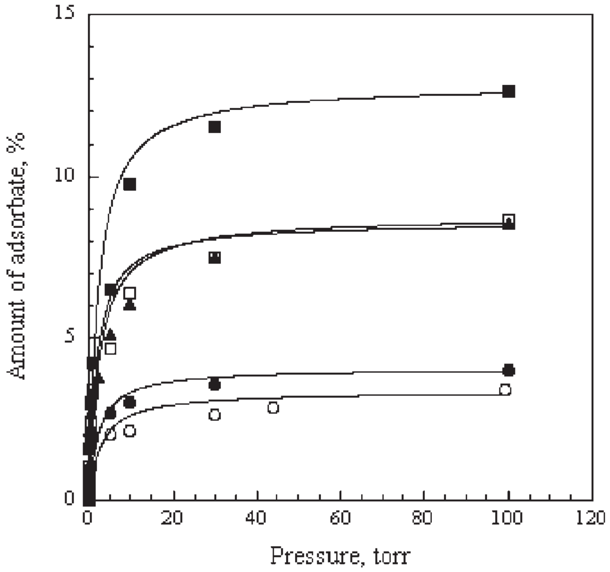

Figure 1. Adsorption isotherms at 25°C of butane (■), ethylene (□), ethane (▲), isobutene (●), isobutane (○) on zeolite 5A. Symbols = experimental points, lines = calculated functions with the Langmuir model.

The low adsorption capacity of zeolite 5A for isobutane and isobutene (Fig. 1) must be most likely ascribed to a molecular sieving effect. In fact, kinetic diameters of these hydrocarbons (4.9–5.0 Å, see Table. 1) are very close to the pore opening of zeolite 5A (~5 Å), resulting in a reduced permeation of the gases into the sorbent. On the contrary, the high adsorption capacity for butane is explainable by the enhancement of the interaction energy between the molecule and the neighboring walls[17] due to the fact that its kinetic diameter (4.3 Å) is smaller but rather close to the pore size of zeolite A.

As regards zeolite H-Beta (Fig. 2), the very high adsorption capacity displayed for isobutene could be explained, considering a contribution of chemisorption phenomena, due to the great chemical reactivity of the C═C double bond of this hydrocarbon.[18] According to the literature, chemisorption involving acidic zeolites (extraframework sites occupied by hydrogen) and unsaturated hydrocarbons would be due to an oligomerization process.[19,20] While the adsorption of isobutene proceeds in the smaller pores, the oligomerization process likely occurs in the larger pores and stops only when the free volume inside the zeolite is filled with the oligomers.

It was shown by van den Berg et al.[21] that both ethylene and isobutene oligomerize on H-ZSM-5 at room temperature (300 K), whereas ethylene is

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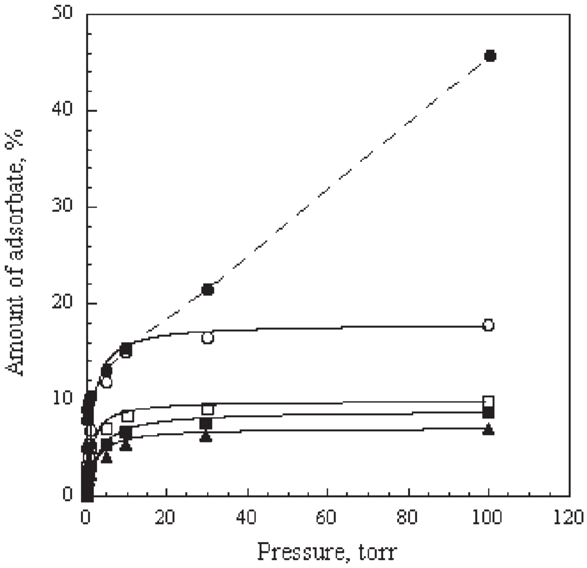

Figure 2. Adsorption isotherms at 25°C of butane (■), ethylene (□), ethane (▲), isobutene (●), isobutane (○) on zeolite H-Beta. Symbols = experimental points, solid lines = calculated functions with the Langmuir model; dashed line = experimental isotherm for isobutene adsorption.

converted slowly (poor reactivity), isobutene reacts very fast. The rectangular shape, typical of physical sorption on microporous materials, exhibited by the ethylene adsorption isotherm on H-Beta (see Fig. 2) indicates the poor reactivity of ethylene and the absence of relevant oligomerization phenomena.

Actually, the deviation from rectangular shape of the isobutene adsorption isotherm on H-Beta might also be due to pore filling phenomena, but in this case a similar behavior also should be expected by *n*-butane and isobutane (especially *n*-butane because of its boiling temperature, which is higher than that of isobutene). Such behavior was not found in this experimentation. Moreover, as pore filling is essentially due to capillary condensation, it occurs when the partial pressure approaches the vapor pressure at working temperature. Do[22] reports that the range of validity for capillary condensation is that in which the relative pressure is between 0.35–0.99. Since at room temperature the pressure to liquefy isobutene is not less than 2000 torr, capillary condensation phenomena become relevant at a partial pressure of roughly 700 torr, compared to the partial pressure of our experiments amounting to only 100 torr (see Fig. 2).

Modeling

The adsorption equilibrium data were analyzed by the Langmuir equation [Eqs. (2) and (3)]. Modeling was not applied to the isobutene adsorption data on H-Beta, because the increasing trend of experimental points (Fig. 2, dashed line) is not compatible with the rectangular shape of the Langmuir-type curve.

Table 2 summarizes the equilibrium parameters, i.e., $q_{\max}$ and b, computed through the modeling procedure. The values of the coefficient of determination, r^2, that are very close to 1, demonstrate that the Langmuir equation is a good model of the experimental equilibrium data. Comparison between model fitting (solid line) and experimental equilibrium data (symbols) is shown in Figs. 1 and 2, for zeolites 5A and H-Beta, respectively.

According to Eq. (4), equilibrium parameters $q_{\max}$ and b allow the Henry's constant K to be calculated. This is an useful parameter to estimate the affinity sequence of the hydrocarbons at the low pressures (e.g., <1 torr), which are typical of the main hydrocarbons present at an automotive engine exhaust.

Processing Eq. (3) gives a correct estimation of $q_{\max}$; the same is not true for $bq_{\max}$ and, therefore for K, because the number of experimental points available in the low-concentration region useful for estimation of $bq_{\max}$ is usually very small. That is why, to obtain a good estimation of Henry's constant (K) it is preferable to use the virial isotherm.[16] Table 3 compares the Henry's constant K values estimated from virial equation [Eq. (5)], from Langmuir equation [Eq. (4)] and directly from the limiting slope of adsorption isotherms [Eq. (1)]. The values computed from the virial equation are very

Table 2. Equilibrium parameters computed from the Langmuir model [Eq. (2)] and coefficients of determination r^2 of straight lines [Eq. (3)].

Zeolite	Adsorbate	$q_{\max}$ (g adsorbate/g zeolite)	b (torr^{-1})	r^2
5A	Ethane	0.086	0.522	0.9974
5A	Ethylene	0.088	0.413	0.9973
5A	*n*-Butane	0.128	0.451	0.9963
5A	Isobutane	0.034	0.343	0.9879
5A	Isobutene	0.041	0.439	0.9967
H-Beta	Ethane	0.071	0.502	0.9981
H-Beta	Ethylene	0.099	0.777	0.9991
H-Beta	*n*-Butane	0.089	0.352	0.9970
H-Beta	Isobutane	0.179	0.701	0.9992
H-Beta	Isobutene	—	—	—

Table 3. Henry's constant values estimated from virial equation (K_V), from Langmuir equation (K_L) and directly from the limiting slope of adsorption isotherms (K_S).

Zeolite	Adsorbate	K_L (torr^{-1})	K_V (torr^{-1})	K_S (torr^{-1})
5A	Ethane	0.045	0.326	0.351
5A	Ethylene	0.036	0.175	0.186
5A	*n*-Butane	0.058	0.190	0.166
5A	Isobutane	0.012	0.094	0.111
5A	Isobutene	0.018	0.063	0.056
H-Beta	Ethane	0.036	0.176	0.221
H-Beta	Ethylene	0.077	0.178	0.173
H-Beta	*n*-Butane	0.031	0.054	0.043
H-Beta	Isobutane	0.125	0.335	0.351
H-Beta	Isobutene	—	1.778	1.813

close to those determined directly from the limiting slope of the experimental isotherms. On the contrary, as expected, values computed from the Langmuir equation appear unreliable.

Inspecting data in Table 3 points out that zeolite 5A shows good affinities for ethane, ethylene, and *n*-butane also at low pressure. As regards zeolite H-Beta, a good performance at low pressure can be expected for all hydrocarbons, except *n*-butane. The high value of *K* for isobutene seems to indicate that oligomerization phenomena already occur in the low-concentration region.

Breakthrough Curves

In order to test adsorption properties in real conditions, dynamic measurements were performed directly at the exhaust of a S.I. engine. Figure 3 reports the breakthrough curves at 40°C and with a space velocity of 30,000 hr^{-1} for zeolites 5A and H-Beta, compared with the previous curves obtained for silicalite, H-ZSM5, and H-Y.[12] It was observed that these curves report hydrocarbon concentration, expressed as ppm of C_3, i.e., as equivalent concentration of hydrocarbon containing three C atoms, measured at the outlet of the adsorbent bed, as a function of time on stream. The adsorption capacity is computed by graphic integration of the area delimited by the curve and a horizontal straight line at the feed value.

Breakthrough curves of Fig. 3 indicate reasonable performances as regards zeolite H-Beta (total adsorption capacity equal to roughly 1.1%), but negligible adsorption capacities for zeolite 5A.

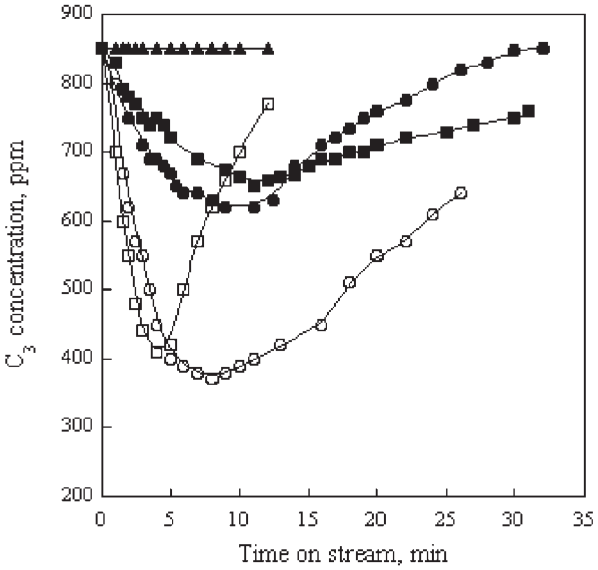

Figure 3. Concentration of total hydrocarbons at the outlet of HY (○), H-ZSM5 (●), silicalite (■), H-Beta (□) and 5A (▲) adsorbent beds vs. time on stream at 30,000 hr^{-1} space velocity and 40°C. Reactor feed: engine exhaust gas. C_3 conc. = equivalent concentration of hydrocarbon containing three C atoms. Data on HY, H-ZSM5 and silicalite from Corbo et al., 2000.[12]

These data can be explained considering that adsorption is mainly affected by two different parameters such as: (i) the hydrophilicity/hydrophobicity and (ii) pore opening, which depend on composition (Si/Al ratio) and structure of the adsorbent, respectively.

As far as the hydrophilicity/hydrophobicity is concerned, zeolite 5A, having a low Si/Al ratio (Si/Al = 1), is hydrophilic, whereas H-Beta (Si/Al = 12.5) can be considered hydrophobic.[10] Also zeolites H-Y (Si/Al = 15), H-ZSM-5 (Si/Al = 15), and silicalite (Si/Al = ∞), reported for reference in the same figure, must be considered hydrophobic. The different behavior towards water is also evident from the data of Fig. 4, which reports the adsorption isotherms of water vapor at 25°C for the zeolites referred to in Fig. 3. It may be concluded, therefore, that the negligible hydrocarbon adsorption shown by zeolite 5A is to be connected to its high affinity for the water vapor molecules present in the engine exhaust gas.

Admitting, on the contrary, that the degree of hydrophobicity is not the prevalent parameter affecting the performance of zeolite H-Beta, compared to H-Y, H-ZSM-5, and silicalite, it can be deduced that the different

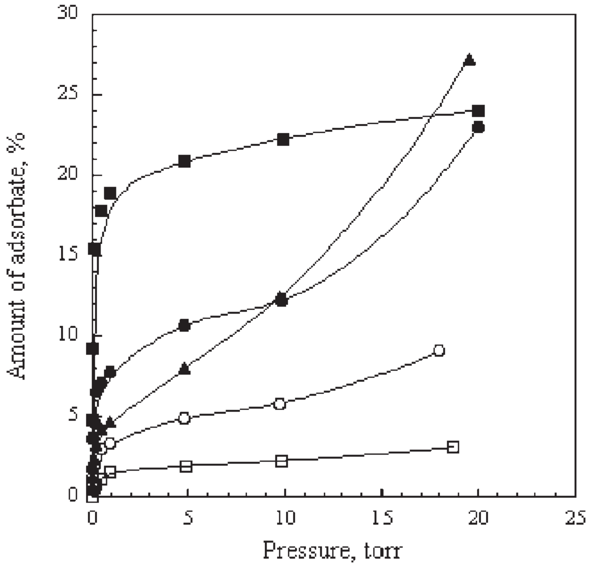

Figure 4. Adsorption isotherms at 25°C of water on H-Y (▲), 5A (■), H-Beta (●), ZSM5 (○), silicalite (□). Data on HY, H-ZSM5 and silicalite from Corbo et al., 2000.[12]

behavior of these zeolites is explained by their different pore openings. In fact, in Fig. 3, the curve depth of the various zeolites essentially increases in the order: H-ZSM5- and silicalite (channels dimensions: 5.3 × 5.6 Å and 5.1 × 5.5 Å), H-Beta (5.5 × 5.5 Å and 7.6 × 6.4 Å), and H-Y (7.4 Å), which is roughly the same order of the increasing pore opening.

Observe, however, that the shape of breakthrough curves and the extent of adsorption, depend also on the affinity of the zeolites for the different hydrocarbons present in the engine exhaust during the cold start. Since this parameter is connected to both chemical composition and structure of the zeolite, the evaluation of its effect on adsorption capacities, especially in real condition, is not immediate.

CONCLUSIONS

The following results have been obtained from the present investigation:

- Equilibrium runs indicate that both zeolite 5A and zeolite H-Beta are able to adsorb light hydrocarbons, such as ethane, ethylene, and butane;

moreover, H-Beta also shows a good affinity for isobutane and isobutene.

- Data fitting of adsorption isotherms indicates that the Langmuir equation is a good model for the rectangular curves, as it gives reliable values of adsorption capacity at saturation; on the contrary it is unable to give a reliable evaluation of adsorption capacity in the region of low pressure, which is possible using the virial equation.
- Dynamic runs with a real engine exhaust point out a reasonable performance of H-Beta in trapping a significant part of the hydrocarbon emission, likely the light fraction; the poor performance shown by zeolite 5A is connected to its preferential affinity for water vapor present in the exhaust.

On the whole, the possibility of use of zeolite H-Beta as a selective adsorbent of light hydrocarbon for reducing cold start emission is envisaged. Taking into consideration the previously collected data regarding the adsorption of aromatics,[12] it may be concluded that future experimental work should focus on the possibility to couple zeolite H-Beta with zeolite H-Y or zeolite H-ZSM5. This coupling might give the best performance in the attempt to adsorb all the variety of hydrocarbons emitted from engine during the start-up.

NOMENCLATURE

b	Langmuir constant (torr^{-1})
K	Henry's constant (torr^{-1})
k_a	Kinetic constant of adsorption ($\text{mol cm}^{-2}\,\text{sec}^{-1}\,\text{torr}^{-1}$)
k_d	Kinetic constant of desorption ($\text{mol cm}^{-2}\,\text{sec}^{-1}$)
p	Partial pressure (torr)
q, $q_{\max}$	Adsorbed amount relative to dry adsorbent, its maximum value (g/g)

Subscripts

L	Estimated from Langmuir equation
S	Estimated from the limiting slope of adsorption isotherms
V	Estimated from virial equation

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