Scientific
Research

# Adsorption of Light Hydrocarbons on LTA and FER Zeolites

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## ABSTRACT

This paper reports the results of an experimental study on adsorption of light hydrocarbons on small pore microporous materials. The choice of hydrocarbons studied was affected taking into consideration the application of adsorption processes in removal of light hydrocarbons from exhaust streams of the petrochemical industry and of light-duty gasoline vehicles under cold start conditions (C4 - C5 paraffins and olefins). The materials investigated were 5A and Ferrierite zeolites, characterized by different pore opening and Si/Al ratio. Equilibrium isotherm curves at room temperature were determined by a gravimetric method on dehydrated zeolites, while breakthrough curves in dynamic tests were used to evaluate the adsorption properties of hydrated zeolites at low hydrocarbon partial pressure (0 - 1 kPa) and in experimental conditions close to those of a HC trap at the engine exhaust. The experimental results regarding the adsorption capacities were discussed with the aim to understand how the physico-chemical characteristics of the adsorbent material could affect its trapping capability in adsorbing different types of hydrocarbons.

**Keywords:** Hydrocarbon Adsorption; Hydrocarbon Trap; Ferrierite; Linde 5A; Engine Cold Start Emissions

## 1. Introduction

The adsorption processes are widely employed for light hydrocarbons (HC) capture in applications that require the recovery of these compounds in high purity (petrochemical industry) [1,2] and have been recently proposed for the abatement of organic pollutants at the exhaust of light-duty gasoline vehicles under cold start conditions [3].

This last application is justified by the future legislative limits for passenger car emissions in EU and USA that will become more and more stringent and will require the development of new technological solutions, including more effective after-treatment devices. It is known that the largest fraction (more than 80%) of the total organic pollutants flows out during the short time following the engine startup (200 seconds). During this period the air/fuel ratio is on the rich side, which 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 between 60 to 120 s to be reached. This means that the compliance with the targets set by the incoming legislation will demand a strong

abatement of hydrocarbon emissions in the cold-start phase [4]. On the other hand, the incoming diffusion of hybrid vehicles increases the importance of the cold-start emissions control, since the number of start-up phases is more frequent in these types of vehicles with respect to conventional ones.

The combination of adsorption traps with catalytic conversion for HC emission control during the cold start phase of gasoline vehicles has been proposed in several patents [5]. These traps are constituted by a bed of adsorbent material which is 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. If the desorption temperature is lower than the light-off catalyst temperature, some hydrocarbons are not oxidized and escape from the tailpipe.

Differently from other commercial adsorbents with high surface area (activated carbons and clays, inorganic gels), zeolites, which are crystalline aluminosilicates, have pores of uniform and molecular size (3 - 10 Å), uniquely determined by the unit structure of the crystal. As a consequence these microporous materials have a high internal surface area (generally higher than 400 m²/g) available

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for adsorption due to channels that uniformly penetrate the entire volume of the solid [6].

This material, which exists in both natural and synthetic form, characterized by different pore opening and Si/Al ratio, has been the object of many studies related with HC trapping, since a particular zeolitic material 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 [7-11].

In this paper the adsorption of different HCs was studied taking into consideration those compounds which need to be recovered in petrochemical applications, and are present in significant concentration at the exhaust of light-duty gasoline vehicles, typically C4 - C5 paraffins and light olefins. Due to the small molecular size of HC considered, Ferrierite (FER) and 5A (LTA) zeolites, characterized by pore opening ranging from 3.5 to 5 Å [12, 13], were examined as adsorbent materials. The evaluation of adsorption properties was affected by equilibrium isotherms and dynamic tests in flow micro-reactor at room temperature.

## 2. Experimental

All adsorption measurements presented in this paper were performed on commercial zeolitic materials in powder form reported in **Table 1**. 5A and Ferrierite were studied in order to evaluate the effect of small pore channel structure on adsorption properties of small size HC molecules.

Adsorption isotherms at room temperature were acquired for ethane, ethylene, n-butane, isobutane and isobutene. They were obtained by a gravimetric technique, and performed with the apparatus sketched in **Figure 1**. 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) for 3 hours (Edwards Diffstak MK2 diffusion pump).

**Table 1. Zeolitic materials used for adsorption tests.**

| Sample | Form | Si/Al | Pore opening, Å |
|---|---|---|---|
| 5A (LTA) | Powder | 1 | 4.2[*] |
| Ferrierite (FER) | Powder | 10 | 4.2 × 5.4[**] <br> 3.5 × 4.8[**] |

[*]Ref. [12]; [**]Ref. [13].



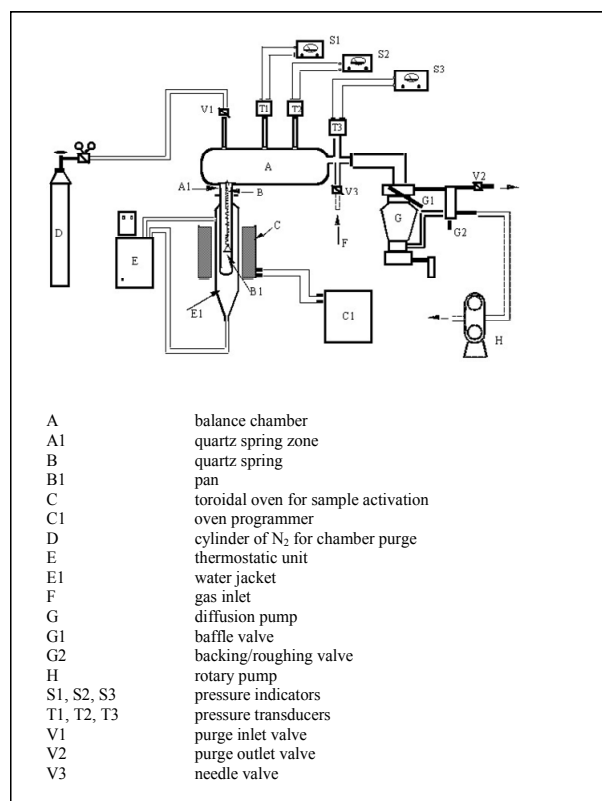| A | balance chamber |
|---|---|
| A1 | quartz spring zone |
| B | quartz spring |
| B1 | pan |
| C | toroidal oven for sample activation |
| C1 | oven programmer |
| D | cylinder of $N_2$ for chamber purge |
| E | thermostatic unit |
| E1 | water jacket |
| F | gas inlet |
| G | diffusion pump |
| G1 | baffle valve |
| G2 | backing/roughing valve |
| H | rotary pump |
| S1, S2, S3 | pressure indicators |
| T1, T2, 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.**

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.

Breakthrough curves were determined with the aim to obtain quantitative indications about the adsorption instantaneous capacities and equilibria values at low hydrocarbon partial pressures (0 - 1 kPa), usually encountered in engine exhaust gases, and to simulate the behavior of a HC trap working at the engine exhaust. Ethylene was selected as the olefin present in major concentration in exhaust gases of a gasoline engine, together with a mixture of C4 - C5 paraffins.

These adsorption tests 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 μm). The gas flow rate (1 l/min) was selected to realise a space velocity value (gas gravimetric flow rate/adsorbent weight) of 30000 $h^{-1}$, a value representative of the space velocities conditions occurring at the engine exhaust on
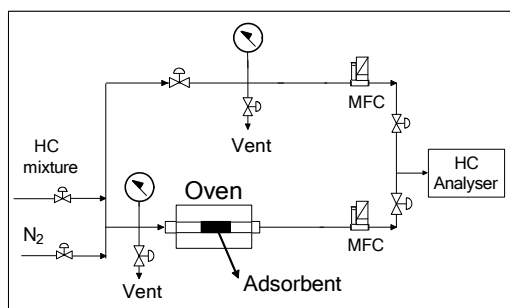
        

Figure 2. Scheme of the experimental apparatus used for measurements of breakthrough curves.

TWC during automotive start up phase. An on line analyzers equipped with flame ionisation detector (Siemens Fidamat 5 E-AP) was used for hydrocarbon concentration analysis before and after the adsorbent bed.

The breakthrough curves were constructed reporting the ratio of hydrocarbon concentration (expressed as C3 ppm) measured at the outlet of the adsorbent bed and the inlet mixture concentration as function of time on stream ($C/C_{in}$). Mixtures of hydrocarbons in nitrogen (850 ppm expressed as C3, corresponding to 0.1 kPa) were fed to the flow microreactor to verify the adsorption properties in experimental condition close to those that could be realized in a HC trap. Taking into account that the adsorption capacity of zeolites is due to a pore filling mechanism, the same concentration of C3 was used for all mixtures in order to realise comparable carbon mass flow rates in different molecular structures.

The adsorption of light paraffins by breakthrough curves was studied for an equimolar mixture of C4 - C5 paraffins (n-butane, i-butane, n-pentane, i-pentane, neo-pentane, total concentration of 850 ppm as C3). 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 intra-crystalline water content when it was exposed to hydrocarbon gas stream.

## 3. Results and Discussion

The experimental results of adsorption tests are reported in **Figures 3-6**, while the equilibrium adsorption capacities at 0.1 kPa and 298 K, expressed as mass of adsorbed HC per 100 g of zeolite, are summarized in **Table 2**. The zeolite 5A with pore opening of 4.2 Å (which allows for the passage of molecules with a kinetic diameter of less than 4.9 Å [12]) and Si/Al = 1 was firstly characterised in equilibrium adsorption gravimetric tests at room temperature with different C2 and C4 hydrocarbons. In **Figure 3** adsorption isotherms of ethylene, ethane, n-butane, isobutane and isobutene at 298 K on 5A are compared.

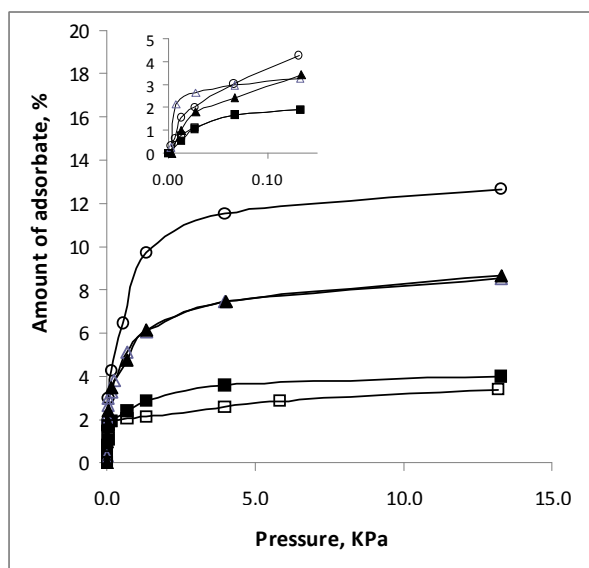A magnification of the low pressure zone (<0.15 kPa)



Figure 3. Adsorption isotherms at 298 K of n-butane (○), ethane (△), ethylene (▲), isobutane (□) and isobutene (■) on zeolite 5A.
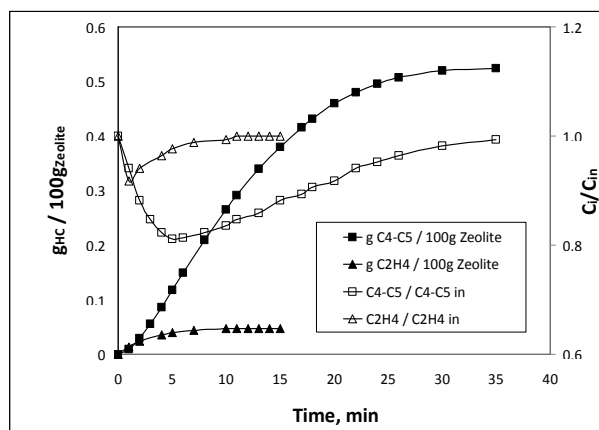


Figure 4. Breakthrough curves (empty symbols) and cumulative adsorption curves (full symbols) at 298 K for ethylene (▲, △) and C4 - C5 paraffin mixture (■, □) on 5A.

is reported on the top. All curves show the typical shape of the adsorption isotherms on microporous solids [14]. In these conditions 5A zeolite showed higher affinity for n-butane and C2 with respect to ramified C4 hydrocarbons, with no significant difference between ethane and ethylene. The saturation adsorption values resulted about 12% for n-butane, 8% for C2 and below 4% for ramified C4. The low adsorption capacity exhibited by zeolite 5A for isobutane and isobutene can be attributed to a molecular sieve effect. In fact, the molecular size of these hydrocarbons (5.5 - 5.6 Å) is larger than the pore opening of zeolite 5A (4.2 Å, see **Table 1**). In the hypothesis that adsorption of hydrocarbons on zeolites at 298 K is essentially due to physical interaction between gas molecule and solid surface (van der Waals interaction)
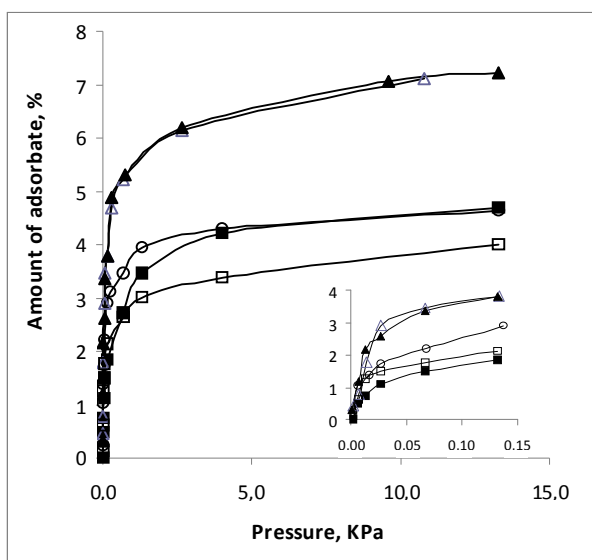
**Figure 5. Adsorption isotherms at 298 K of n-butane (○), ethane (△), ethylene (▲), isobutane (□) and isobutene (■) on Ferrierite.**
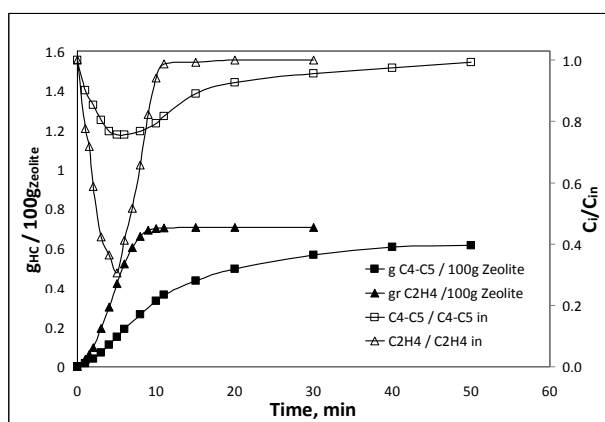


**Figure 6. Breakthrough curves (empty symbols) and cumulative adsorption curves (full symbols) at 298 K for ethylene (▲, △) and C4 - C5 paraffin mixture (■, □) on Ferrierite.**

**Table 2. Equilibrium adsorption capacities at 0.1 kPa and 298 K obtained by gravimetric tests (gt) and breakthrough curves (bc) for different HCs on 5A and Ferrierite, wt%.**

|  | 5A | | Ferrierite | |
|---|---|---|---|---|
|  | gt | bc | gt | bc |
| Ethane | 3.13 | - | 3.62 | - |
| Ethylene | 2.92 | 0.05 | 3.58 | 0.70 |
| n-Butane | 3.67 | - | 2.53 | - |
| Isobutane | 1.83 | - | 1.94 | - |
| Isobutene | 1.82 | - | 1.67 | - |
| C4 - C5 paraffins | - | 0.52 | - | 0.61 |

the absence in the molecule of any permanent dipole moment implies a weaker contribution of coulombic forces to the overall van der Waals interaction [14].

The predominance of this effect seems can explain the adsorption capacity exhibited by 5A for C2 hydrocarbons, while the higher adsorption capacity shown for n-butane can be explained observing that its molecular width (4.9 Å) is equal to the maximum value of the kinetic diameter allowed for the molecules to pass through the pores of 5A zeolite [12]. 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 [14].

The breakthrough curves were determined for ethylene and the C4 - C5 hydrocarbon mixture described in Experimental. The first hydrocarbon was selected as representative of light olefins at the engine exhaust, while a paraffin mixture was preferred in dynamic tests to individual compounds in order to verify the adsorption capacity of hydrated zeolites in conditions close to those of a real HC trap, in terms of space velocity, low partial pressure and simultaneous presence of different compounds.

**Figure 4** reports the breakthrough curves obtained for 5A zeolite at 298 K and 30000 h$^{-1}$, together the values of hydrocarbon cumulative adsorption, calculated as mass of adsorbed *HC* per 100 g of zeolite. The formula used for these calculations was the following:

$$\frac{g_{HC}}{100\,g_{\text{zeolite}}} = \sum_{i=1}^{n}\left[\left(C_{in} - C_i\right)\left(t_i - t_{i-1}\right)\right] Q\, M_{\text{C3H8}} 100$$

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 $t_i$, $Q$ is volumetric flow rate of the gas stream in nl/min, $M_{\text{C3H8}}$ is the molecular weight of propane.

The equilibrium adsorption capacity of 5A at 0.1 kPa and 298 K resulted scarce towards ethylene (0.05%, see also **Table 2**), and appreciable for C4 - C5 paraffins (0.52%). This selectivity towards paraffins can be attributed to the presence in the mixture of n-butane, as suggested by results of **Figure 3**. On the other hand, the adsorption values obtained by breakthrough curves resulted very lower with respect to gravimetric tests, in particular the adsorption of ethylene on 5A was almost two order of magnitude lower in dynamic tests (0.05% versus 2.92%). Taking into account that the zeolite micro-channels contained intra-crystalline water molecules during flow adsorption runs (see Experimental), these lower adsorption capacities can be attributed to the competition inside the zeolite micro-channels between intra-crystalline water and HC adsorbate.

The breakthrough curves of **Figure 4** show that the minimum HC concentration at the bed outlet was de-

      

tected after about 5 minutes for C4 - C5 paraffins (about 20% of trapping capacity), and only after 1 minute for ethylene (for a trapping capacity lower than 10%), while the relative bed saturations were reached after about 30 and 10 minutes.

A more interesting applicative result was obtained with Ferrierite zeolite, characterized by a pore opening < 5 Å and Si/Al ratio = 10. The isotherm curves are shown in **Figure 5** for C2 and C4 hydrocarbons. Microchannel size of Ferrierite determined higher affinity for C2 compounds than for C4. In fact, while the saturation adsorption values for C2 resulted similar to those obtained on 5A zeolite (about 7%), the value for n-butane was about three time lower (4.2%), and 3% - 4% for ramified C4. The lower capacity shown by Ferrierite for n-butane with respect to 5A can be explained invoking the effect of molecular sieving already discussed for ramified C4 on 5A.

The magnification of the low pressure zone (<0.2 kPa) reported in **Figure 5** (right bottom), together with the values of **Table 2**, evidences the higher affinity of Ferrierite towards C2 with respect to 5A (about 3.6% for both ethane and ethylene), while the behavior observed for C4 on Ferrierite at saturation was confirmed at low partial pressure.

The adsorption measurements in dynamic tests (**Figure 6**) showed high selectivity of Ferrierite for ethylene (0.70% adsorption capacity), while no significant difference for C4 adsorption was detected between Ferrierite and 5A (0.61% versus 0.52% in **Table 2**).

The best performance of Ferrierite towards ethylene was also confirmed by the high removal efficiency (about 70%) that can be realized after about 5 minutes of time on stream, to be compared with 8% of removal efficiency observed on 5A (**Figure 4**). The breakthrough curve obtained for C4 - C5 paraffins on Ferrierite reproduces the same profile observed on 5A zeolite. The comparison of the breakthrough profiles reported in **Figures 4** and **6** evidence a more favorable adsorption kinetic for ethylene with respect to paraffins mixtures on both zeolites investigated, which makes the small pore zeolites, and particularly the Ferrierite, attractive for the removal of light olefins by HC trap technology.

## 4. Conclusions

Adsorption properties of 5A and Ferrierite zeolites towards light paraffins and olefins have been investigated at 298 K by equilibrium isotherms obtained by gravimetric and by dynamic tests in flow microreactor.

The equilibrium isotherms have evidenced an elevated affinity of 5A towards n-butane, with a value of saturation adsorption higher than 12%. The adsorption of ethane and ethylene resulted was comparable on the two zeolites, with saturation values comprised between 7 and 8%. Regarding the ramified C4 hydrocarbons saturation, values of 3% - 4% were obtained on both zeolites. At a low partial pressure, some behavior differences were observed for C2 hydrocarbons, which were adsorbed in higher amounts on Ferrierite (about 20% more than 5A).

Adsorption capacities obtained with breakthrough curves resulted very lower than the maximum value reachable by gravimetric tests, due to the presence of intra-crystalline water in zeolite samples.

High selectivity for ethylene was observed on Ferrierite, with a removal efficiency of 70% reached after about 5 minutes of time on stream, while a removal efficiency of only 8% was observed for ethylene on 5A after 2 minutes of time on stream. In spite of this significant difference in removal capacity, both zeolites showed comparable adsorption kinetics. Taking into account the intervenetion times of a TWC catalysts during the start-up phase of gasoline engine (about 120 s), the above results suggest that both small pore zeolites investigated could be considered as suitable materials for light olefins removing by HC trap technology.

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