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SELECTIVE PHENOL ADSORPTION FROM HYDROCARBON FOR ULTRA-CLEAN BIOFUEL

*Karine Thomas**, *Ibrahim Khalil*, , *Francoise Maugé*

Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen Normandie, CNRS, 6, bd du Maréchal Juin, 14050 Caen, France

*E-mail: karine.thomas@ensicaen.fr

ABSTRACT

The purification of biofuels becomes a challenging issue because of the harmfulness of remaining phenolic molecules for human health and engines. To this end, protonic Y zeolites with different Si/Al ratios and mesoporous materials were explored as effective adsorbent materials to remove phenol from isooctane solution. Phenol was selectively removed from isooctane over HY and HUSY zeolites with a maximal adsorption capacity of 2.2 mmol.g⁻¹. The adsorption equilibrium was reached faster over dealuminated zeolites, due to the presence of large pores at the expense of microporosity as well as a low density of acidic sites. We further evidence that the presence of acid sites limits the regeneration capacity since phenol strongly adsorbed on both Brønsted and Lewis acid sites. The USY zeolite with the highest Si/Al ratio presents the best regeneration capacity because of its slower aluminum loading, although is not performing in presence of toluene. The solid gathering the best performances regarding both selective adsorption and regeneration is the HY2.9.

Keywords: Bio-Fuel, Phenol, Y zeolites, adsorption, FT-IR

INTRODUCTION

The fight against global warming and the increasing scarcity of oil resources are leading to a growing interest in renewable energies. In this respect, biofuels can substitute a fraction of fossil fuels without major modifications to current engines. However, the incorporation of products of plant origin introduces oxygenated impurities, mainly of the phenolic type [1,2], into the fuels to be disposed of. The study consists in studying, on different solids, the adsorption of phenol in a hydrocarbon mixture representative of a gasoline cut. The adsorption and regeneration capacities of three families of solids were compared: HY zeolites (HY2.5, HY2.9 and USY40), mesoporous silica, activated carbon and metal oxide (Al₂O₃).

EXPERIMENTAL

Na⁺Y zeolite with Si/Al ratio = 2.5 as well as both NH₄⁺Y zeolites with Si/Al ratio of 2.5 and 2.9 were supplied by Union Carbide. Ultra stable Y (USY) zeolites (over H⁺ and NH₄⁺ form) with various Si/Al ratios (22 – 40) were supplied by Zeolyst International. MCM-41 was prepared using the procedure of Grün *et al.*[3]. Amorphous silica (Aerosil 200, Degussa) was mixed with water and then calcined at 673 K before being used. The activated carbon, used as reference adsorbent, was provided by Norit. The gamma alumina and the amorphous silica-alumina (ASA) solid were supplied respectively by Sasol and Grace Davison. The textural properties of the adsorbents were characterized by N₂ adsorption isotherms at 77K using ASAP2020 from Micrometrics.

The quantification of hydroxyl groups as well as the characterization of the acidic sites was performed by infrared (IR) spectroscopy of pyridine adsorption. Adsorption experiments were

performed either in batch or in flow reactor with a mixture (phénol - isooctane). Phenol purchased from Aldrich (99.5% purity) was used as a model molecule for all the adsorption studies. Further the selective adsorption of phenol was studied by adding various concentrations of toluene (1% - 10% - 40 wt. %) to the initial mixture. Solids were pretreated at 623K for 4 hours under argon flow before performing the adsorption experiments at room temperature and atmospheric pressure.

In batch condition, 0,3 g of solid with a particle size between 200 and 400 μm was stirred into 20 mL of the hydrocarbon mixture. The flow adsorption tests were performed in a glass column (300 mm of high and 6 mm of internal diameter) with 0.5 g of adsorbent. The solution to purify was fed into the column using a Gilson pump allowing a constant flow rate of 1 $\text{ml}\cdot\text{min}^{-1}$. The capacity of the adsorbents to be re-used is tested by a new adsorption cycle performed after a thermal desorption at 473 K for 4 hours under Argon flow ($90 \text{ cc}\cdot\text{min}^{-1}$).

RESULTS AND DISCUSSION

The phenol adsorption ($7\text{g}\cdot\text{L}^{-1}$ in isooctane) was studied for different solids as faujasites (NaY2.5, HY2.5, HY2.9, USY 22, USY40), silica solid (MCM-41, Aerosil 200), ASA, Al_2O_3 and activated carbon (AC). Whatever the adsorbent, the adsorption phenomena is quick and the equilibrium state is reached in few minutes. Figure 1 gives the percentage of phenol adsorbed after 1 hour over the solids. The most efficient adsorbents are mesoporous silica and activated carbon since they present the highest percentage of adsorption at equilibrium (c.a 75-77 %). Both solids present high specific surface area and large total pore volume. However, these parameters are not the only responsible of their great capacity of adsorption. Indeed, for USY 40 that has both a high specific surface area and a high pore volume, the amount of adsorbed phenol (42%). is 1.8 times lower. To identify the parameters that drive adsorption, each adsorbent series has been considered separately.

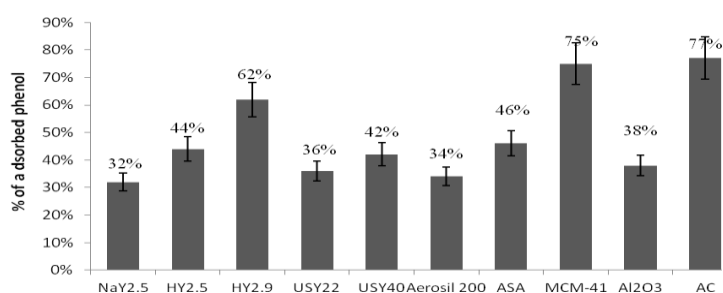


Figure 1: Percentage of phenol adsorbed in batch condition after 1 h of stirring

On activated carbon, that presents only micropores, the adsorption is due to capillary condensation of phenol inside the pores. On other solids, other adsorbents characteristics influence the adsorption phenomena.

For the siliceous-based solids (Aerosil 200, ASA, MCM-41) that do not present micropores, the percentage of adsorbed phenol increases with the specific surface area on which silanol groups are present. A linear relationship is obtained between the amount of adsorbed phenol and the amount of silanol groups measured by IR. Thus, the amount of silanol groups is one of the parameters to take into account.

For FAU series, the amount of adsorbed phenol under batch condition is quite similar (between 32 - 44 %), except for the HY2.9 zeolite (62%), although the Si/Al ratio is different. In a previous work [4] we have showed that micro and mesopores influences the amount of phenol adsorbed. Whatever the HFAU considered, a constant value of 3 phenol molecules were adsorbed per supercage. But phenol is also adsorbed on the silanol groups of the mesopores formed on the HFSY. As for NaY 2.5 its lower adsorption capacity compared to HY 2.5 zeolites while their microporous volumes are similar can be explained by the different size of the cations.

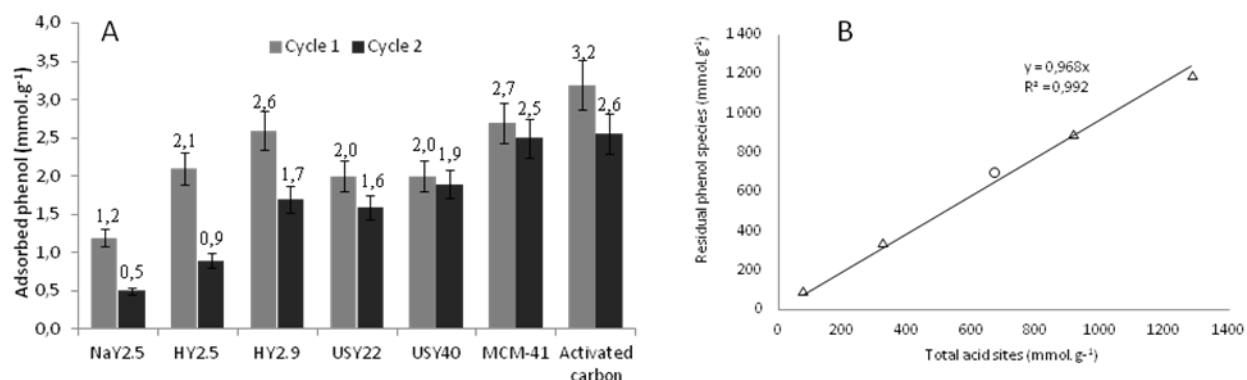


Figure 2: Amount of adsorbed phenol after 2 adsorption cycles performed in flow conditions (A); Residual phenol species in function of the total acid sites amount of studied zeolites (B).

Under flow adsorption (Figure 2A, cycle 1), trends are close to those measured in batch conditions., NaY2.5 presents the lowest adsorption capacity, the Si/Al ratio seems not to affect the adsorption capacity over HFAU (HY2.5, USY22 and USY40) and finally the more performing solids are HY2.9 zeolite, activated carbon and MCM-41 since they presents the highest retention volume. If the amount of adsorbed phenol is the only considered parameter the adsorption capacity over activated carbon is estimated at 3.2 mmol.g⁻¹. This value is higher than those obtained over the HY2.9 zeolite (2.6 mmol.g⁻¹) and MCM-41 (2.7 mmol.g⁻¹). This result is not surprising since activated carbon is known by its high surface area and its high capacity of desorption [17,20,28] due to the capillary condensation inside the pores.

Figure 2 (cycle 2 vs cycle 1) show that, over the studied zeolites, desorption capacity increases with the Si/Al ratio of zeolites. The amount of residual phenol (non desorbed phenol species) increases with the amount of acid sites quantified by IR (Figure 2B). The obtained slope is almost equal to 1, showing that one residual phenol molecule is strongly adsorbed over one acid site [4]. From these results one can conclude that Brønsted sites and Lewis acid sites (Al³⁺ or Na⁺ ions) are the main parameter that limits the regeneration capacity over the different zeolites.

The selectivity toward phenol adsorption was tested in different mixtures containing various amount of toluene (until 40wt.% which is representative of the amount of aromatic compounds present in biofuel). The more affected solids by toluene addition are NaY2.5 and activated carbon while the less affected solid are HY2.5 and HY 2.9. These behaviors can be explained by the differences in the modes of adsorption of the phenol molecule on the solids. The energy of phenol adsorption depends on its configuration of adsorption, and therefore the stability in presence of toluene. Toluene molecules can only be adsorbed by their aromatic cycle whereas phenol molecules can be adsorbed by the OH groups or the aromatic cycle.

CONCLUSION

In absence of toluene in the mixture, the most performing solids for phenol adsorption are HY2.9 zeolite, MCM-41 and activated carbon which present both high adsorption and regeneration capacities. The presence of toluene in high amount affects this order. In such conditions, the Y zeolites with high aluminum content (HY2.5 and HY2.9) as well as Al_2O_3 were the more selective toward phenol adsorption. In term of selectivity the best adsorbent must present a certain aluminum loading over which phenol molecules can be selectively adsorb by their OH groups. In term of regeneration we saw that the phenol is strongly adsorbed over the acid sites. Moreover, the fully crystalline zeolites (HY2.5 and NaY2.5) did not present high regeneration capacity due to the difficulty to remove adsorbed phenol molecules from a well microcrystalline network. To improve the regeneration, the zeolite structure should present a partial destruction to facilitate the access of phenol molecules during adsorption and desorption. For such reasons the HY2.9 zeolite has grouped a high adsorption capacity and selectivity as well as an acceptable regeneration.

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Table 1 – Chemical and textural properties of the studied adsorbents.

Adsorbents	Surface area (m ² .g ⁻¹)	Pore volume (cm ³ .g ⁻¹) ^e		
		total	micro	meso
NaY 2.5	1015 ^b	0.39	0.36	0.03
HY2.5	1063 ^b	0.39	0.36	0.03
HY2.9	897 ^b	0.39	0.30	0.09
USY22	932 ^b	0.51	0.31	0.20
USY33	928 ^b	0.47	0.28	0.19
USY40	937 ^b	0.52	0.31	0.21
SiO ₂	203 ^c	1.13	-	1.13
ASA	352 ^c	1.46	-	1.46
MCM-41	984 ^d	0.65 ^d	-	0.65 ^d
Al ₂ O ₃	326 ^c	0.78	-	0.78
Activated carbon	1076 ^c	0.61	0.54	0.07

[5] ^b Determined using Langmuir isotherm ; ^c Determined using BET nitrogen sorption;
^d Determined using α -plot ²⁵ ; ^e Determined using t-plot