Adsorption of Ethanol on hydrophobic zeolites

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Introduction

Volatile Organic Compounds (VOCs), released in many different industries [1], contribute to the depletion of the stratospheric ozone layer and the formation of photochemical smog, besides presenting harmful effects to human health. Among the different technologies for VOCs control, several advantages make adsorption a promising technology: it is suitable for streams with low VOCs concentrations, it is a non-destructive technique (therefore, recovery of valuable VOCs is possible), and it does not form by-products.

Activated carbons have been actively studied and used as VOCs adsorbents, displaying very-large adsorption capacities [2]. Nevertheless, they present some major disadvantages. Specifically, activated carbons are flammable and hydrophilic materials, and regeneration is often difficult. Zeolites have been studied as alternative adsorbents due to their high adsorption capacity, hydrophobic character, high thermal and hydrothermal stability, and an easy regeneration [3]. Several studies have been reported in literature dealing with this subject. However, most works evaluate the adsorption capacity using an "equilibrium approach" (e.g., adsorption isotherms). In this contribution we quantify and compare the adsorption of ethanol (as a model of polar VOC) on different hydrophobic zeolites using a "dynamic approach" (e.g., breakthrough curves), and determine the behavior of the regeneration using temperature-programmed desorption (TPD).

Materials and Methods

Commercial MFI and Y-type zeolites with large Si/Al ratios were selected for the study: silicalite (H-ZSM-5, SiO_2/Al_2O_3=280, surface area=400 m^2/g), and super-dealuminated USY (H-Y, SiO_2/Al_2O_3=80, surface area=780 m^2/g). Adsorption capacity was evaluated by using breakthrough curves. Basically, 200–500 mg of adsorbent (particle size, 180 - 250 µm) were placed in a quartz reactor and degassed by pretreatment with pure N_2 flow (450°C for 2 hr prior to the adsorption tests). An ethanol-laden N_2 stream (200-1000 ppm EtOH) was then passed through the fixed bed of adsorbent. Outlet concentration was continuously monitored by means of a GC and/or a FT-IR multicomponent gas analyzer. Once the saturation of the bed was attained (which is indicated by outlet concentration equal to the inlet concentration), ethanol was switched off and only pure N_2 was fed in order to purge the bed. Finally, the TPD was initiated (20-450°C at 5°C/min). Outlet concentration of ethanol (and other compounds that may be present) was recorded throughout the process. Adsorption capacity was determined from the breakthrough curve. Experiments were conducted at different W/F ratios and ethanol concentrations.

Results and Discussion

The steep shape of the breakthrough curves (not shown) suggests a favorable interaction between the sorbate and both adsorbents. Zeolite USY displays a larger sorption capacity than silicalite: 0.60 mmol/g and 0.48 mmol EtOH/g, respectively, which might be ascribed to the larger cell parameters of Y zeolites. TPD experiments were conducted to evaluate the regenerability of the adsorbent. Figure 1 shows the TPD profiles of ethanol adsorbed on silicalite and USY. TPD of silicalite features sharp, distinct peaks, whereas TPD on USY presents a broad, somewhat single peak. In addition, desorption from silicalite occurs in a lower temperature range than USY. Even though TPD data suggests the presence of different adsorption sites on silicalite, it may be concluded that physical interactions of ethanol with silicalite are rather weak. This could be explained by the smaller number of framework aluminum atoms in the silicalite, compared to the USY sample. Consequently, silicalite would be a more favorable adsorbent. However, TPD of silicalite also revealed the formation of species different from ethanol at relatively low temperatures (e.g., below 200°C). In fact, ethanol undergoes dehydration and decomposition on pure and promoted ZSM-5 catalysts [4]. Formation of such species may not be advantageous if VOCs recovery is important and/or the adsorbent bed is directly before a catalytic combustion bed. On the other hand, we have not yet found species other that ethanol in our TPD experiments on USY. Finally, preliminary results on the reuse of silicalite suggest that the adsorption capacity increases when the sample is reused. We are conducting further testing to assess and explain this behavior.

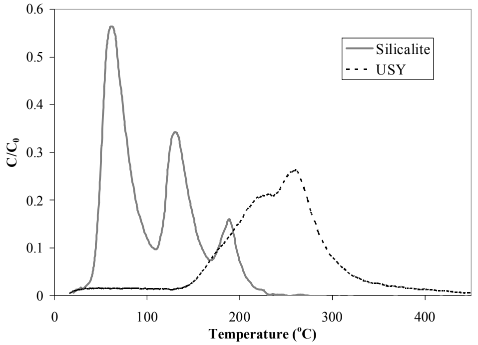

Figure 1. TPD of ethanol on silicalite and USY. TPD was conducted immediately after completing breakthrough tests. C_0= inlet concentration during the breakthrough test.

Significance

Both adsorption capacity (e.g., cell parameters) and regenerability (e.g., Si/Al ratio) should be considered in selecting a microporous adsorbent. In addition, breakthrough curves may provide engineering-relevant parameters for simulating and designing pilot-plant scale adsorbents. Our group is currently obtaining such parameters.

References

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