J|A|C|S
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Absolute Molecular Sieve Separation of Ethylene/Ethane Mixtures with Silver Zeolite A

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Supporting Information

ABSTRACT: Absolute ethylene/ethane separation is achieved by ethane exclusion on silver-exchanged zeolite A adsorbent. This molecular sieving type separation is attributed to the pore size of the adsorbent, which falls between ethylene and ethane kinetic diameters.

Ethylene is currently produced from hydrocracking of fossil fuels. The separation of ethylene from light hydrocarbons, including ethane, is performed by distillation, which is the most energy-demanding step in the whole production chain.[1,2]

Ethylene/ethane separation by adsorption on a solid adsorbent is an energy-efficient alternative. Adsorbents can be classified into two categories depending on separation mechanisms involved: (i) selective adsorption and (ii) molecular sieving. The first class of adsorbents, which is by far the most studied, relies on the preferential uptake of the olefin. Adsorbents for the separation of olefin from paraffin often include high surface area, porous materials (zeolites, carbons, resins clays) which have been treated with metal species, typically copper and silver, capable of π-complexation with olefins.[3−9] Among them, silver-exchanged faujasites (AgX, AgY) have been extensively studied.[3,5−11] On the other hand, the molecular sieving mechanism relies on the exclusion of one component based on size criteria.[12−14] The development of an adsorbent with molecular sieving property is a challenge for this application due to the small molecular diameter difference that exists between C_2H_4 and C_2H_6 (4.163 and 4.443 Å, respectively).[15]

An evolution in pore size control for crystalline molecular sieves began with the discovery of Engelhard Titanosilicate-4 (ETS-4).[16] The crystal lattice of ETS-4 systematically contracts upon dehydration at elevated temperatures. These structural changes can be used to control the lattice dimensions and the channel apertures of ETS-4 to "tune" the effective size of the pores. This phenomenon, known as the molecular gate effect, has achieved commercial success in natural gas purification.[17] For example, Sr-ETS-4 (CTS) adsorbents have been applied to difficult size-based separations including N_2/CH_4 (3.64 vs 3.76 Å, respectively) on an industrial scale.[17] Kuznicki and co-workers have exploited CTS adsorbents for the size exclusion of ethane.[18−20] However, the contraction process damages the ETS-4 framework and reduces the capacity of the adsorbent.[18,19] Hence, the control exerted on pore size fine-tuning of robust zeolites by cation exchange and/or thermal treatment is limited.[16]

Here we report the absolute separation of ethylene from ethane with a silver zeolite A (AgA). The results are compared with those obtained with silver faujasite zeolite (AgX). Although the adsorption of ethylene in silver-exchanged zeolite is well known, ethane/ethylene molecular sieving has not been reported. We show that the exceptional behavior of AgA arises from the combination of preferential adsorption of the olefin over the paraffin and the steric size exclusion of ethane.

Ion-exchange is performed by exposing the as-received commercial zeolite powders (5A and NaX) to an excess of silver nitrate aqueous solution (Supporting Information). For AgA, elemental analysis (ICP-OES) indicates an exchange yield of around 92%, with a remaining of 0.48% of Ca^{2+} cations (Supporting Information).

The isotherm data of the adsorption of ethylene and ethane on Ag zeolites AgA and AgX are presented in Figure 1.

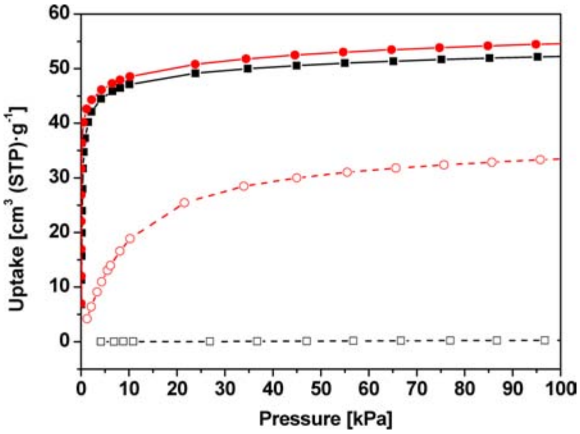

Figure 1. Adsorption isotherms of ethylene (closed symbols) and ethane (open symbols) measured by volumetric method on AgA (black squares) and AgX (red circles) at 303 K.

Clearly, ethane adsorption does not occur on AgA at the pressure ranges investigated, whereas the gas is adsorbed on AgX. In contrast, the adsorption of ethylene on the two silver-exchanged zeolites is quite similar. The adsorption capacity at 100 kPa reaches 2 mol/kg, which is among the highest values found for zeolite-based adsorbents and comparable to that of CuCl dispersed in NaX crystals.[7] Silver-ETS-10 reaches about 1 mol/kg at the same pressure range.[4,17,20] On the basis of

Received: June 11, 2012
Published: August 22, 2012

dx.doi.org/10.1021/ja305663k | J. Am. Chem. Soc. 2012, 134, 14635−14637

adsorption isotherms measured at different temperatures, we can estimate the enthalpy of ethylene adsorption to be $\Delta H_{303K} = -95$ kJ/mol, which corresponds to those of other Ag zeolites.[21] The loading of ethylene at low pressures is attributed to strong interactions between ethylene and silver clusters inside the zeolite.[22,23] The adsorption of ethylene takes place similarly in AgA and AgX. On the other hand, ethane can diffuse in AgX, whereas it cannot in AgA.

Based on respective uptake ratios at 10 kPa, the ethylene/ethane ideal selectivity is infinite for AgA and only 2.5 (50/20) for AgX. Reproducibility experiments were carried out to confirm the lack of ethane adsorption by AgA. Consecutive single adsorption−desorption isotherms of ethylene and ethane were performed without removal of sample from the measurement cell and with no additional thermal pretreatment between measurements. These cycling tests show no changes in the ethylene adsorption capacity of AgA and, more importantly, confirm the absence of ethane adsorption (Supporting Information).

The outstanding adsorption properties of AgA are confirmed with breakthrough experiments carried out on an ethane/ethylene mixture. Figure 2 shows the breakthrough curves of a mixture of ethylene/ethane/nitrogen (10:10:80) through a column filled with 0.9 g of AgA at 303 K and 1 atm. After the first seconds, ethane breaks through the AgA column. The exclusion of ethane in the AgA column is consistent with the absence of adsorption of ethane observed in volumetric measurements. During the first 15 min, the adsorbent retains ethylene and the outlet stream contains pure ethane. After 25 min, the concentration of the outlet gas reflects the feed gas composition, indicating the saturation of AgA. By integration, the amount of ethylene adsorbed was found to be 57 cm^3/g, which is in agreement with volumetric measurements.

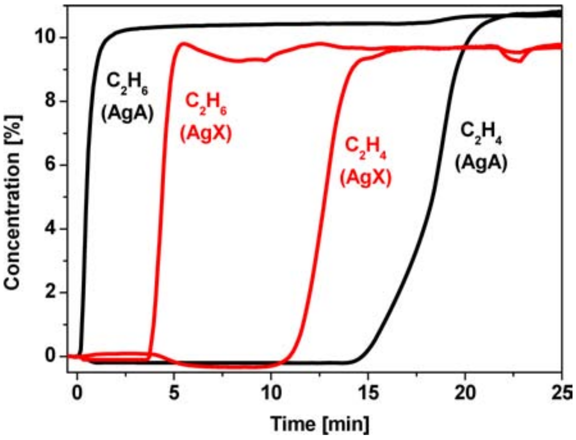

Figure 2. Breakthrough curves of an ethane and ethylene mixture in nitrogen (10:10:80 kPa), 25 mL (STP)/min at 303 K on 0.9 g of AgA (black lines) and AgX (red lines) zeolite.

From separation results on AgX in breakthrough experiments, we can observe that ethane and ethylene are adsorbed simultaneously in the first minutes, in contrast to AgA (Figure 2). Ethane breaks through the column after 4 min. This is consistent with single gas isotherm measurements (Figure 1). It results in lower ethylene/ethane selectivity with respect to AgA. We can also observe for AgX that ethylene breaks through earlier than for AgA (Figure 2). The lower ethylene capacity for AgX in mixture conditions is due to the co-adsorption of ethane.

Hence, the ethane exclusion observed for AgA in mixture condition results in the enhancement of both ethylene selectivity and capacity with respect to AgX.

The molecular sieving mechanism, e.g., size exclusion of ethane, was investigated by powder X-ray diffraction and Ar adsorption on the starting zeolite 5A and silver-exchanged AgA.[24,25] Note that, similarly to AgX and in contrast to AgA, ethane and ethylene are adsorbed on zeolite 5A (Supporting Information). Rietveld refinement performed on powder X-ray diffractograms of both AgA and 5A solids provides free diameters of the channel apertures, 4.24 and 4.84 Å for zeolite 5A, and 4.35 and 4.36 Å for zeolite AgA (Supporting Information).

The free diameter data for AgA are clearly larger than the kinetic diameter of ethylene (4.163 Å) and smaller than that of ethane (4.443 Å). As a consequence, ethylene can penetrate in the porous structure of AgA, whereas ethane is excluded, in perfect agreement with adsorption and separation observations. Furthermore, ethane and ethylene can both diffuse into the porous structure of zeolite 5A since their kinetic diameters are smaller than the free diameters measured for zeolite 5A. The smaller pore size for AgA with respect to 5A has been confirmed by Ar adsorption isotherms at 77 K, which shows a decrease of approximately 0.6 Å in the mean diameter. Although silver exchanged on zeolite 5A results in a slight decrease of free diameter, it can account for the observed cutoff between ethylene and ethane.

We have shown for the first time that absolute ethylene/ethane separation is achieved by ethane exclusion on silver-exchanged zeolite A adsorbent. This molecular sieving type of separation is attributed to the pore size of the adsorbent, which falls between the kinetic diameters of ethylene and ethane. In terms of separation, it results in 100% ethylene selectivity and maximum ethylene capacity with respect to total adsorption capacity. The AgA adsorbent can be applied in VSA/TSA-type processes similarly to AgX.[26,27] We believe that AgA could be a valuable adsorbent for the capture of ethylene from streams involved in the oxidative coupling of methane where diluted ethane/ethylene mixtures are present.[28] A technico-economic assessment of the process will be reported elsewhere.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Material preparation, elementary analysis, single adsorption measurements, and breakthrough experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors appreciate scientific services of IRCELYON. This paper reports work undertaken in the context of the project “OCMOL, Oxidative Coupling of Methane followed by Oligomerization to Liquids”. OCMOL is a Large Scale Collaborative Project supported by the European Commission in the 7th Framework Programme (GA no. 228953). For further information about OCMOL see http://www.ocmol.eu.

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