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Propane/Propene Separation by SBA-15 and π-Complexated Ag-SBA-15

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Abstract. Synthesis, characterization and adsorption properties of propane/propylene on mesoporous SBA-15 are reported. This material was also used as high surface area material for silver deposition to enhance propylene adsorption improving selectivity towards the olefin. Two different silver loadings were tested: $Ag/SiO_2 = 0.5$ and $Ag/SiO_2 = 1.0$. With the lower silver content, better selectivity and amount adsorbed was obtained. Preliminary studies were done for the use of this adsorbent in Vacuum-Pressure Swing Adsorption (VSA-PSA) units. With a four-step cycle comprising feed, pressurization, rinse and blowdown recovery of 97% propylene with chemical grade purity (91%) was obtained and also fuel grade HD-5 propane at high pressure. If higher propylene purity is required, a five-step cycle has to be used (pressurization, feed, rinse, co-current depressurization to intermediate pressure and counter-current blowdown). In this case, purity of 99% was obtained with 63% recovery.

Keywords: SBA-15, π-complexation, propylene, adsorption, Pressure Swing Adsorption

1. Introduction

Splitting of propane/propylene is a very difficult separation actually practiced by cryogenic distillation with columns containing over 150 trays. Alternative processes such as Pressure Swing Adsorption (PSA) are interesting to reduce energetic costs. In this process, the difficulty to overcome is that propylene is the most adsorbed compound and has to be recovered at low pressure, requiring a very selective adsorbent.

Commercial adsorbents such as zeolites 4A, 5A, 13X, silica gel and carbon molecular sieves were tested for this system (Da Silva and Rodrigues, 1999; Yang, 2003; Grande et al., 2003). Only zeolite 4A has good selectivity towards propylene. For this reason, specific materials are being developed for this separation. One of the research line with higher impact was the one followed by professor Ralph T. Yang using transition metal ions to form a π-bond with the olefin that is weak enough to be broken by a change of pressure like in PSA units (Yang, 2003).

SBA-15 is a mesoporous silica already tested for propane/propylene separation with low selectivity towards propylene (Choudary et al., 2003). This material has a very large surface area and large macropores with interconnecting microporosity that can be changed by simple modifications in the preparation protocols.

In this work we have prepared a sample of SBA-15, characterize it and measure pure propane and propylene adsorption equilibrium and kinetics. To improve

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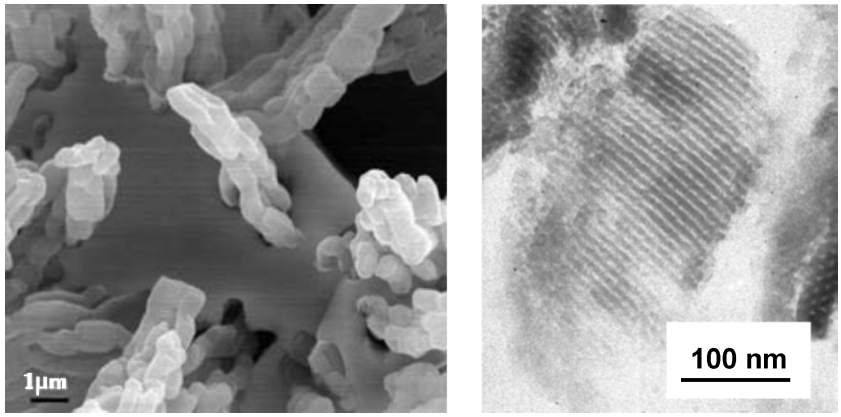

Figure 1. SEM micrograph of Ag/Si = 1.0 showing cylindrical crystals of silver-modified SBA-15 and TEM image of Ag/Si = 0.5 showing no modification of the ordered structure of SBA-15 after silver impregnation.

the selectivity of the mesoporous material, we have dispersed silver ions in two different loading ratios: $Ag/SiO_2 = 0.5$ and $Ag/SiO_2 = 1.0$. Samples were also characterized and tested for propane and propylene adsorption. The material with higher selectivity for propylene was used in PSA simulations for propylene purification.

2. Materials

SBA-15 has been prepared using tetraethyl orthosilicate (TEOS) and $EO_{20}PO_{70}EO_{20}$ as the structure–directing agent (Zhao et al., 1998). Metal dispersed samples were prepared by impregnation of SBA-15 with silver nitrate, followed by drying and calcination at 383 K for 24 h. Characterization of the materials was done by SEM, XRD, EDAX, TEM and nitrogen adsorption at 77 K.

After preparation of the materials XRD analyses of the samples were measured. The XRD patterns shown the low angle peaks corresponding to SBA-15 mesoporous ordered material and also metallic silver was not detected. In the $Ag/SiO_2 = 1.0$ sample reflections corresponding to silver nitrate were observed while these reflections were very weak in the $Ag/SiO_2 = 0.5$ sample. To confirm the ordered structure of the SBA-15 material, TEM images were recorded. Images were also recorded in the silver-modified samples to verify that ordered structure was not damaged with the impregnation. Also, SEM images were taken to determine the size of the crystals to be used in kinetic measurements. The crystal structure also was not altered by the impregnation, although some traces containing higher amounts of ionic silver were found in the $Ag/SiO_2 = 1.0$ sample. As all the images are similar, we show in Fig. 1 a SEM image of the $Ag/SiO_2 = 1.0$ showing the crystals of modified SBA-15 with some segregated silver in ionic form and a TEM image of the $Ag/SiO_2 = 0.5$ sample where is shown that the ordered structure of SBA-15 was not altered. From the SEM images cylindrical crystals with 0.4 μm diameter were observed. EDAX and nitrogen adsorption analyses revealed that Ag/Si ratio and superficial area was 0.54 w/w and 594 m^2/g in the $Ag/SiO_2 = 0.5$ and 1.09 w/w with 297 m^2/g in the $Ag/SiO_2 = 1.0$ sample. Superficial area of the pure SBA-15 was 996 m^2/g.

The characterization of the materials showed a good silver dispersion with no detectable metallic silver, even after propane and propylene adsorption experiments. As shown in Fig. 1, the Ag/Si = 1.0 sample showed some aggregates with ionic silver with amorphous shape and a small amount of silica detected by EDAX.

3. Adsorption Equilibrium and Kinetics of Pure Gases

Adsorption equilibrium and kinetics of pure propane and propylene on these three materials was already reported (Grande et al., 2004). In the analysis of adsorption equilibrium, we have to consider a model that takes account of physical adsorption and also the enhanced adsorption due to chemisorption. In this work, the Toth model was used to describe physical adsorption while π-complexation was described with a

Langmuir model assuming adsorption sites with uniform energy distribution (Yang and Kikkinides, 1995). The complete model is:

$$q = \frac{q_m K P}{[1 + (K P)^n]^{1/n}} + \frac{q_{mc}}{2s} \ln \left[\frac{1 + b_c P e^s}{1 + b_c P e^{-s}} \right] \quad (1)$$

where K is the physical adsorption constant, q_m and q_{mc} are the maximum adsorbed phase concentrations of physical adsorption and chemisorption, respectively, b_c is the chemisorption constant and s is the spread of energy distribution. Both adsorption constants have exponential dependence of temperature described by:

$$K = K^o \exp\left(\frac{-\Delta H}{RT}\right)$$
$$b_c = b_c^o \exp\left(\frac{\Psi}{RT}\right) \quad (2)$$

where K^o and b_c^o are the infinite adsorption constants, $(-\Delta H)$ is the enthalpy of adsorption and Ψ is the mean variance of the uniform energy distribution (Yang and Kikkinides, 1995).

The physical adsorption on the silica surface was assumed to be the same for propane and propylene and thus the adsorption equilibrium of the binary mixture is described by:

$$q_i = \frac{q_{mi} K_i P y_i}{\left[1 + \sum (K_i P y_i)^{n_i}\right]^{1/n_i}} + \frac{q_{mc}}{2s} \ln \left(\frac{1 + b_c P e^s}{1 + b_c P e^{-s}} \right) \Bigg|_{C_3H_6} \quad (3)$$

The parameters used for the fitting of Eq. (1) to pure component data are shown in Table 1.

As an example of adsorption equilibrium of propane and propylene on these materials, we show in Fig. 2 the isotherms measured at 343 K in the three materials. The propylene adsorption on the impregnated materials is more important at lower pressures but not very much near atmospheric pressures. Although, is clear the diminution in the amount of propane adsorbed in the silver-modified samples improving the selectivity of these materials towards the olefin. As the amount of propylene adsorbed on the Ag/SBA-15 = 0.5 sample is higher than on the other sample and the propane amounts are comparable, the selectivity of the Ag/SBA-15 = 0.5 material is higher and would be preferably used for further studies. The adsorption of

Table 1. Adsorption equilibrium parameters of propane and propylene on SBA-15 and Ag-SBA-15 samples.

Adsorbent	Gas	q_m (mmol/g)	K^o (1/kPa)	ΔH (kJ/mol)	n (−)	q_{mc} (mmol/g)	b_c^o (1/kPa)	Ψ (kJ/mol)	s (−)
SBA-15	C_3H_6	2.041	$3.55 \cdot 10^{-6}$	−24.240	0.87	–	–	–	–
	C_3H_8	2.062	$3.55 \cdot 10^{-6}$	23.885	0.91	–	–	–	–
Ag/Si = 0.5	C_3H_8	0.221	$1.04 \cdot 10^{-6}$	−34.028	0.53	–	-	–	–
	C_3H_6	0.221	$1.04 \cdot 10^{-6}$	−34.028	0.53	1.870	2.0×10^{-14}	−78.352	3.58; 5.52; 6.91
Ag/Si = 1.0	C_3H_8	0.189	$1.04 \cdot 10^{-6}$	−36.866	0.36	–	–	–	–
	C_3H_6	0.189	$1.04 \cdot 10^{-6}$	−36.866	0.36	1.475	2.0×10^{-14}	−75.893	2.66; 4.84; 6.45

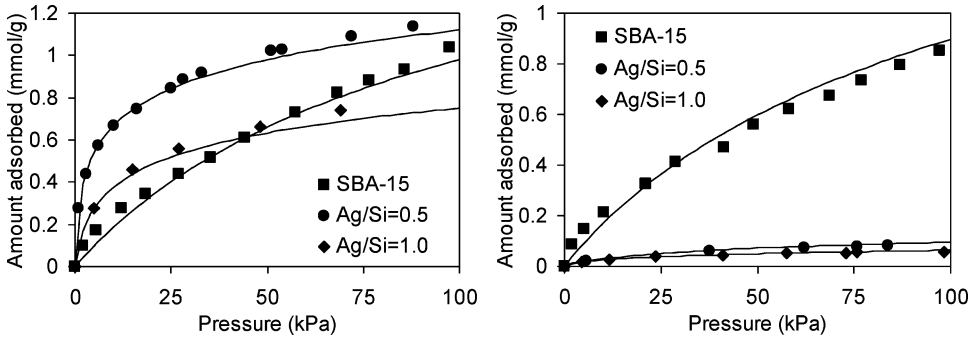

Figure 2. Adsorption equilibrium of propylene (a) and propane (b) on SBA/15, Ag/Si = 0.5 and Ag/Si = 1.0 samples at 343 K.

propylene on this sample is comparable with previous report using silver-exchanged SBA-15 with Ag/Si = 0.4 although the amount of propane adsorbed in our samples is much smaller resulting in a more selective material (Choudary et al., 2003). The selectivity to propylene was reported to increase by complexation with silver in other reports using different adsorbent structures like silica, alumina and zeolites (Yang, 2003).

Propane and propylene adsorption kinetics in the same temperature range (323, 343 and 373 K) was studied in a previous report by means of diluted breakthrough curves; 1.1% of pure hydrocarbon diluted in helium and at atmospheric pressure (Grande et al., 2004). In the three samples, breakthrough curves were controlled by Knudsen diffusion. In the fitting of these curves, pore diffusivities were calculated with the pore values measured from TEM measurements. The important result of these curves is that no additional resistance was observed after impregnation of the samples and diffusion of both hydrocarbons is very fast even in the impregnated materials. Propylene also exhibited a self-sharpening of the concentration wave due to the strongly non-linearity of the adsorption isotherms, even at this very low concentration.

4. Pressure Swing Adsorption Simulations

The final application of these materials is a process for propane and propylene separation. One process with good industrial knowledge background is Pressure Swing Adsorption (PSA). As propylene is very strongly adsorbed under atmospheric pressures will be required and in this cases these units are termed Vacuum Pressure Swing Adsorption (VSA-PSA).

The use of these materials into a VSA-PSA unit requires a final shape into pellets because powder adsorbents will produce very large pressure drop into the column that is not desired. It was reported in literature that even when the pore walls of SBA-15 are thicker than the MCM materials, the resistance to pressure is higher in the MCM materials. Even though, in the case of pure SBA-15, a compression of 52 MPa only produced a loss of area of 10% (Hartmann and Vinu, 2002). If the diffusion of both hydrocarbons remains high, the equilibration will be very fast and main diffusion limitations will be produced by the macropores formed in the compacting procedure. Another alternative are new techniques of SBA-15 crystal growing over solid surfaces of an inert matrix, which may be developed in the near future.

A LDF model was used to simplify the description of the diffusion process. The entire model (component mass balances, energy balances over the solid, gas phase and wall of the column and Ergun equation) was previously published elsewhere (Da Silva, 1999). Purity, recovery and productivity were calculated using definitions from elsewhere (Rota and Wankat, 1990).

A cycle with four steps was initially tested. The steps are: 1. Pressurization up to the final pressure of 250 kPa, 2. Feed at constant pressure where propane is recovered at the top of the column, 3. Rinse with pure propylene to improve product purity, 4. Countercurrent blowdown at 10 kPa where propylene product is retired from the system and adsorbent is partially reconditioned for a new cycle. The temperature chosen for simulations was 343 K as an example temperature. A bed of 1 m $\times$ 0.0210 m was used. Flowrates of feed and purge was 1.50 SLPM (standard liters per minute) and 0.75 SLPM for the rinse step. Feed and pressurization is done with an equimolar stream of propylene and propane. Adsorbent properties (density and thermal parameters) were calculated as 80% of silica and 20% alumina (as binder).

In Table 2 we present some results obtained for propane-propylene separation by VSA-PSA. To describe more in detail a simulation, we chosen run 1. In Fig. 3, propylene concentration (a) and temperature (b) at the end of each step when cyclic steady state (CSS) was reached is plotted. In the entire cycle temperature has oscillations of around 20 K degrees. The length of mass transfer is limited by axial dispersion and by temperature effects. Molar flowrate at the outlet of the column is shown in Fig. 4. In this figure, is noted that propane leaving the column in the feed and rinse step has a very small concentration of propylene (less than 2%) which means that it can be considered as fuel

Table 2. VSA-PSA purity and recovery for different cycle conditions.

Run	P_{low} (kPa)	t_{pres} (s)	t_{feed} (s)	t_{rinse} (s)	t_{blow} (s)	Purity (%)	Recovery (%)
1	0.05	50	60	40	140	90.9	97.8
2	0.10	50	60	40	140	91.0	92.6
3	0.15	50	60	40	140	91.2	74.7
4	0.10	50	70	40	140	92.2	81.8
5	0.10	50	60	50	140	94.2	85.1

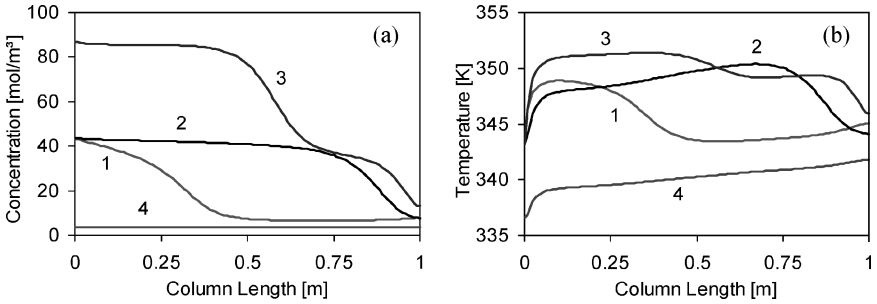

Figure 3. VSA-PSA simulation (run 1). (a) propylene concentration and (b) temperature at the end of each step in cyclic steady state: 1.pressurization (50 s); 2. feed (60 s); rinse (40 s); counter-current blowdown (140 s).

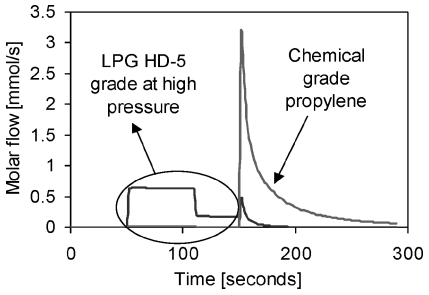

Figure 4. Molar flowrate of propane and propylene from run 1. LPG HD-5 propane flowrate in the feed and rinse step is circled and chemical grade propylene is indicated from the blowdown step.

grade HD-5 propane (EPA, 1995). This propane is at higher pressure requiring less effort for compression into LPG (liquefied petroleum gas) cylinders. On the other side, in the blowdown step, propylene with purity over 91% is obtained reaching only chemical grade propylene. Even though, to obtain these products, a low value of the blowdown pressure was used. A higher value previously used for this separation shows lower recovery and propane contamination with propylene is unacceptable for fuel grade propane (>5%).

If the objective is to obtain polymer grade propylene an additional step (intermediate blowdown or co-current depressurization to intermediate pressure) has to be included between the rinse step and the counter-current blowdown. Purity of 99% was obtained with this cycle configuration (step times like in run 1 with a depressurization to intermediate pressure of 50 kPa for 20 seconds) but recovery falls to 63%, although the outlet of this new step has almost the same composition of the feed and can be recycled to increase recovery, although this scheme was not yet studied. Also, propane contamination with propylene is higher than 5% and thus requiring additional purification for fuel grade.

5. Conclusions

Mesoporous material SBA-15 was successfully prepared and impregnated with two different loadings of silver. The sample having the ratio Ag/SBA-15 = 0.5 has a very large selectivity toward propylene in the temperature range of 323–373 K. This sample was used for simulating VSA-PSA (Vacuum Pressure Swing Adsorption) unit operation at 343 K. With a four-step cycle comprising feed, pressurization, rinse and blowdown recovery of 97% propylene with chemical grade purity (91%) was obtained and also fuel grade HD-5 propane at high pressure. If higher propylene purity is required, a five-step cycle has to be used (pressurization, feed, rinse, co-current depressurization to intermediate pressure and counter-current blowdown). In this case, purity of 99% was obtained with 63% recovery.

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