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Propane/propylene separation by selective olefin adsorption on Cu/SBA-15 mesoporous silica

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Abstract Samples of mesoporous silica, SBA-15, were prepared under hydrothermal conditions and Cu cations were incorporated into the framework by two different impregnation techniques. The corresponding adsorption/desorption isotherms of propylene, propane, and N_2 were measured to evaluate the material's effectiveness in the separation of propane/propylene mixtures.

Adsorption uptake of propylene increased and that of propane decreased in Cu containing samples as compared to the uptakes observed in undoped SBA-15 samples. It was demonstrated that the presence of Cu atoms in the adsorbent lattice led to a greater selectivity towards propylene. Furthermore, the highest level of Cu(I) were obtained in samples prepared by equilibrium impregnation, which in turn improved the olefin/paraffin uptake ratio. Under some working conditions, the amount of propylene adsorbed in selected samples is totally reversible while propane uptake was negligible.

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Introduction

Recently, Newalkar et al. [1] investigated the adsorption properties of SBA-15 to evaluate its potential for the separation of commercially important light hydrocarbons. They showed that the SBA-15 framework possesses a higher affinity for alkenes than for the corresponding alkanes. Despite the fact that no metal cations are present in this structure, the authors noted that this behavior was in line with those observed on π -complexation systems [2]. In addition, previous studies performed in our laboratories demonstrated that SBA-15 mesoporous silica containing transition-metal cations can be used as an effective adsorbent for propylene/propane separation [3, 4]. It was proved that the presence of Cu or Ag in the adsorbent lattice led to a greater selectivity towards propylene. Although the Cu-containing samples showed a higher capacity for propylene, the methodology used for Cu incorporation was not studied in detail. These adsorbents usually consisted of an active component dispersed on a support via impregnation, with a high specific surface area. On these basis of these reports, the present work studies the effect of impregnation methodology on the nature of Cu species on SBA-15 type materials and consequently on the olefin/paraffin adsorption properties. The samples were characterized by XRD, TPR, SEM, TEM, XPS and N2 adsorption (77 K).

Experimental

SBA-15 was prepared according to [3], using tetraethyl orthosilicate (TEOS; Aldrich) and poly(ethylene glycol)-

block-poly(propylene glycol)-block-poly(ethylene glycol), $H(-OCH_2CH_2)_x[-OCHCH_3CH_2-]_v(-OCH_2CH_2-)_zOH$ (average $M_w = 5800$, Aldrich) as the organic structure-directing agent. A gel having the required composition was stirred overnight at 35°C and submitted to hydrothermal conditions at 80°C for 16 h. The resulting solid phase was filtered, washed, dried at 110°C, and calcined at 590°C in air for 6 h. The Cu/mesoporous silica samples were prepared as follows: samples 5089-2 and 5089-1 were obtained by incipient wetness impregnation, while sample 5089-4 was obtained by equilibrium impregnation in a 6-fold volume excess of impregnating solution. To improve the dissolution of the cuprous salt and to prevent oxidation of the Cu⁺ cations, in the case of the 5089-1 and 5089-4 samples, the impregnation was conducted using an acidic solution containing HCl and NaHSO₃. After the Cu incorporation, the samples were dried at 100°C overnight. All samples were characterized by XRD, TEM, SEM, XPS and N₂ adsorption (77 K) methods. XRD patterns were recorded with a Philips APD 1700 diffractometer, using CuK α radiation, at 40 kV, 30 mA, 0.02° step size and 1 s step time. The size and morphology of solid particles were observed by scanning electron microscopy (SEM) using a Philips 505 microscope. TEM analysis was carried out with a JEOL 100 CXII, using an acceleration voltage of 100 kV and a clear field observation technique. XPS spectra were obtained with a Physical Electronics PHI5700 instrument. To avoid Cu(II) to Cu(I) photo-reduction, Cu2p signal analysis was done using an irradiation time less than 600 s.

The equilibrium adsorption isotherms of propylene, propane, and N₂ were measured in a conventional highvacuum volumetric device, totally made of Pyrex glass and equipped with grease-free valves. The high vacuum $(<10^{-4}$ Torr) was achieved with a turbo molecular pump (TSH 062, Balzers), and pressures were recorded with two types of pressure transducers (Balzers) over different ranges: TPR 017 (10^{-4} –5 Torr) and APR 011 (1–1000 Torr). Before equilibrium measurements, the samples were activated in situ at 350°C in an oven to a residual pressure of $<6 \times$ 10^{-4} Torr and kept for 3 h under these conditions. After sample dehydration, the temperature was decreased to the desired value and the sample was allowed to stabilize for at least 1.5 h before beginning the measurements. Adsorbed amounts (mmol/g) of gases were normalized to 1 g of dehydrated adsorbent. The weight losses of the adsorbents were previously evaluated by heating the samples to 300°C at atmospheric pressure in a conventional oven. All the gases used in this study were UHP grade (purity >99.99%).

Prior to the study of C_3H_6 and C_3H_8 adsorption, N_2 adsorption-desorption isotherms were determined at 77 K to evaluate the surface area and pore size distribution of the samples and, therefore, to estimate the influence of the treatment with CuCl solution on the adsorption properties

of the SBA-15 sample. To establish the accuracy and reproducibility of the volumetric system, all the measurements were repeated twice.

Results and discussion

Characterization of samples

The XRD pattern (range $0.5 < 2\theta < 4$) of the undoped SBA-15 precursor (Fig. 1) showed a peak at $2\theta = 0.94^{\circ}$, corresponding to the (100) reflection and two weak reflections at about 1.6 and 1.7°. These results are in agreement with patterns previously reported for this mesostructure [3]. Additionally, the XRD patterns (range $10 < 2\theta < 60^{\circ}$ of Cu-containing samples 5089-2, 5089-1 and 5089-4 are depicted in Fig. 2. Reflections corresponding to the cuprous salt used for impregnation were not observed. The three samples showed reflections corresponding to different hydroxylated chloride compounds containing Cu⁺⁺ cations (CuCl₂·3Cu(OH)₂; Cu₂(OH)₃Cl). Increased peak intensities were observed for sample 5089-4, which was prepared by equilibrium impregnation.

Figure 3 shows SEM and TEM micrographs of the undoped SBA-15 sample. It can be seen that the morphology is similar to that previously reported for SBA-15 type materials [3]. Furthermore, from this analysis, an approximate spacing of 8 nm can be estimated.

The influence of the methodology used for Cu incorporation on the valence state of Cu^+ ions was investigated by XPS. The patterns for 5089-1 and 5089-4 samples are shown in Fig. 4, and the results are presented in Table 1. As can be seen, the Cu(I)/Cu(II) ratio and the total Cu percentage are clearly increased in sample 5089-4 prepared by equilibrium impregnation.

Nitrogen adsorption/desorption isotherms at 77 K for the samples showed a H1 hysteresis loop, which is typical of





Table 1XPS analyses ofdoped samples

Cu 2p _{3/2} sig	gnal and Cu(I) y Cu	(II) percentages				
Sample	Cu 2p _{3/2} (eV)	I Cu 2p _{3/2} /I satelite	Cu(I) (%)	Cu(II) (%)		
5089-1	933.2 (935.2)	1.93	48	52		
5089-4	933.4 (935.5)	2.34	69	31		
Atomic con	centrations (%)					
Sample	C 1s	O 1s	Cu 2p	Si 2p	Cl 2p	Na 1s
5089-1	1.76	65.02	0.64	30.39	1.30	0.89
5089-4	1.18	65.74	0.82	29.34	1.96	0.96
Atomic rati	os					
Sample	Cu/Cl	Cu/Si	O/Si			
5089-1	0.49	0.021	2.14			
5089-4	0.85	0.028	2.24			

Fig. 2 XRD analysis of SBA-15 after Cu incorporation. $5 < 2\theta < 60$.



Fig. 3 SEM (a) and TEM (b) images of SBA-15 before Cu impregnation. In (a) the total image width is of 6.43 μ m, while in (b) the estimated red parameter (distance between the centers of two neighboring channels) is approx. 8 nm.

Table 2Textural properties ofSBA-15 and Cu/SBA-15samples from N2 adsorption	Sample	$S_{\rm BET}$ (m ² /g)	C _{BET}	V_{Σ}^{a} (cm ³ /g)	\bar{r}_p (Å)	E (kJ/mol)	V_0 (cm ³ /g)	V_0/V_{Σ} (%)	Cu (%) (g/100 g)
data at 77 K	SBA-15 5089-1	635 477	1535 510	0.7508 0.6173	24 26	4.9 5.0	0.2611 0.1857	34.8 30.1	- 12.34
${}^{a}V_{\Sigma}$ was assessed from the amount adsorbed at P/P ₀ = 0.98	5089-4 5089-2	393 310	247 100	0.5388 0.5371	27 35	4.8 3.7	0.1466 0.1223	27.2 22.8	16.21 35.6

mesoporous solids [4]. Textural properties of the samples are summarized in Table 2. The average pore radius (\bar{r}_n) was calculated from the ratio between the total pore volume (V_{Σ}) and the BET surface area (S_{BET}) according to the following equation: $\bar{r}_p = 2V_{\Sigma}/S_{\text{BET}}$. The sharp increase in nitrogen adsorption at $P/P_0 < 0.1$ and the high BET C values for all samples studied indicated the presence of micropores. The micropore volume (V_0) was assessed using the D-R (Dubinin-Radushkevich) equation. The data of Table 2 show that all textural properties diminished with increasing Cu contents: SBA-15 < 5089-1 < 5089-4 < Cu/SBA-15. The maxima in the pore size distributions (PSD) of the samples, which were evaluated by analyzing the desorption branches of the hysteresis loops using the BJH method [5] (Fig. 5), are slightly moved to the right as the contents of Cu increased. The sharp drop in S_{BET} , C_{BET} , and V_0 (Table 2), especially for the Cu/SBA-15 sample, means that impregnated Cu atoms occupied certain positions within the micropores. The influence of Cu impregnation on the adsorption uptake of N₂ at 77 K is more marked in the mono and multilayer regions. The adsorption/desorption isotherms for the SBA-15 and Cu/SBA-15 samples showed a hysteresis loop, extended to very low relative pressures ($P/P_0 < 0.3$). A relatively slow adsorption of N₂ in the region $P/P_0 < 0.35$ is observed, with an average time required to reach the adsorption equilibrium always exceeding 20 min.

Figures 6 and 7 show the equilibrium adsorption isotherms of pure propylene and propane at 20° C and 55° C, respectively. These figures show that the quantities adsorbed increase continuously with pressure, and decrease as expected with increasing temperature. All adsorption isotherms in Fig. 6 were described by the Freündlich equation. In addition,



Fig. 4 XPS patterns of 5089-1 and 5089-4.

Fig. 5 Pore size distribution (BJH) of samples.







adsorption isotherms for propane at 55°C were well represented by the empirical Henry equation and those for propylene (Fig. 7) were well described by the Langmuir model in the range P < 100 Torr. Propylene showed the highest affinity for the adsorbents because of the specific interactions of the π -bonds with the adsorbents' surfaces. Differences between the C₃H₆ and C₃H₈ adsorption isotherms for the SBA-15 sample decreased as temperature increased from 20 to 55°C, whereas for the Cu/SBA-15 samples the

opposite trend was observed. Furthermore, adsorption uptake for propylene increased and for propane decreased in the order SBA-15 < 5089-1 < 5089-4 < 5089-2, i.e. increasing Cu content in the adsorbent lattice led to a corresponding improvement in selectivity towards propylene. It is evident that the enhanced selectivity showed for 5089-4compared to 5089-1 is related to the higher level of Cu(I) in the former as a consequence of the equilibrium impregnation.

P (Torr)

Fig. 8 Isosteric heat of adsorption with loading for propylene (solid lines) and propane (doted lines). L is the average molar heat of condensation. •, \circ (SBA-15); •, \triangle (5089-1); (5089-4); •, \Box (5089-2).



In addition, the isosteric heats of adsorption (Q_{st}) of propylene and propane were evaluated from the adsorption isotherms using the Clausius-Clapeyron equation. Figure 8 shows Q_{st} as a function of adsorption uptake. In all samples, the values of Q_{st} for propylene are found to be higher than those for propane over the entire adsorption coverage. The difference $\Delta Q_{st} = Q_{st}(C_3H_6) - Q_{st}(C_3H_8)$ for SBA-15 was very small (average 4 kJ/mol), whereas the difference was significant for Cu-containing samples. In particular, at low coverage, ΔQ_{st} increased in the order: SBA-15 < 5089-1 < 5089-4 < 5089-2. Thus, the Cu(I) ions are the specific adsorption sites for the adsorption of propylene in SBA-15 silica.

Conclusions

Adsorption uptake for propylene increased and for propane decreased in Cu-containing samples, as compared to that observed for the corresponding Cu-free samples. The presence of Cu(I) in the adsorbent lattice led to a greater selectivity towards propylene, and equilibrium impregnation yielded higher Cu(I) levels than incipient wetness impregnation. Therefore, the Cu/SBA-15 adsorbents are promising solids for separation of propane/ propylene mixtures at 55°C.

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