Cu-Based π-Complexation Adsorbent for Paraffin/Olefin Separation in Slurry Bed

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Summary: The solid phase transition pressure swing sorption and the liquid phase complexing sorption integration technology is used to separate paraffin/olefin in the slurry bed reactor. The characterizations of the adsorbents are conducted by the N_2 adsorption/desorption, FT-IR, XRD and TG techniques. The effects of different preparation method, a CuCl loaded coefficient and calcination temperature are studied. The results showed that specific surface area and total pore volume of the adsorbents are significantly decreased when compared to those of SiO_2 and AC (active carbon). Furthermore, the adsorbents prepared by the impregnation method with SiO_2 as carrier, CuCl loaded coefficient of 25.0 wt% and calcinated at 400 ºC showed higher separation effects. The propylene/propane selectivity coefficient is reached 2.26, and this implied that the feasibility of adsorbents utilized in slurry bed for paraffin/olefin separation.

Keywords: Cu-based, Adsorbent, Separation, π-complexation, Slurry bed.

Introduction

Olefins are important products in the petrochemical industry, and its products account for more than 70% of petrochemical products. In petroleum industry, the light hydrocarbons in the FCC dry gas are usually applied as fuel gas or separated as the raw material for petrochemical products. The separation technologies for light hydrocarbons include the cryogenic distillation, low temperature oil adsorption, NORP and pressure swing adsorption as well as combination technologies [1]. However, the above-mentioned methods suffer from many drawbacks such as high cost of equipment, and hard to separate paraffin/olefin in the mild condition [2]. Gilliland [3] found that the transition metals and olefins could form organic transition metal complex via the π-complexation. The copper containing MOFs like $Cu_3(BTC)_2$ [4,5] has high paraffin/olefin separation effects in C4 or C5 mixtures, this provided a novel route to separate paraffin/olefin in the practical applications.

At present, the adsorbents are applied in the paraffin/olefin complexing separation process mainly included: Al_2O_3 [6], zeolite [7], Cu-BTC (MOFs) [4,8], nano-typesetting active carbon [9] and active carbon. The adsorbents exhibited high selectivity and stability for paraffin/olefin separation. Besides, there are many literature studies on developing or optimizing the adsorbent that is required to improve the effects of complexing separation. Modification has widely used to adjust the separation effects of these adsorbents. Anson [10] found that the isotherms of Na-, K- and Ag-ETS-10 are to be nearly rectangular the adsorbents showed strong separation effects. Paraffin/olefin could be separated by ion-exchanged forms of the Na-X membranes [11], ETS-4 and silica membranes. Bux [12] found that the newly developed MOF membranes ZIF-8 have higher paraffin/olefin separation effects at room temperature for 1 bar feed pressure. Also, fixed bed technology is used in the complexing separation and has the disadvantages of intermittent operation and low throughput.

In this paper, we used a facile and low cost method to separate paraffin/olefin by a process involving the solid phase transition pressure swing adsorption and the liquid phase complexing adsorption. In the study, CuCl is used as the active component and propylene/propane as feed gas. These complexing adsorbents prepared by two preparation methods (i.e., the impregnation dispersion method and the thermal method) used to test the complexing separation effects. The effects of different CuCl loaded coefficient and calcination temperatures are also tested.

Experiment

Materials and Reagents

Al_2O_3, SiO_2, CuCl, paraffin liquid and active

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carbon (denoted as AC) were all purchased from Tianjin Hengxing Chemical Reagent Co., Ltd, China. AC modification was obtained by the H_2O_2 and HNO_3 impregnation (denoted as AC-H_2O_2), and dried at 115 ^oC for 4 h. Propylene /propane gas is purchased from Qingdao Petrochemical Technology co., Ltd, China.

Adsorbents Preparation

Thermal dispersion method: CuCl and carriers are mixed with the mass ratio of 10 wt%, 20 wt%, 25 wt%, 30 wt% (*m*(CuCl)/*m*(carrier)). Then these mixtures are triturated in a grinding miller sufficiently for 3 min (3000 $r\cdot min^{-1}$). After being calcined in Argon at 400 ^oC for 4 h and followed with H_2 deoxidized at 120 ^oC for 3 h and cooled to room temperature.

Impregnation method: CuCl is added into the ammonia solution to produce saturated CuCl solution. Then a certain amount of carriers is added into saturated solution and stirred at room temperature for 6 h. Then these mixtures are vigorously stirred at 100 ^oC to obtain solid samples. After being calcined in air at 400 ^oC for 4 h, and different samples are obtained, and followed with H_2 deoxidized at 120 ^oC for 3 h.

Complexing Separation Process

The propylene/propane complexing separation is performed in the slurry bed. Firstly, the adsorbents and solvents (the mass ratio of 15:85) are fed into slurry bed and stirring efficiently, and then Ar is used to purge the whole system for 5 min. Subsequently, propylene/propane gas (*V*(propylene)/*V*(propane)=1) with the gas flow rate of 100 $mL\cdot min^{-1}$, and reacted for 50 min. Gas desorption reaction is performed at room pressure and different temperatures. Desorption gas content is measured by wet flow meter and analysis by GC.

Characterization

FTIR spectra is recorded by the Nicolet 380 spectrometer in the range of 4000~500 cm^{-1}. Each spectrum represented the average of thirty-two scans. Textural properties of the samples are determined by the N_2 adsorption/desorption at –196 ^oC using an automated measurements (Micromeritics Corp., Tristar II 3020, US). Specific surface area (S_{BET}) is calculated by using Brunauer–Emmett–Teller (BET) equation, and total pore volume (V_t) is calculated at P/P_0=0.98. Thermogravimetric (TG) is performed to study the stability of the used samples (Mettler Toledo, TGA/SDTA851e, US). In the TG analysis, the sample is heated in a flow of N_2 from 20 ^oC up to 900 ^oC (20 $^oC\cdot min^{-1}$). X-ray diffraction (XRD) patterns are recorded on an X-ray diffractometer Max2500PC (MAC Science corp., Japan) with a step of $8^o\cdot min^{-1}$ from 5^o to 75^o.

Results and Discussion

Characterization of Adsorbents

Table 1 shows textural properties of CuCl-SiO_2, CuCl-AC, SiO_2 and AC. It is found that the S_{BET} of CuCl-AC and CuCl-SiO_2 is reached 180.5 and 289.8 $m^2\cdot g^{-1}$, which is decreased evidently when compared to 486.4 and 332.3 $m^2\cdot g^{-1}$ of AC and SiO_2, respectively. And V_t of CuCl-SiO_2 and CuCl-AC is corresponding decreased when compared to that of AC and SiO_2. This might be because CuCl has distributed on the carriers surface, which resulting in S_{BET} and V_t varied a lot. Nevertheless, the pore size of CuCl-AC and CuCl-SiO_2 has changed little.

Table-1: Textural property of the adsorbents.

Adsorbent	S_{BET} /$m^2\cdot g^{-1}$	V_t /$cm^3\cdot g^{-1}$	Pore size /nm
AC	486.4	0.6	2.4
CuCl-AC	180.5	0.3	2.9
SiO_2	332.3	1.0	6.0
CuCl-SiO_2	289.8	0.9	5.9

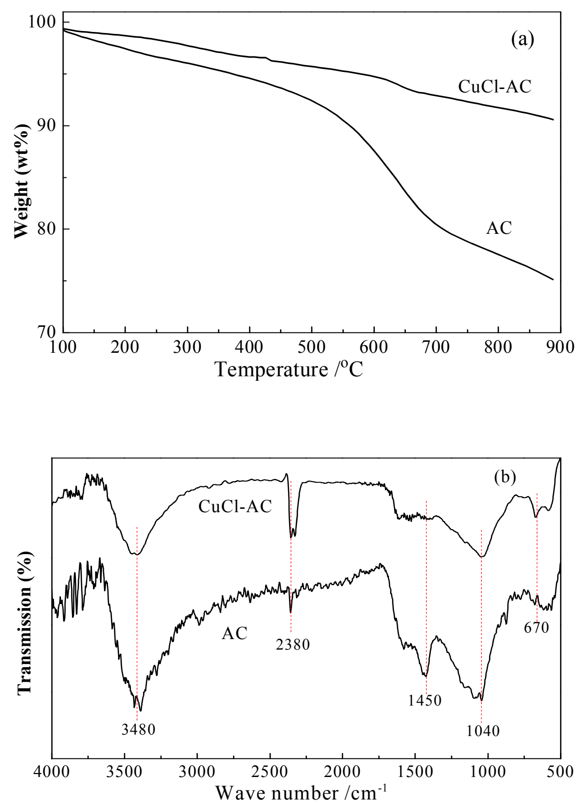

Fig. 1: TG (a) and FTIR (b) patterns of CuCl-AC and AC.

In this section, FTIR and TG analysis of CuCl-AC and AC are conducted, and the results are proposed in Fig.1. Fig.1 (a) shows TG curves of two samples are both showed weight losses, while that of CuCl-AC reduced less than AC. This might be because CuCl is distributed on the surface of AC, and further prevented weight loss. Fig.1 (b) shows the patterns of CuCl-AC and AC, a broad O-H stretching vibration peak at 3480 cm^{-1}, corresponding to the O-H bonds of free water and hydrogen bonds of structural hydroxyl [13]. A weak C=O bending vibration peak at 2380 cm^{-1} is observed due to the oxidation modification increased the density of C=O bond. Besides, a weak C-Cl stretches vibrational peak is observed in the pattern of CuCl-AC, and the C=O/C-N/-NO_2 stretches peak is disappeared at 1450 cm^{-1}. This demonstrated that CuCl has distributed on the surface of carriers.

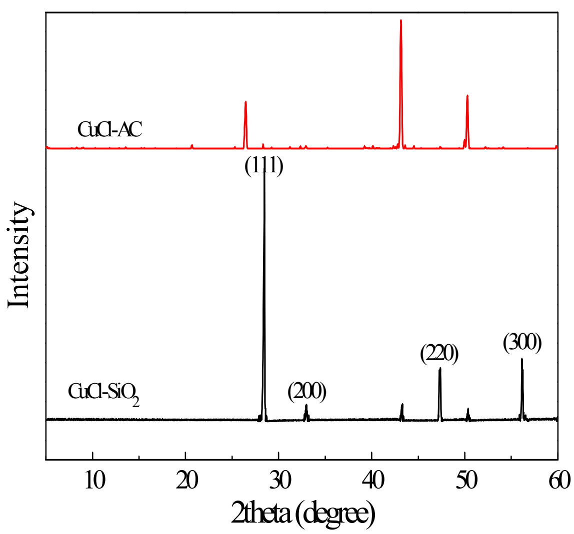

Fig. 2: XRD patterns of CuCl-AC and CuCl-SiO_2.

Fig.2 shows that the XRD patterns of CuCl-AC and CuCl-SiO_2. The observed two well -resolved peaks at 43.0° and 50.5° in these two adsorbents, corresponding to the peaks of Cu(I). This might be because the disproportionation or reduction reaction of Cu(I) is occurred during the preparation process. Besides, four well-resolved peaks over CuCl-SiO_2 are observed, which are indexed as (111), (200), (220) and (300) reflections associated with the diffraction peak of CuCl. This demonstrated that CuCl is dispersed on the surface of carrier, which is in agreement with the results of TG and FTIR.

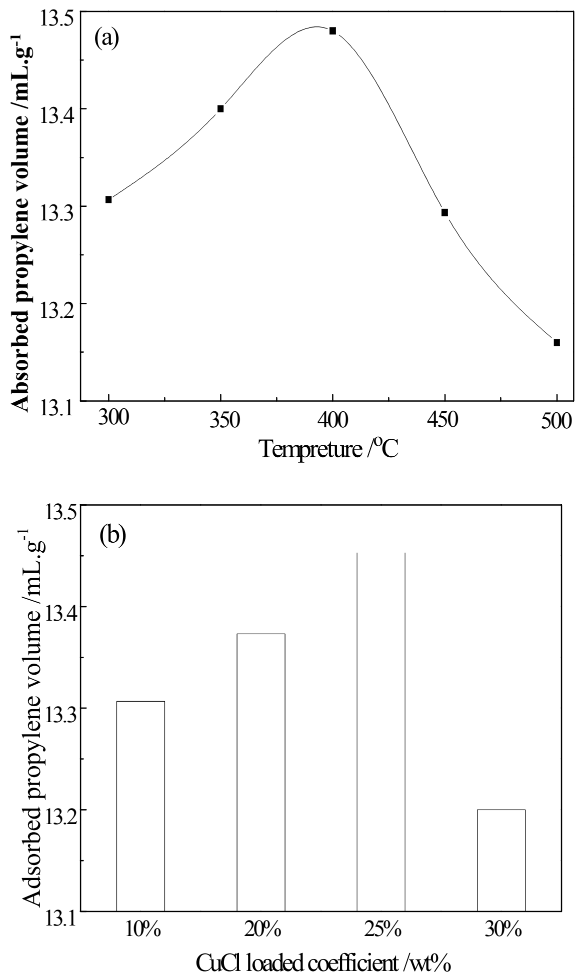

Fig. 3: Effects of temperature and CuCl loaded coefficient on the absorbed propylene.

Effect of Temperature and CuCl Loaded Coefficient

In this section, the adsorbents are prepared by the impregnation method and with SiO_2 as carrier, and the adsorbed effect is shown in Fig.3 (a) and Fig.3 (b). Fig.3 (a) shows the adsorbed volume is significantly increased when the temperature less than 400 °C. This might be because low temperature could not maintain CuCl move freely and well-proportioned dispersed on the carrier surface, and thus led to the lower adsorbed effect. Propylene adsorbed volume is reduced evidently when the temperature is above 400 °C. This might be because the Cu(I) is oxidized in the preparation process, and thus decreased the complexing separation effects.

Table-2: Effects of different preparation methods and adsorbents.

Adsorbent	Impregnation method			Thermal dispersion method		
	V(propylene) /ml·g^{-1}	*V*(propane) /ml·g^{-1}	SC [a]	*V*(propylene) /ml·g^{-1}	*V*(propane) /ml·g^{-1}	SC [a]
CuCl-SiO_2	13.17	5.82	2.26	12.99	6.46	2.01
CuCl-AC	12.76	6.26	2.04	12.62	6.60	1.91
CuCl-Al_2O_3	13.33	6.10	2.19	12.67	5.94	2.13
CuCl-AC-H_2O_2	13.58	6.25	2.17	12.84	6.15	2.09

[a] SC stands for Selectivity coefficient, and SC=*V*(propylene)/*V*(propane)

Fig.3 (b) shows the propylene adsorbed volume is evidently increased with increasing the CuCl loaded coefficient. The reason might be because the distribution of CuCl did not reach the maximum dispersion threshold value [14], which resulting in the complexing adsorption effect is increased evidently. However, when CuCl loaded coefficient is above 25.0 wt%, the adsorbed volume is obviously decreased. This might be because overfull CuCl dispersed on the surface of carrier, which led to the physical adsorption effect is stronger than the complexing adsorption. With all of the above results, we concluded that the adsorbent with a CuCl loaded coefficient of 25.0 wt% had good adsorption effects.

Effect of Preparation Methods and Adsorbents

Table-2 shows the adsorption effects of the adsorbents prepared by different methods and adsorbents, while the effects of all adsorbents in literature are shown in Table 3. The SC of all adsorbents prepared by the impregnation method is above 2.04, while those of above 1.91 are gained by the thermal dispersion method. For the impregnation method, the CuCl-SiO_2 showed highest SC of 2.26, which might be because the d-orbit hold ratio increased, and thus facilitated the π-complexation adsorption effects of Cu(I) and propylene. The CuCl-Al_2O_3 had the SC of 2.19, which is slightly lower than that reported by Yang [15], and higher than the copper series absorbents found by Grande [16] and Zhu [17]. For the thermal dispersion method, CuCl-Al_2O_3 showed highest SC of 2.13, while the other adsorbents are only about 2.01. Hence, this implied that the adsorbents prepared by the impregnation method represented better separation effects than those prepared by the thermal dispersion method [18].

Table-3: Effects of different complexing adsorbents in literature.

Adsorbent	*V*(propylene) /ml·g^{-1}	*V*(propane) /ml·g^{-1}	SC [a]	Ref
CuCl-Al_2O_3	17.47	4.85	3.60	[15]
Cu-BTC	8.00	6.30	1.30	[16]
NJ-Cu	14.60	6.80	2.14	[17]

Conclusion

The present investigation into the development of π-complexation adsorption to separate propylene/propane lead to the following conclusions:

It is found that CuCl has distributed on the carrier surface, which is verified by XRD, TG and FTIR. Textural properties of the adsorbents are decreased evidently compared to those of SiO_2 and AC. Besides, the adsorbents prepared by the impregnation method with a CuCl loaded coefficient of 25.0 wt% and SiO_2 as carrier shows higher propylene/propane separation effect. Propylene/propane selectivity coefficient is reached 2.26, and this implied that the feasibility of the adsorbents utilized in slurry bed for paraffin/olefin separation process.

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