



Synthesis of Alumina-Containing Hexagonal Mesoporous Silica and Its Application in the Adsorption of Gossypol

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Mesoporous molecular catalyst alumina-containing hexagonal mesoporous silica (Al-HMS) of different Si/Al ratios have been synthesized by neutral templating method and characterized by X-ray powder diffraction and Brunauer-Emmett-Teller (BET). These data confirmed the hexagonal mesoporous structure formation at different Si/Al ratios. The Al-HMS as catalyst applying to adsorb gossypol in cottonseed oil and gossypol adsorption increased with the amount of Al loading. Under the optimal conditions, the gossypol adsorption was more than 60 %.

Key Words: Gossypol, Alumina, Hexagonal mesoporous silica, Adsorption.

INTRODUCTION

Gossypol was discovered by J.J. Longmore and first purified by L. Marchlewski at end of the 19th century¹. The gossypol (1,1',6,6',7,7'-hexahydroxy-5,5'-diisopropyl-3-3'-dimethyl-2,2'-binaphthalene-8,8'-dicarboxaldehyde) contained in pigment glands and is a polyphenolic binaphthyl dialdehyde^{2,3}, which are distributed the cottonseed. Gossypol is a toxic substance of phenolic compound to young ruminants and monogastric animals⁴. It limits most of the cottonseed products to human and animals. Cottonseed oil is extracted from seeds of the cotton plant and belonged to vegetable oil. Due to the presence of toxic gossypol in cottonseed oil and this oil has a colour fixed which is characterized by a reddish brown colour and is difficult to refine^{5,6}, it can not be used for edible and can infertility in humans. It is necessary for extracted oil and as meal used to be further processed to removal gossypol.

In order to efficiently removal gossypol from cottonseed oil, a number of studies have been carried out, usually through caustic reining⁷ and adsorption on solids, such as activated alumina⁸ and activated montmorillonite-containing clays⁹. Richard *et al.*¹⁰ investigated that aluminas and silicas as adsorbents for reducing the gossypol from cottonseed oil, they found gossypol has a high affinity for alumina surface. Zhao *et al.*¹¹ recent studies reported that alumina-containing hexagonal mesoporous silica (Al-HMS) mesoporous molecular sieve showed good adsorption as a solid catalyst applied to non-methane volatile organic compounds (VOCs).

In this paper, we describe the synthesized of immobilized Al on hexagonal mesoporous silica (HMS) sieve by a hydrothermal synthesized method. The aluminium-hexagonal mesoporous silica was applied as a solid catalyst for the adsorption of gossypol and characterized by X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET). The loading of Al on hexagonal mesoporous silica, the amount of catalyst, the reaction time and reaction temperature were investigated to optimize the reaction conditions for adsorption of gossypol.

EXPERIMENTAL

The powder X-ray diffraction (XRD) data was collected on a Brunker D8 Advance X-ray diffractometer using Cu-K α irradiation ($\lambda = 1.5406 \text{ \AA}$) as source at 40 kV and 40 mA. The samples were recorded from 1 to 20° (2 θ) with a step scan of 0.01°/s.

Brunauer-Emmett-Teller (BET) surface area analysis was performed from the nitrogen adsorption isotherms at 77 K using a Micromeritics Model ASAP 2020 instrument. All samples were degassed at 110 °C under vacuum for 6 h. Average pore diameter (d) and pore volume were calculated based on the Barret-Joyner-Halenda (BJH) method.

The NH₃-temperature programmed desorption (NH₃-TPD) data were collected using a ChemBet 3000 analyzer. About 120 mg samples were activated under flowing heat (650 °C) for 1.5 h and cooled to 80 °C under continuous evacuation. The sample was equilibrated with gaseous NH₃ at 0.04 kPa and the temperature increased by 10 °C/min under flowing heat 20 cm³/min.

The laboratory centrifugation was supplied by An Ting scientific instrument factory, Shanghai and model is TDL80-2B. The gossypol was detected on high performance liquid chromatography (Waters model 2487, USA).

Pure drug sample of gossypol was kindly supplied by Ci Yuan Bio Co., Ltd. (Xi'an, China); the cottonseed oil was kindly supplied by Shihezi edible oil refinery. All chemicals were of analytical reagent grades, methanol is chromatographically pure and distilled water was used throughout.

Catalyst preparation: The aluminium-hexagonal mesoporous silica aluminium-hexagonal mesoporous silica catalyst was synthesized according to a procedure described by Zhao *et al.*¹¹. To a vigorously stirred mixture solution of dodecylamine (DDA) in ethanol (EtOH) and deionized water was added at a time a homogenous mixture of 0.2 mol tetraethyl orthosilicate (TEOS) in EtOH and alumina isopropoxide [Al(O-*i*-Pr)₃] at room temperature.

The mixture was vigorously stirred at room temperature for 24 h, the as-synthesized hexagonal mesoporous silica and aluminium-hexagonal mesoporous silica were filtered, washed with deionized water and dried at room temperature for 24 h. The obtained samples were calcined in a muffle furnace at *ca.* 550 °C for 5 h.

Adsorption of gossypol: For the purpose of this study, gossypol soluble in refined cottonseed oil and prepared to 0.17 mg/g gossypol solution. The gossypol solution stored at 2 °C in a brown bottle. At the beginning of the reaction, the aluminium-hexagonal mesoporous silica catalyst was handed by ultrasonic dispersion. The adsorption experiments were conducted at room temperature as follows: gossypol solution was charged in a stoppered Erlenmeyer flask and a known amount of the catalyst aluminium-hexagonal mesoporous silica was added to the flask which then shaken vigorously for a significant time. Allowing the catalyst reach to adsorption equilibrium, followed by laboratory centrifugation for 10 min at 5000 *xg*. The precipitation was filtered through Whatman No. 1 filter paper. The resultant bottom layer was composed of catalyst and gossypol and the supernatant layer was cottonseed oil and retained gossypol which was taken using high performance liquid chromatography to detect.

Detection method: The detection method of gossypol in cottonseed oil according to a procedure described previously¹². The chromatographic conditions: a C18 reversed-phase column was used. The particle size was 5 µm and the column dimensions were 4.6 mm × 150 mm, the mobile phase were methanol and 2 % phosphoric acid solution (90:10), the column temperature was 40 °C, the flow rate was 1 mL/min and the gossypol was detected by a Waters 2487 UV detector at 235 nm, the sensitivity is 0.01-0.02 absorbance unit full scale (AUFS) and the injection volume is 20 µm. The supernatant layer was mixed with 1 mL of hexane and 5 mL of solvent mixture which was N,N-dimethyl formamide:water (70:30, v/v). The samples were stirring for 10 min and standing for 15 min. The bottom layer was filter and injected into the HPLC.

RESULTS AND DISCUSSION

Fig. 1 displays the typical XRD pattern for the aluminium-hexagonal mesoporous silica samples with different ZS loading.

It can be clearly seen that the patterns all contain an intense diffraction peak about $2\theta = 2.5^\circ$ and exhibited a single (100) peak. The XRD patterns had the typical characteristic peaks of a mesoporous molecular sieve in agreement with the literature reports^{13,14}. It can be note that the XRD diffraction peaks of aluminium-hexagonal mesoporous silica (Si/Al = 25) are much weaker than that of other samples and with the increase of Al content the d spacing decrease. Cause of this phenomenon is due to the catalyst reduction in hexagonal order¹⁵.

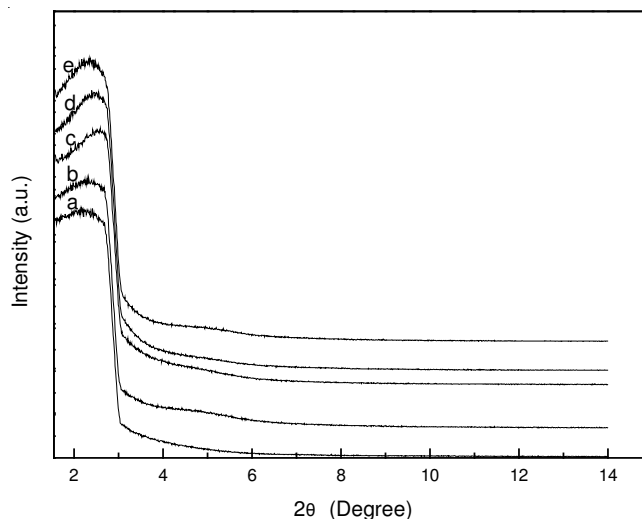


Fig. 1. XRD patterns of aluminium-hexagonal mesoporous silica material for different Si/Al ratios: (a) Si/Al ratios = 25, (b) Si/Al ratios = 20, (c) Si/Al ratios = 75, (d) Si/Al ratios = 100 and (e) Si/Al ratios = 150

Table-1 shows surface area and pore size distribution data of the aluminium-hexagonal mesoporous silica samples. It is noted that the surface area and pore volume decreases with increase of Al into the hexagonal mesoporous silica structure. Some Al³⁺ ions escape from the catalyst framework and some inter-particle pores are damaged reduced to the pore volume decreased¹¹. As higher Al loads, the dealumination of framework during calcinations or the increase of the wall thickness of aluminium-hexagonal mesoporous silica catalyst¹⁶. The pore volume reduced from 1.44 cm³/g to 0.95 cm³/g. Fig. 2 shows pore size distributions of the obtained various aluminium-hexagonal mesoporous silica samples. It can be seen that the pore sizes of the aluminium-hexagonal mesoporous silica catalyst decrease with increment of Al loading. These results were in agreement with the XRD date which hexagonal order is decreasing with the decrease of Si/Al ratio.

TABLE-1
STRUCTURE OF VARIOUS Al-HMS SAMPLES

Sample	S _{BET} (m ² /g)	d (nm)	Pore volume (cm ³ /g)
Si/Al = 25	1315	4.1	1.44
Si/Al = 50	1279	4.2	1.42
Si/Al = 75	1219	4.2	1.28
Si/Al = 100	1138	4.4	1.17
Si/Al = 150	1100	4.4	1.18

Fig. 3 shows the N₂ adsorption-desorption isotherms of the aluminium-hexagonal mesoporous silica samples with different Al loading. The samples of aluminium-hexagonal

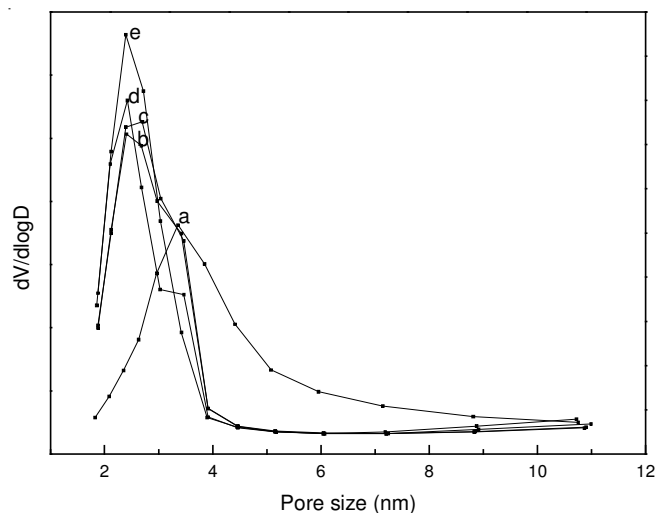


Fig. 2. Pore size distributions for different Si/Al ratios: (a) Si/Al = 25, (b) Si/Al = 20, (c) Si/Al = 75, (d) Si/Al = 100 and (e) Si/Al = 150

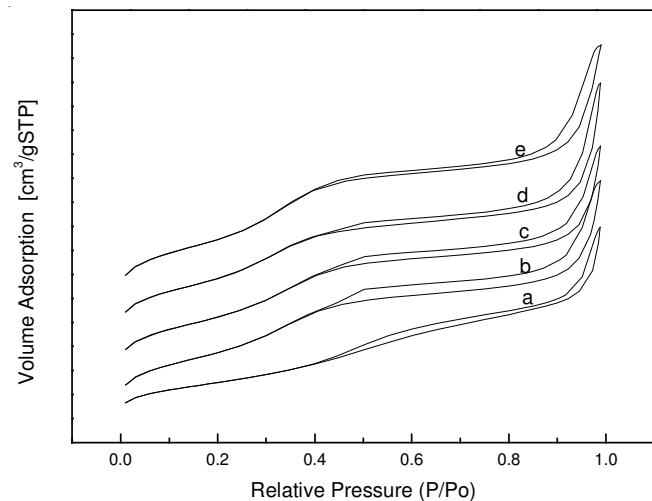


Fig. 3. Nitrogen adsorption isotherms for different Si/Al ratios: (a) Si/Al = 25, (b) Si/Al = 50, (c) Si/Al = 75, (d) Si/Al = 100 and (e) Si/Al = 150

mesoporous silica catalysts exhibited the shape of II isotherms according to the IUPAC classification for nitrogen adsorption-desorption isotherms. All samples exhibit a well-defined hysteresis loop in the adsorption curve at about $P/P_0 = 0.42$, which is indicative of the filling of framework-confined mesopores.

There are a number of methods for acidity measurements^{17,18}. The solid acid sites are determined by TPD which adsorption of ammonia to determine total acidity and acid strength distribution. It is evident from the NH_3 -TPD profiles that aluminium-hexagonal mesoporous silica materials of Si/Al ratios ranging from 25 to 150 are shown in Fig. 4. It can be inferred that the acidity was increased on increasing the Al loading on hexagonal mesoporous silica content. Falaras *et al.*⁹ reported that adsorption phenomenon in cottonseed oil is mainly involves the pigment such as gossypol, carotene and so on; the pigment attraction to the acid sites in the adsorbent.

The effects of mass loading the Al on hexagonal mesoporous silica (molar ratio) for gossypol adsorption present in Fig. 5. At ambient temperature, 2 g cottonseed oil and the gossypol content of 0.17 mg/g, the amount of aluminium-hexagonal

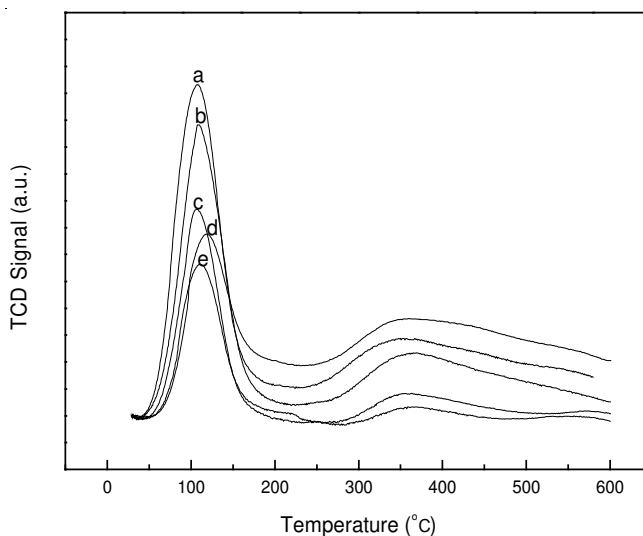


Fig. 4. NH_3 -TPD curves for (a) Si/Al = 25, (b) Si/Al = 50, (c) Si/Al = 75, (d) Si/Al = 100 and (e) Si/Al = 150

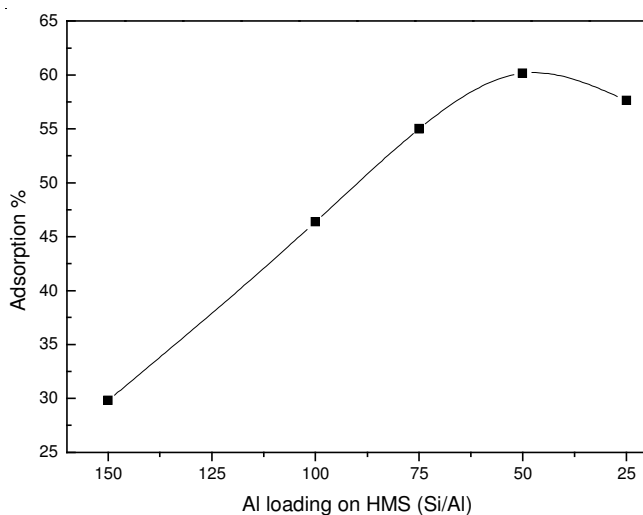


Fig. 5. Catalytic activities of solid acid catalysts with different Al loading on hexagonal mesoporous silica for adsorption of gossypol

mesoporous silica catalyst was 0.05 g. The mixture was stirred at 200 rpm for 0.5 h. It is shown that the adsorption rate of gossypol increased with increasing Al loading on the hexagonal mesoporous silica molecular sieve and when Si/Al was 150, the aluminium-hexagonal mesoporous silica catalyst adsorbed gossypol is 29.82 %; Si/Al was 100, the adsorbed gossypol is 46.37 %; Si/Al was 75, the adsorbed gossypol is 55 %; Si/Al was 60.15 %, the adsorbed gossypol is 60.15 % and Si/Al was 25, the adsorbed gossypol is 57.64 %. When Si/Al was 50, no further increase was observed at more Al loading on hexagonal mesoporous silica.

At the same time, the amount of aluminium-hexagonal mesoporous silica catalyst used in the adsorption process affected the gossypol adsorption efficiency. The effect of the aluminium-hexagonal mesoporous silica catalyst dose on the adsorption efficiency is shown in Fig. 6. At ambient temperature, with Si/Al = 50 of aluminium-hexagonal mesoporous silica catalyst, 2 g cottonseed oil and the gossypol content of 0.17 mg/g. The mixture was stirred at 200 rpm for 0.5 h. The

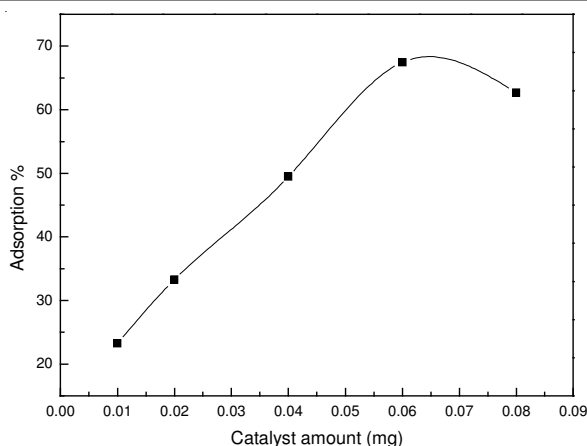


Fig. 6. Effect of catalyst amount on the adsorption of gossypol

adsorption efficiency of gossypol increased with increasing aluminium-hexagonal mesoporous silica catalyst amount. When the aluminium-hexagonal mesoporous silica catalyst amount was 0.01 g, the gossypol adsorption efficiency was 23.3 %; the amount was 0.02 g, the gossypol adsorption efficiency was 33.3 %; the amount was 0.04 g, the gossypol adsorption efficiency was 49.5 %; the amount was 0.06 g, the gossypol adsorption efficiency was 67.5 % and the amount was 0.08 g, the gossypol adsorption efficiency was 62.7 %. While addition of additional aluminium-hexagonal mesoporous silica catalyst, the gossypol adsorption efficiency did not increase.

The effects of time for gossypol adsorption show in the Fig. 7. At the room temperature, with Si/Al = 50 of aluminium-hexagonal mesoporous silica catalyst, 2 g cottonseed oil and the gossypol content of 0.17 mg/g, the amount of aluminium-hexagonal mesoporous silica catalyst was 0.06 g. The mixture was stirred at 200 rpm for different time (10-50 min). The mixture was stirred for 10 min the gossypol adsorption was 26.92 %; stirred for 20 min the gossypol adsorption was 44.99 %; stirred for 30 min the gossypol adsorption was 63.14 %; stirred for 40 min the gossypol adsorption was 65.32 % and stirred for 50 min the gossypol adsorption was 61.04 %. The adsorption increased with reaction time and gradually peaked at 30 min (Fig. 7).

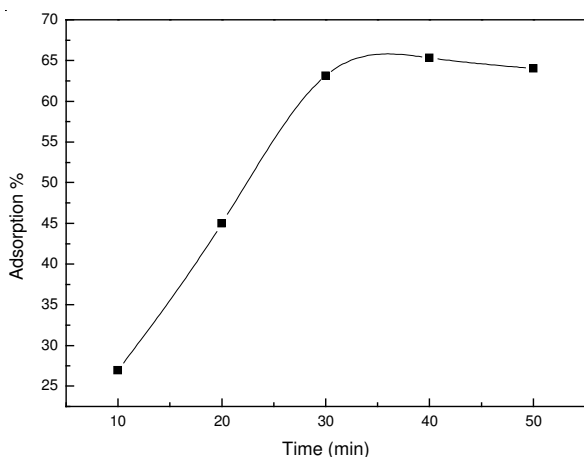


Fig. 7. Effect of reaction time on the adsorption of gossypol

Conclusion

We have synthesized mesoporous molecular sieves aluminium-hexagonal mesoporous silica catalyst with different Si/Al ratios and synthesized using dodecylamine as surfactant by neutral templating method. The aluminium-hexagonal mesoporous silica catalysts samples were examined by XRD and BET that shows good dispersion. With the increase in the content of alumina, the adsorption of the catalysts increased. When Al loading on hexagonal mesoporous silica was Si/Al = 50, the amount of the catalyst was 0.06 mg for gossypol adsorption process of 30 min, the adsorption rate more than 60 %.

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