Original Article

Effect of silica sources in nanoporous silica synthesis on releasing behavior of indigo carmine

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Abstract

Nanoporous silica was applied in controlled releasing experiments. Different physical properties of the nanoporous silica, related to variations of the silica sources, affected the releasing behaviour. Two different silica precursors in nanoporous silica synthesis were investigated, tetraethoxysilane and sodium silicate. The nanoporous silica, which was obtained by tetraethoxysilane, gave the highest surface area (800 m^2/g) and pore volume (1.2 cc/g). On the other hand, the nanoporous silica obtaining from sodium silicate showed the largest pore size (9 nm). The nanoporous silica with larger pore volume can load a higher amount of indigo carmine, which resulted in a fast release due to the large driving force between the silica particle and media solution. However, the releasing rate was not only affected by the pore volume, but also by the interaction between the silanol groups on the silica surface and molecules of indigo carmine.

Keywords: nanoporous silica, control release, drug delivery

1. Introduction

Nanoporous silica is a challenging material in many applications. Since, it has attractive features, such as large pore volume, uniform pore size distribution large surface area, and high stability. All these properties promoted in many research themes. Mesoporous silica was used as catalyst support (Subrahmanyam *et al.*, 2004; Ooi *et al.*, 2005), CO_2 capture (Khatri *et al.*, 2005), heavy metal removal in waste water (Sayari *et al.*, 2005), and template for carbon nanotube synthesis (Zhu *et al.*, 2002).

In applications related to drug delivery, nanoporous silica is a very interesting material because its adjustable textural properties were able to control the drug releasing rate (Qu *et al.*, 2006). Furthermore, nanoporous silica is a

non-toxic and biocompatible material, which can be applied in the human body (Trewyn *et al.*, 2008). The mesoporous silica was tested in the encapsulation and releasing of direct blue dye (Ren *et al.*, 2007). Some types of mesoporous silica were found that can encapsulate the dye. Porous hollow silica was used as a drug carrier (Chen *et al.*, 2004 and Li *et al.*, 2004). Qu and coworkers (2006) used mesoporous silica type MCM-41 to study the effect of pore regulation and morphology on the controlled release of captropil. The largest pore size gave the highest releasing rate because the steric diffusion resistance was absented. The type of coating materials on nanoporous silica has an impact on the release rate, because it changes the functional group of the silica surface (Wu *et al.*, 2007). The hybrid system between organic and inorganic materials was applied to improve the functional surface of silica, which controlled the rate of release (Fugundes *et al.*, 1998). Therefore, the releasing rate was not only controlled by the physical properties of nanoporous silica, but it was also affected by the functional group on the

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silica surface. The functional group of silica can be improved to be specific with the target (Pasqua *et al.*, 2007). The differences of silica precursors are an interesting factor, because they are related to the various amounts of the silanol group (Si-OH) and physical properties. Therefore, this research investigated the effect of silica precursors in nanoporous silica synthesis on releasing behaviour using indigo carmine as a drug model.

2. Experiment

2.1 Synthesis of nanoporous silica

The mixture of 2 g pluronic P123 (Aldrich, USA) and 72 ml of 2 M HCl (Ajax Finechem, New Zealand) was dissolved and stirred at the various reaction temperatures (30-60°C) for 4 hrs. The silica source and Pluronic P123 (Aldrich, USA) mixtures at the ratio of 3:1 poured in the previous mixture and stirred for different reaction times (2-4 hrs). Tetraethoxysilane, TEOS (Fluka, Italy) and sodium silicate, SS (Panreac, Spain) were used as two types of silica source. Hydrothermal treatment was applied after the end of reaction time. The mixture was filtered to obtain the silica solid particle. The solid particle was dried at 100°C for 6 hrs and calcined at a temperature of 600°C for 4 hrs. The sample name was designated by silica source - synthesis temperature - reaction time such as TEOS-30°C-4h, which means that this is a nanoporous silica synthesized from TEOS at a synthesis temperature of 30°C and a reaction time of 4 hrs. The textural properties of nanoporous silica were characterized by nitrogen adsorption desorption technique using autosorb-1c (Quantachrome, USA). The pore diameter and pore volume were calculated by Barret-Joyner-Halenda (BJH) model. The surface area was given by Brunauer-Emmet-Teller (BET) model. The silanol group (Si-OH) was characterized by Fourier transform infrared spectrometer (Spectrum GX, Perkin Elmer).

2.2 Loading and releasing study

The nanoporous silica was dried at 100°C for 6 hrs and soaked in 0.5% wt of indigo carmine (Himedia, India)

for 48 hrs under vacuum condition. It was filtered and dried at a temperature of 60°C for 6 hrs. The amount of drug loading was calculated by the weight difference before and after drug loading. In the releasing study, five hundred milligrams of drug loaded nanoporous silica was placed in to 100 ml phosphate buffer (pH=7) as a simulated body fluid. The release of indigo carmine was measured by UV-vis spectrophotometer (CECIL, CE1010) at λ = 610.2 nm. One millilitre of simulated fluid was taken every minute for the first thirty minutes; after that one time in every thirty minutes (Sahiner *et al.*, 1998).

3. Results and Discussion

3.1 Physical properties of nanoporous silica

Table 1 presents the pore diameter, pore volume, and surface area of nanoporous silica, which was synthesized from tetraethoxysilane (TEOS) and sodium silicate (SS). Most of the nanoporous silica synthesized from sodium silicate gave a larger pore diameter; however, they show a relative low pore volume and surface area. Since the sodium silicate has a lower reactivity than tetraethoxysilane, the nanoporous silica from tetraethoxysilane shows a higher polymerization degree. A result is that the structure of silica shrinks resulting in a smaller pore structure. The nanoporous silica from tetraethoxysilane provided a larger pore volume and a higher surface area thus having a higher porosity. The effects of synthesis conditions on the physical properties were reported by Samart *et al.* (2008). The reaction time and reaction temperature also affected the textural properties. The surface area increased when the reaction time was longer. Further, the reaction temperature also affected the surface area. Figure 1 shows the FT-IR spectra of nanoporous silica synthesized from tetraethoxysilane and sodium silicate. The O-H stretching peak was related to the wave number 3400-3600 cm^{-1}, which represented the amount of the remaining silanol group on the silica surface. The tetraethoxysilane as silica resource provided the larger O-H stretching peak, which indicated a higher remaining silanol group than the nanoporous silica from sodium silicate.

Table 1. Physical properties of mesoporous silica

Sample name	Pore volume (cc/g)	Pore diameter (nm)	Surface area (m^2/g)	Sample name	Pore volume (cc/g)	Pore diameter (nm)	Surface area (m^2/g)
TEOS-30°C-2h	0.73	4.48	697	SS-30°C-2h	0.89	6.76	526
TEOS-30°C-3h	0.48	4.35	497	SS-30°C-3h	0.62	6.14	403
TEOS-30°C-4h	1.18	6.30	789	SS-30°C-4h	0.51	6.60	344
TEOS-60°C-2h	0.80	4.54	742	SS-60°C-2h	0.72	6.46	448
TEOS-60°C-3h	0.55	4.94	523	SS-60°C-3h	0.66	8.92	296
TEOS-60°C-4h	0.98	5.23	801	SS-60°C-4h	0.77	7.90	390

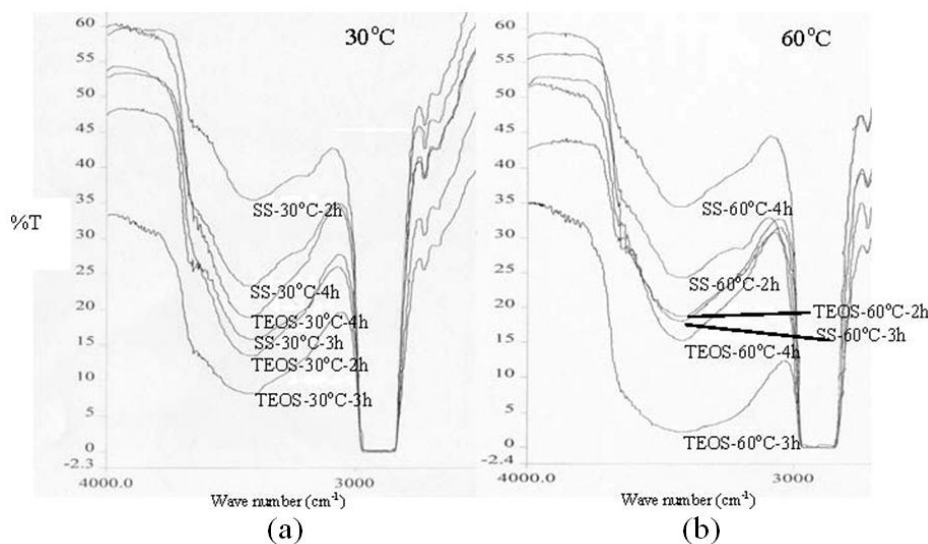Note: Sample name was designated by silica source - synthesis temperature - reaction time

Figure 1. FT-IR Spectra of nanoporous silica synthesis from tetraethoxysilane and sodium silicate at synthesis temperature of 30°C and 60°C

Table 2. Percentage of indigo carmine loading

Sample name	Percentage of indigo carmine loading	Sample name	Percentage of indigo carmine loading
TEOS-30°C-2h	6.7	SS-30°C-2h	57.5
TEOS-30°C-3h	12.2	SS-30°C-3h	39.1
TEOS-30°C-4h	19.1	SS-30°C-4h	25.4
TEOS-60°C-2h	5.8	SS-60°C-2h	43.1
TEOS-60°C-3h	9.2	SS-60°C-3h	18.4
TEOS-60°C-4h	12.2	SS-60°C-4h	8.5

3.2 Study of loading and releasing indigo carmine

Table 2 shows the percentage of indigo carmine loading in nanoporous silica. The amount of loaded indigo carmine was mainly affected by the pore volume. The decrease of pore volume as shown in nanoporous silica, which was synthesized by sodium silicate (Table 1), reduced the percentage of indigo carmine loading. Nevertheless, the amount of the silanol group also influenced the indigo carmine loading, for example, TEOS-30°C-3h had a smaller pore volume than TEOS-30°C-2h as shown in Table 1, whereas TEOS-30°C-3h gave a higher percentage of indigo carmine loading than TEOS-30°C-2h, because the larger amount of silanol group can collect more indigo carmine within the pores (Figure 1). The releasing profiles of indigo carmine from nanoporous silica synthesized from various silica resources are shown in Figure 2. The indigo releasing rates were affected by the concentration of the silanol group and the indigo carmine loading. Higher amounts of indigo carmine loading gave a faster releasing rate, because of a larger driving force from the concentration between silica particles and buffer solution. Therefore, large pore volume

nanoporous silica, which collected higher amounts of indigo carmine, provided a fast releasing rate as show in Figure 2d (TEOS-60°C-4h). On the other hand, a lower loading (SS-30°C-2h) resulted in a smaller driving force thus had a slower release. The effect of the silanol group was related to the hydrogen bonding between the silanol group on the silica surface and the amino group of the indigo carmine molecule as shown in Figure 3. The releasing behaviours of high silanol nanoporous silica (SS-60°C-2h) and low silanol nanoporous silica (SS-60°C-4h) were considered as shown in Figure 1b. The high silanol nanoporous silica (SS-60°C-2h) had smaller pore volume but gave larger indigo carmine loading, because the large amount of silanol group had numerous interactions between the indigo carmine molecules and the silanol groups on the silica surface.

4. Conclusions

The silica sources affected the indigo carmine release. The two silica sources provided different physical properties, like pore volume, pore diameter, and the amount of silanol group. These properties influenced the indigo carmine re-
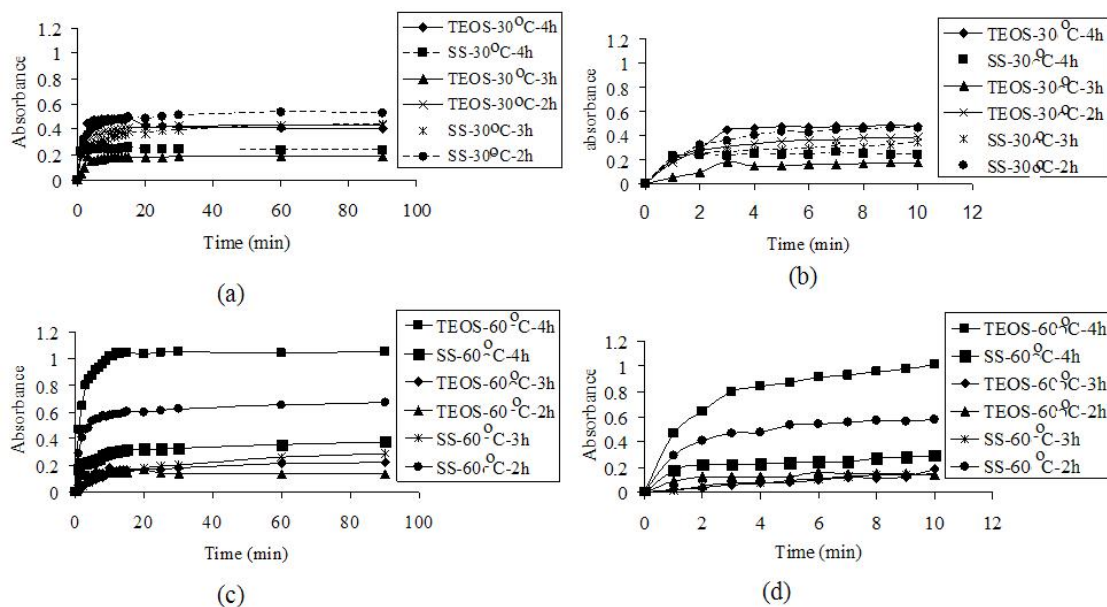
Figure 2. Releasing profiles of indigo carmine from nanoporous silica synthesized from various silica sources and synthesis times; synthesis temperature and releasing time (a) 30°C and 120min, (b) 30°C and 10min, (c) 60°C and 120min, and (d) 60°C and 10min.
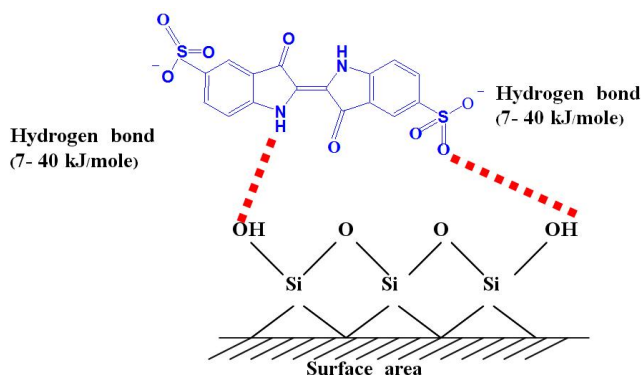

Figure 3. Interaction between silanol group and indigo carmine molecule

leasing behaviour. The pore volume was the major parameter affecting the indigo carmine loading, which affected the driving force of the concentration between the silica particle and the buffer solution. The silanol group also affected the loading and releasing behaviour, because the hydroxyl group interacts with indigo carmine molecule by hydrogen bonding.

Acknowledgement

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