Synthesis of Inorganic and Zeolite-Hybrid Desiccant by Sol-Gel Method

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ABSTRACT

In this work the inorganic and zeolite-hybrid desiccants were synthesized by the sol-gel method at room temperature and atmospheric pressure. The sol-gel method leads to the formation of highly cross-linked and transparent gels. Inorganic salts, i.e., NaCl, KCl, CaCl2, ZnCl2, MgCl2, MgSO4 and Mg(ClO4)2 were added to investigate the capacity of water vapor adsorption. It was found that CaCl2 gave the best result. Therefore, CaCl2 of 20%, 30% and 40% by weight were varied. The longer the aging time is, the higher the adsorption efficiency becomes. Subsequently, zeolite (JRC-Z-HY5.3) of 10%, 20%, 30% and 40% by weight were added to obtain the porosity and strength of the desiccant. The adsorption capacity of the synthesized desiccant increased with an increase in calcium chloride. From SEM micrographs, the surfaces of the desiccants adding calcium chloride of 20% and 30% by weight were not smooth and showed porous structures after adding zeolite. The adsorption capacity of the desiccant adding calcium chloride and zeolite increased, when the contents of zeolite increased to 40% by weight. The SiO2-30-wt% CaCl2-40-wt% zeolite showed the highest adsorption capacity at 100% RH. The water vapor adsorption of the SiO2-30-wt% CaCl2-40-wt% zeolite at 40%, 60%, 85% and 100% RH were 32.14%, 54.48%, 74.30% and 96.84%, respectively.

KEYWORDS
zeolite, desiccant, sol-gel method, adsorption

INTRODUCTION

The desiccant is an important adsorbent in the industries which involve the humidity control of products, for instance, agricultural seeds, chemical or pharmaceutical products, natural gas, etc. The adsorbents mostly used in industries are silica gel, alumina gel, activated carbon and zeolite. In Thailand, some desiccants are imported so they are rather expensive. Many researchers have reported the synthesis of the adsorbents by sol-gel polymerization. The silica aerogels were synthesized via the sol-gel polymerization of tetramethlyorthosilicate (TMOS) by basic conditions and followed by supercritical drying with carbon dioxide (Tamon, et al., 1997). They found that the aerogels were mesoporous materials with high surface area. The mesopore can be controlled by changing the NH3/TMOS ratio. In addition, these aerogels were used to adsorb ethane, ethylene, propane and propylene. The amounts of the adsorbates adsorbed on the aerogels depended on the NH3/TMOS ratio. The water vapor adsorbents or the desiccants were also developed by the sol-gel route (Mrowiec-Bialon, et al., 1997 and 1999). Calcium chloride (CaCl2) was added to the sol-gel materials to improve the water vapor adsorption capacity. They found that the water adsorption capacity of SiO2-CaCl2 sol-gel composites could reach 1 kg of water/kg
of adsorbent, and remained stable during at least one hundred adsorption-desorption cycles. Other applications of sol-gel technology in coating, corrosion protection, ceramic synthesis and membrane synthesis are stated (Wright et al., 2001).

In this study, the inorganic and zeolite-hybrid desiccant was synthesized by the sol-gel method. The composition of inorganic compound and zeolite which gave the highest water vapor adsorption capacity was determined. Moreover, the regeneration temperature of the derived desiccant was also investigated.

MATERIALS AND METHODS

Preparation of silica xerogels (SiO$_2$) were synthesized by the sol-gel polymerization of tetraethylorthosilicate (TEOS). TEOS was diluted by ethanol (EtOH), deionized water (H$_2$O) and hydrochloric acid (HCl). The mixture was then stirred by the magnetic stirrer and hydrolyzed at the temperature of 50°C for 1 hour. The molar ratio of TEOS:EtOH:H$_2$O:HCl was 1:4.5:4:8x10$^{-4}$. After hydrolysis, EtOH and NH$_4$OH at molar ratio of TEOS:EtOH:NH$_4$OH =1:4.5:8x10$^{-3}$ was added to the mixture for condensation. The mixture was further stirred about 1 minute until the sol became gel. Then, the gel was aged for 7 days and 30 days at room temperature and dried in hot air oven at the temperature of 110 °C for 4 hours.

The silica xerogels were upgraded by adding the inorganic compound based on its water vapor adsorption capacity. The following inorganic compounds: sodium chloride (NaCl), potassium chloride (KCl), calcium chloride (CaCl$_2$), zinc chloride (ZnCl$_2$), magnesium chloride (MgCl$_2$), magnesium sulfate (MgSO$_4$) and magnesium perchlorate (Mg(ClO$_4$)$_2$) were used. The 20%, 30% and 40% by weight (dry basis) of the inorganic compound with the highest water vapor adsorption capacity was added to the silica xerogels in the condensation step. The aging times for 7 days and 30 days were also studied. Subsequently, zeolite (JRC-Z-HY5.3) of 10%, 20%, 30% and 40% by weight (dry basis) were added.

Adsorption experiment

The synthesized desiccants were used to adsorb water vapor at relative humidity (RH) of 40%, 60%, 85% and 100%. The experiments were done at room temperature in the adsorption chamber in which a digital balance connected with a computer was used. The weight of the desiccant during the adsorption process was recorded by the Winwedge program until the adsorption reached the equilibrium condition.

Physical characterization

Surface morphologies of the desiccants were investigated by the Scanning Electron Microscopy (SEM, 1455VP) at 8,000-time magnification. The regeneration temperature of the desiccant was determined by means of the thermal gravimetric analysis (TGA, ELR 23329C).

RESULTS AND DISCUSSION

The silica xerogel was synthesized by the sol-gel polymerization without adding the inorganic compound. After 7-day aging, the weight of SiO$_2$ was about 11.75 % of the initial gel weight. The surface morphology is shown in Figure 1. The SiO$_2$ was used to adsorb the water vapor and found that the water vapor adsorption was 46.60 %. The adsorption capacity of SiO$_2$ was improved by adding the inorganic compound during the condensation step. The amount of water vapor adsorbed of the inorganic
compounds were shown in Figure 2. From Figure 2, CaCl\(_2\) has the highest adsorption capacity (ca. 1.6 g of water/g of CaCl\(_2\)). Thus, CaCl\(_2\) was chosen. The inorganic-hybrid desiccants of CaCl\(_2\) 20\%, 30\% and 40 \% by weight were synthesized. It was found that the gelation time depended on the amount of CaCl\(_2\).

![Figure 1. The SEM photograph of SiO\(_2\).](image)

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![Figure 2. The water vapor adsorption capacities of various inorganic compounds.](image)

**Figure 2.** The water vapor adsorption capacities of various inorganic compounds.

The SEM micrographs of the inorganic-hybrid desiccants SiO\(_2\)-20-wt\% CaCl\(_2\), SiO\(_2\)-30-wt\% CaCl\(_2\) and SiO\(_2\)-40-wt\% CaCl\(_2\) were shown in Figures 3-5. It was observed that the surfaces of the SiO\(_2\)-20-wt\% CaCl\(_2\) and SiO\(_2\)-30-wt\% CaCl\(_2\) were rougher than that of SiO\(_2\). The SiO\(_2\) inorganic-hybrid desiccants and commercial silica gel were used to adsorb water vapor at 100 \%RH. The adsorption efficiencies were shown in Figure 6. The increase in CaCl\(_2\) to the SiO\(_2\) can improve the water vapor adsorption. The highest adsorption value of 85.52\% was observed from the SiO\(_2\)-40-wt\% CaCl\(_2\). The water vapor adsorptions of the inorganic-hybrid desiccants were higher than that of the commercial silica gel. After the adsorption, the desiccants were determined the rate of water vapor desorption for the regeneration temperature. From Figure 7 the desorption rate of the commercial silica gel was much lower.
Figure 3. The SEM photograph of the SiO₂-20-wt% CaCl₂.

Figure 4. The SEM photograph of the SiO₂-30-wt% CaCl₂.

Figure 5. The SEM photograph of the SiO₂-40-wt% CaCl₂.

Figure 6. The water vapor adsorption efficiencies of the inorganic-hybrid desiccants at 100 %RH.
Figure 7. The desorption rates of SiO₂ and SiO₂-CaCl₂.

than those of the inorganic-hybrid desiccants. However, the desorption rate of the inorganic-hybrid desiccants were almost the same. The regeneration temperature slightly increased with the increase in CaCl₂. The regeneration temperatures of the SiO₂, SiO₂-20-wt% CaCl₂, SiO₂-30-wt% CaCl₂ and SiO₂-40-wt% CaCl₂ were 89.15, 104.88, 108.56 and 154.23°C, respectively.

The effect of aging time on the water vapor adsorption of the desiccants is shown in Figure 8. The adsorption efficiencies of the desiccants with 30-day aging were higher than those of the desiccants with 7-day aging for both SiO₂ and SiO₂-20-wt% CaCl₂. Thus, the longer the aging time is, the higher the adsorption efficiency becomes.

Figure 8. The water vapor adsorption efficiencies of SiO₂ and SiO₂-20-wt%CaCl₂ at aging times of 7 and 30 days.

As found above, the water vapor adsorption of the inorganic-hybrid desiccant increased when CaCl₂ increased. However, the SiO₂-40-wt% CaCl₂ lost the dimensional strength after the water vapor
adsorption reached the equilibrium condition. Thus, the SiO₂-30-wt% CaCl₂ was chosen for further study. Zeolite (JRC-Z-HY5.3) which has high porosity were added to the inorganic-hybrid desiccant. It is found that the gellation time increased to more than 30 minutes and the phase separation occurred after adding the zeolite. The amount of NH₄OH in the mixture must be increased to reduce the gellation time. The inorganic and zeolite-hybrid desiccants were white, rigid, brittle and rough crystals. The SEM micrographs of the SiO₂-30-wt% CaCl₂-10-wt% zeolite, SiO₂-30-wt% CaCl₂-20-wt% zeolite, SiO₂-30-wt% CaCl₂-30-wt% zeolite and SiO₂-30-wt% CaCl₂-40-wt% zeolite were shown in Figures 9-12. The increase in voids or cavities increased with the amount of zeolite added.

![Figure 9. The SEM photograph of the SiO₂-30-wt%CaCl₂-10-wt% zeolite.](image)

![Figure 10. The SEM photograph of the SiO₂-30-wt%CaCl₂-20-wt% zeolite.](image)

![Figure 11. The SEM photograph of the SiO₂-30-wt%CaCl₂-30-wt% zeolite.](image)

![Figure 12. The SEM photograph of the SiO₂-30-wt%CaCl₂-40-wt% zeolite.](image)

Figure 9. The SEM photograph of the SiO₂-30-wt%CaCl₂-10-wt% zeolite.

Figure 10. The SEM photograph of the SiO₂-30-wt%CaCl₂-20-wt% zeolite.

Figure 11. The SEM photograph of the SiO₂-30-wt%CaCl₂-30-wt% zeolite.

Figure 12. The SEM photograph of the SiO₂-30-wt%CaCl₂-40-wt% zeolite.

The water vapor adsorption at 100%RH of the SiO₂-30-wt% CaCl₂ with different amounts of zeolites are shown in Figure 13. It is found that the adsorption efficiency at the equilibrium condition and the adsorption rate increased when the contents of zeolite increased. The maximum value of 96.84 % was obtained from the SiO₂-30-wt% CaCl₂-40-wt% zeolite, which was higher than that of the SiO₂-30-wt% CaCl₂ around 27 %. This may be due to the high porosity of zeolite. Figure 14 shows the water vapor desorption rates. The desorption rates and the regeneration temperatures of each desiccant were not significantly different. The regeneration temperature slightly increased with the increase in zeolite. The
regeneration temperatures of the SiO$_2$-30-wt% CaCl$_2$-10-wt% zeolite, SiO$_2$-30-wt% CaCl$_2$-20-wt% zeolite, SiO$_2$-30-wt% CaCl$_2$-30-wt% zeolite and SiO$_2$-30-wt% CaCl$_2$-40-wt% zeolite were 122.94, 126.32, 121.25 and 141.52°C, respectively.

In addition, the effect of the relative humidity on the water vapor adsorption was shown in Figure 15. The water vapor adsorption and the equilibrium time increased with the relative humidity. This was due to the effect of mass transfer. The high concentration of the water vapor increased the driving force to diffuse into the pore of the desiccant. The water vapor adsorption of the SiO$_2$-30-wt% CaCl$_2$-40-wt% zeolite at 40%, 60%, 85% and 100 %RH were 32.14%, 54.48%, 74.30% and 96.84 %, respectively.
Figure 15. The water vapor adsorption efficiencies of SiO₂-30-wt%CaCl₂-40-wt% zeolite at various relative humidities.

The amounts of water vapor adsorbed on the SiO₂-30-wt% CaCl₂-40-wt% zeolite at various relative pressures (p/p₀) were fitted well by Langmuir equation as shown in Figure 16.

Figure 16. Logarithmic Langmuir equation for water vapor adsorption of SiO₂-30-wt% CaCl₂-40-wt% zeolite.

CONCLUSIONS

The silica xerogels used as the desiccant can be synthesized by sol-gel polymerization using the TEOS:H₂O:EtOH:HCl molar ratio of 1:4.5:4:8x10⁻⁴. The advantages of sol-gel polymerization are that the preparation procedures are not complicated and consume low energy. The water vapor adsorption of the desiccant was rather low (ca. 46%). Its capacity was enhanced by adding CaCl₂ and zeolite. The appropriate compositions of CaCl₂ and zeolite were 30% and 40% by weight (dry basis), respectively. The SiO₂-30-wt% CaCl₂-40-wt% zeolite has the high porosity and dimensional strength. The highest water vapor adsorption is 96.84%. The aging time of the desiccant affects the adsorption capacity. The
desiccant with the aging time of 30 days can adsorb water vapor more than the desiccant with aging time of 7 days.

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REFERENCES