



Calcined hydrotalcite-like compounds as catalysts for hydrolysis carbonyl sulfide at low temperature

Hongyan Wang, Honghong Yi*, Ping Ning, Xiaolong Tang, Lili Yu, Dan He, Shunzheng Zhao

Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming, 650093, PR China

ARTICLE INFO

Article history:

Received 6 March 2010

Received in revised form 11 October 2010

Accepted 12 October 2010

Keywords:

Hydrotalcite-like compounds

Coprecipitation

Carbonyl sulfide

Hydrolysis

Mesoporous

ABSTRACT

Catalytic systems based on mixed oxides catalysts derived from a series of hydrotalcite-like compounds through the coprecipitation method were investigated for hydrolysis of carbonyl sulfide (COS) in a fixed-bed reactor. The effects of pH, temperature of synthesis and hydrothermal treatment on catalytic activity were studied. Furthermore, the samples were characterized by pH titration, X-ray diffraction (XRD) and Brunauer–Emmett–Teller method (BET). The results showed that the catalysts could be prepared by precipitating solution of (Co + Ni)/Al at pH 9.0, synthetic temperature at 25 °C, and then hydrothermal treatment at 50 °C for 12 h. The XRD patterns showed the precursors had typical hydrotalcite structure and the catalysts were mixed oxides. All catalysts could be considered mesoporous.

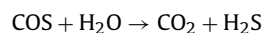
© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Over the past decades it has become increasingly apparent that emissions of sulfur compounds into the atmosphere have been unacceptably high and the removal of sulfur-containing compounds is one of the most important technologies. Especially, carbonyl sulfide (COS) which widely exists in natural gas, petroleum gas, water gas and semiwater gas is one of the major components of organic sulfur compounds [1–6]. Not only does COS affect the environment by leading to the formation of acid rain, but also it presents problems within industry itself. Trace amount of COS results in the deactivation of catalysts and leads to corrosion of reaction equipments. Besides, untreated COS transports into the stratosphere, where it can form sulfur dioxide (SO₂) and accelerate photochemical reaction, converts into sulfate aerosols eventually. Therefore, it is of great significance to remove COS.

Conventional desulfurization technologies do not remove or significantly affect COS. Since COS is normally small quantity and inactive compared to hydrogen sulfide (H₂S), removal of COS is not concerned yet as much as H₂S. In addition, the removal of COS has been reported to be more difficult at low temperature in the range from room temperature to around 200 °C, since COS is rather inactive probably due to its neutrality and similarity to carbon dioxide (CO₂) [7–10]. The hydrolysis of COS has recently been focused on because the hydrolysis products, CO₂ and H₂S, are much easier to

be removed than COS [11]. Catalytic hydrolysis of COS follows the reaction:



The hydrotalcite-like compounds (HTLCs) are a class of naturally occurring anionic clays. The general formula is $[\text{M}^{(II)}_{1-x}\text{M}^{(III)}_x(\text{OH})_2]_x(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^(II) and M^(III) are divalent and trivalent cations, respectively, which occupy octahedral sites in the hydroxide layers. The value of *x* is equal to the ratio M^(III)/(M^(II) + M^(III)), whereas Aⁿ⁻ is an exchangeable anion [12,13]. The positive charges in the hydroxide sheets result from substitution of trivalent cations for divalent cations, and the M^(III)/(M^(II) + M^(III)) ratio (i.e., *x*) represents the layer charge density. The interlayer spaces between hydroxide sheets are filled by water and anions (Aⁿ⁻) that counter balance the positive charges in the hydroxide sheets [14]. The natural occurrence of these materials is rare, but their synthesis can be conducted in laboratory at relatively low cost by varying the preparation conditions [15].

It is well known that once the HTLCs are calcined, the layered array collapses and mixed oxides are obtained. The products of calcinations which are usually called calcined layered double hydroxide (LDO) containing highly disperse, small crystals of reducible metal oxides may show interesting catalytic properties [16]. The LDO have been paid more attention owing to their larger surface area and less diffusion resistance than those of HTLCs. Moreover, LDO have the advantage of porous structure and both of abundant acid and basic sites [17]. Therefore, the HTLCs have been studied as catalysts or catalyst precursors to a great extent.

* Corresponding author. Tel.: +86 0871 5170905; fax: +86 0871 5126319.
E-mail address: yhhtxl@126.com (H. Yi).

Previous papers have been devoted to the study of COS hydrolysis on metal oxides such as Al_2O_3 , ZrO_2 , TiO_2 or their mixtures [18]. Many investigations showed that the alkaline was in favor of hydrolysis of COS and the basic sites were the active centers [19–23]. As a result, it is necessary to research the base environment-friendly catalysts for COS hydrolysis. Given the LDO have abundant acid and basic sites and we did not find any systematic work on the hydrolysis of COS on these materials, this paper presents a study of the catalytic hydrolysis of COS by Co/Ni/Al mixed oxides obtained by calcining the corresponding HTLCs. It appears as a promising catalyst for the hydrolysis reaction of COS. The main advantages of these materials are their easy preparation and low cost. The main object of this paper is to investigate the effect of preparation conditions of HTLCs precursor on catalytic activity at relatively low temperature (50°C), including pH, temperature of synthesis and hydrothermal treatment.

2. Methods and materials

2.1. Catalyst preparation

The precursor Co/Ni/Al HTLCs were synthesized by the hydrothermal method reported previously [9]. A mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($[\text{Co}^{2+}] + [\text{Ni}^{2+}] + [\text{Al}^{3+}] = 0.075 \text{ mol}$) was dissolved with distilled water. Unless specified otherwise, the Co/Ni molar ratio was 0.25 and $M^{(II)}/M^{(III)}$ was 2. A second solution containing NaOH (calculated amount required for complete reaction with the divalent and trivalent metal ions) and Na_2CO_3 (0.075 mol) in distilled water was prepared. The metal nitrates solution was added to the aqueous alkali slowly under mechanical stirring at different synthetic temperatures, and then the solution was stirred for another 30 min after synthesis. The pH of the solution was adjusted by HCl and Na_2CO_3 . The resulting slurry was aged at different temperatures for 12 h. The precipitate was then filtered with distilled water until the filter liquor attained a pH of 7. The resulting solid was dried at 60°C . To produce mixed oxides, the HTLCs were calcined in air at 350°C for 2 h.

2.2. Characterization

X-ray diffraction (D/MAX-2200) pattern were obtained with a Rigaku diffractometer operated at 36 kV and 30 mA by using Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) at a rate of $5^\circ/\text{min}$ from $2\theta = 20^\circ$ to 80° . The powdered samples were analyzed without previous treatment after deposition on an agate mortar. The identification of crystalline phases was made by matching the JCPDS files.

Specific surface areas and pore size distribution for the samples were determined by N_2 adsorption using a Autosorb-1-C instrument. The samples were first outgassed at 573 K for more than 12 h before adsorption isotherms were generated by dosing nitrogen (at 77 K) on the catalysts.

2.3. Measurement of catalytic activity

The catalytic activity tests were carried out in a fixed-bed quartz reactor (4 mm i.d. \times 100 mm length) under atmospheric pressure. Fig. 1 shows the fixed-bed catalytic system used for COS hydrolysis. For COS hydrolysis, the COS from gas cylinder (1% COS in N_2) was diluted by nitrogen (99.99%) to set concentration. Delivery of the feed gases to the reactor was controlled by means of flowmeters except H_2O , which was introduced through a saturator. Then the reactants reacted in the reactor. In view of environment, the off-gas was absorbed by NaOH solution. The gas hourly space velocity (GHSV) was controlled by mass flow controllers and the

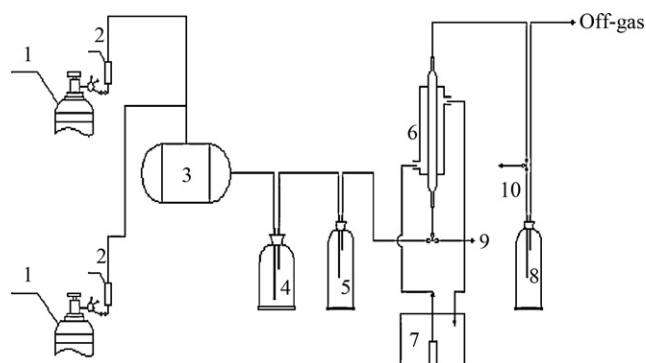


Fig. 1. The catalytic system for COS hydrolysis. (1) Cylinder gas (N_2 , COS), (2) mass flow meter, (3) mixer, (4) extractor, (5) saturator, (6) reactor, (7) circulating pump, (8) tail gas absorber, (9) inlet sample point and (10) outlet sample point.

temperature of this reactor was controlled to 50°C over its entire length by water-bath with circulating pump, with accuracy $\pm 1^\circ\text{C}$. The conversion of COS was determined by analyzing the inlet and outlet concentration of COS using a GC-508 gas chromatography with a flame photometric detector (FPD). The COS conversion was obtained by the following equation:

$$\text{COS conversion (\%)} = \frac{\text{COS}_{\text{inlet}} - \text{COS}_{\text{outlet}}}{\text{COS}_{\text{inlet}}} \times 100\%$$

3. Results and discussion

3.1. Effect of the pH values

3.1.1. pH titration curves

The pH value was changed with adding precipitants to the various metal ions coexist system, which could result in fractional precipitation of metal ions. Changing of pH value directly affect the layered structure of hydrotalcite-like compounds and crystalline phase. The evolution of pH during the coprecipitation of Ni and Al species and the nature of the precipitates were also carefully studied in precious work [24,25]. In this paper, the pH titration curves of Co/Ni/Al simplex solution at room temperature with 1.0 mol/l NaOH titrating 1.0 mol/l $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1.0 mol/l $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.5 mol/l $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ are shown in Fig. 2.

As seen in Fig. 2, the pH titration plateau of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ranges from 6.5 to 8.2, indicating the $\text{Ni}(\text{OH})_2$ precipitation is generated at 6.5 and finished at 8.2. The extent of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

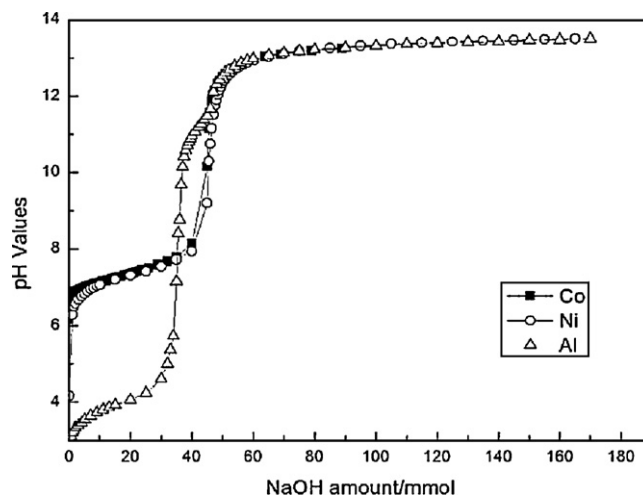


Fig. 2. The pH titration curves of Co/Ni/Al simplex solution.

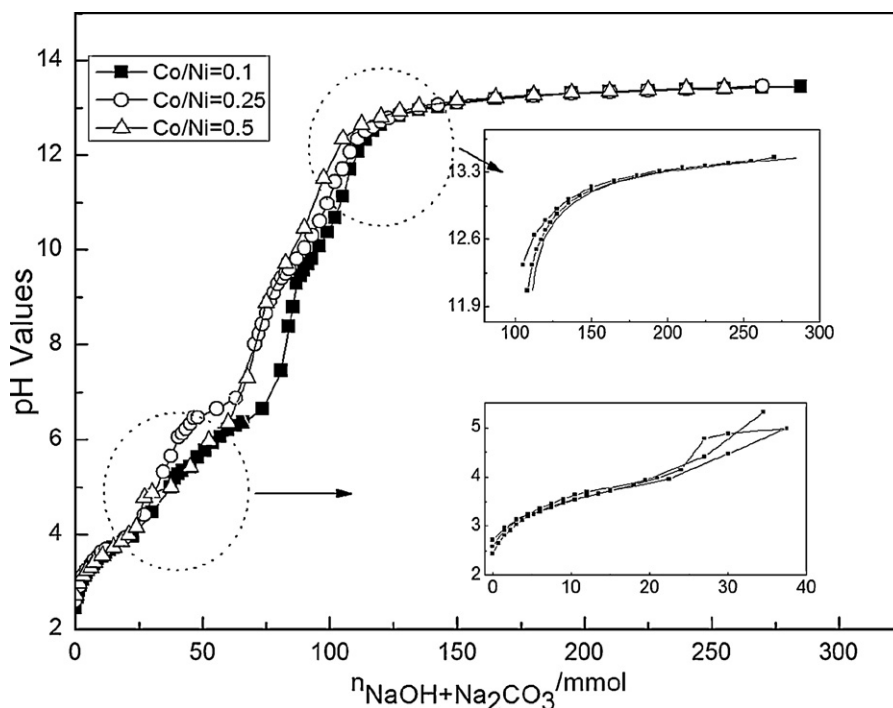


Fig. 3. The pH titration curves of Co/Ni/Al mixed solution.

generating $\text{Al}(\text{OH})_3$ is 3.3–4.8. The plateau of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ approaches to that of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. From Fig. 2, the pH range of divalent and trivalent ions generating precipitation is quite different. Fig. 3 is the pH titration curves of different ratios of Co/Ni solution by adding mixed solution of $\text{NaOH}-\text{Na}_2\text{CO}_3$ with fixed $n(\text{Co} + \text{Ni})/n(\text{Al}) = 2$. As shown in Fig. 3, there are three unobvious plateaus in the titration, and there is only difference in the size range of plateaus with different ratios. The plateau of 3.0–4.2 is the polymerization and precipitation of Al^{3+} [24,25]. However, excessive amount of metal ions in the form of hydroxides and a certain amount of hydrotalcite existed in the range of 12.8–13.4. And the middle plateau may be the stage of HTLCs formation.

3.1.2. Effect of the pH values on catalytic activity

As mentioned above, the pH value of system is a key factor in the synthesis of HTLCs and LDO. The relationships between the pH and activities of hydrolysis COS are shown in Fig. 4 at 50°C , 3000 h^{-1} .

As shown in Fig. 4, there is a significant difference of activity among the catalysts. The conversion of more than 99% COS is found to increase at 7–9.5, and then decrease. Moreover, the change of activity is insignificant at pH of 9–11. The results indicate that there is an optimal value of pH around 9–11. In order to investigate the structure of the catalysts, the phase and crystalline orientation of the HTLCs precursors were determined by XRD and presented in Fig. 5. All the diagrams recorded are consistent with the presence of typical patterns of HTLCs, showing the three characteristic basal reflections due to planes (003), (006), (009) and (110). The diffraction peaks in the diagrams of the precursors at low pH are very sharp and intense, while those of high pH samples show a small deviation for plane (003), especially for the sample pH 11, suggesting a low crystallinity and less organized stacking arrangement. However, though the crystallinity of 11 was not good as the sample of 7, the activity was much better than it. More than 95% conversion of COS could sustain for about 420 min at 11. In contrast,

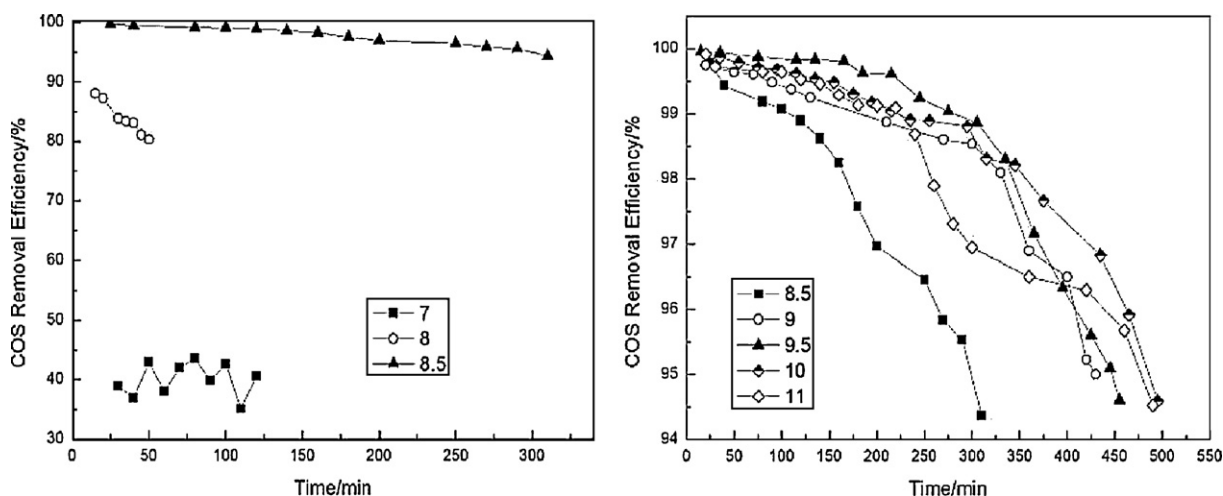


Fig. 4. Effect of pH values on COS removal efficiency.

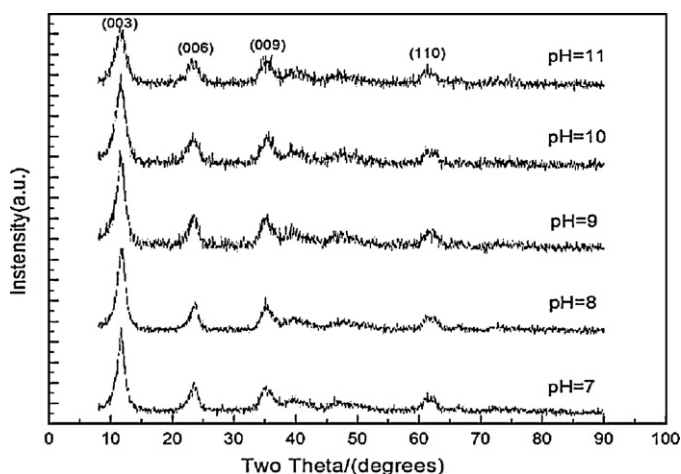


Fig. 5. XRD patterns for Co/Ni/Al HTLCs precursors synthesized at different pH values.

the conversion of 7 was less than 40% for 30 min. The phenomenon may relate to that the alkaline is in favor of hydrolysis of COS and the basic sites are the active centers, which promotes the hydrolytic reaction.

3.2. Effect of synthetic temperature

In order to obtain the HTLCs precursor with large particles and integrated structure, mixing salt and alkali under constantly mechanical stirring using special hot solution is necessary. Therefore, the temperature may have impact on the precursor. In order to investigate the effect of synthetic temperature on hydrolysis, the samples were synthesized at 25 °C, 35 °C and 45 °C. From Fig. 6, the efficiency decreased along with the temperature increasing. It can conclude that high temperature is not in favor of the reaction and the optimal synthetic temperature is 25 °C. As seen in Fig. 6, the temperature has little influence on the conversion, especially at the range of 25–35 °C. In the case of the 25 °C and 35 °C samples, the conversion above 99% was about 100 min and the 95% conversion was observed for about 420 min. In contrast, for 45 °C it was above 99% for 20 min and 95% could only sustain about 300 min.

Table 1 summarizes the surface area, pore volume and pore diameter of samples at different synthetic temperatures. The dif-

Table 1

Structure parameters of catalysts at different synthetic temperatures.

Synthetic temperature	Surface area	Total pore volume	Average pore diameter
25 °C	289.8 m ² /g	4.424E-01 cm ³ /g	6.106 nm
35 °C	234.5 m ² /g	3.939E-01 cm ³ /g	6.718 nm
45 °C	289.5 m ² /g	4.814E-01 cm ³ /g	6.650 nm

ference of porosity is not clear. The sample of 35 °C has the lowest surface about 234.5 m²/g. However, there is little difference between 25 °C and 45 °C, with 289.8 m²/g and 289.5 m²/g, respectively. It is interesting that the material of 35 °C has the lowest surface area and pore volume, however, the average pore diameter is biggest. On the other hand, although surface area changed inconspicuously in the case of 25 °C and 45 °C, the total pore volume and average pore diameter increased with the increase of temperature, which is supported by the results of pore size distributions presented in Fig. 7.

Pore size characteristics of as-synthesized catalysts presented in Fig. 7 shows the absence of any significant pore structure. It is clear that all of these materials can be considered mesoporous, i.e., having pores at 39.68–59.51 Å. It should also be noted that, despite the change in surface area and pore volume got, all of materials studied have the same pore size distribution. Fig. 8 shows the adsorption and desorption isotherms of samples. All samples present type IV isotherms according to IUPAC classification [26], which corresponds to mesoporous solids. Micropore surface area is extremely small and tends to zero which is preferred from the metal ion adsorption point of view. The same type of isotherms was exhibited by the other materials prepared in this study. Furthermore, hysteresis loops are type H3, indicating the presence of slit-shaped pores with non-uniform size and shape, created by the collapse of brucite-like sheets upon calcinations [27].

3.3. Effect of temperature of the hydrothermal treatment

According to the theory of crystallochemical, there are two steps in the process of crystal formation, including nucleation and crystal grain-growth. When the precipitant and salt solution mixed under certain conditions, a large number of crystal nucleus form and constantly grow into precipitate particles. Moreover, further crystallization is in favor of the process. Hydrothermal treatment can maintain a good crystalline structure and high particle uniformity. The results obtained from COS hydrolysis at different tempera-

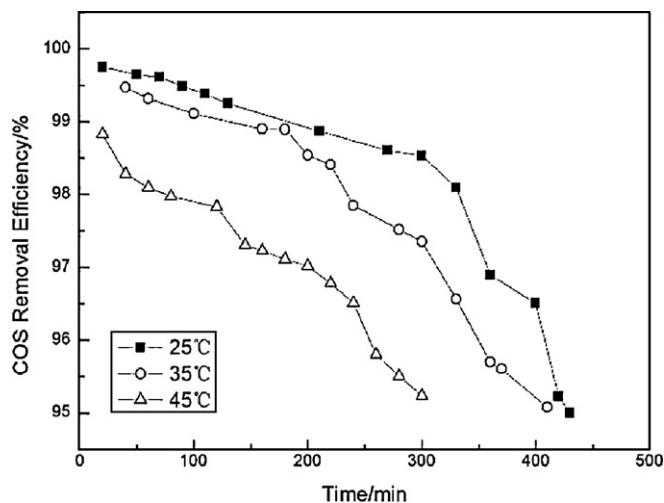


Fig. 6. Effect of synthetic temperature on COS removal efficiency. Reaction condition: reaction temperature = 50 °C, GHSV = 3000 h⁻¹, temperature of saturator = 25 °C.

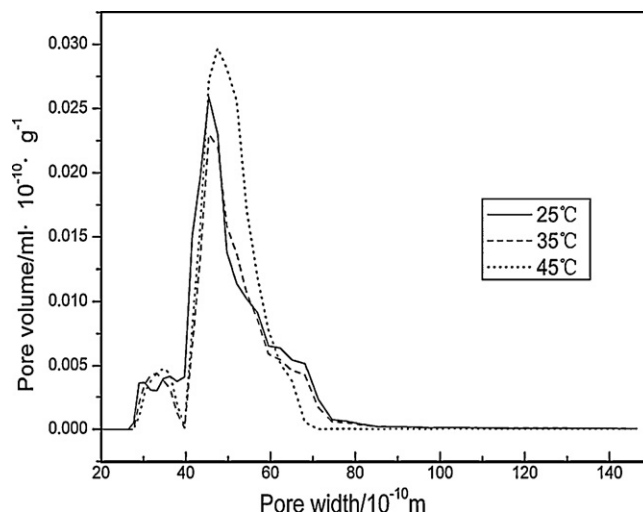


Fig. 7. Pore size distribution of catalysts synthesized at different temperatures.

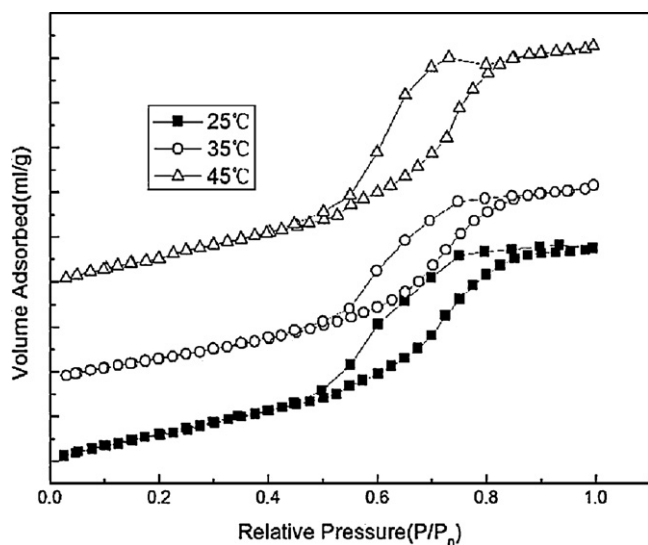


Fig. 8. N_2 adsorption-desorption isotherms of catalysts at different synthetic temperatures.

Table 2

Structure parameters of catalysts at different temperatures of hydrothermal treatment.

Synthetic temperature	Surface area	Total pore volume	Average pore diameter
40 °C	229.8 m ² /g	4.118E-01 cm ³ /g	7.168 nm
50 °C	205.3 m ² /g	4.031E-01 cm ³ /g	7.854 nm
60 °C	226.7 m ² /g	4.758E-01 cm ³ /g	8.396 nm
70 °C	260.2 m ² /g	6.354E-01 cm ³ /g	9.760 nm

tures of hydrothermal treatment at 50 °C, 3000 h⁻¹ are collected in Fig. 9. From the results shown in Fig. 9, the change of conversion is little at different temperatures of the hydrothermal treatment. The 95% conversion can sustain more than 480 min at this range for all samples, which indicates that the temperature range of the hydrothermal treatment can meet the reaction.

The textural properties and pore size distributions of catalysts are typically shown in Table 2 and Fig. 10, respectively. From Table 2, the surface area and total pore volume initially decreases

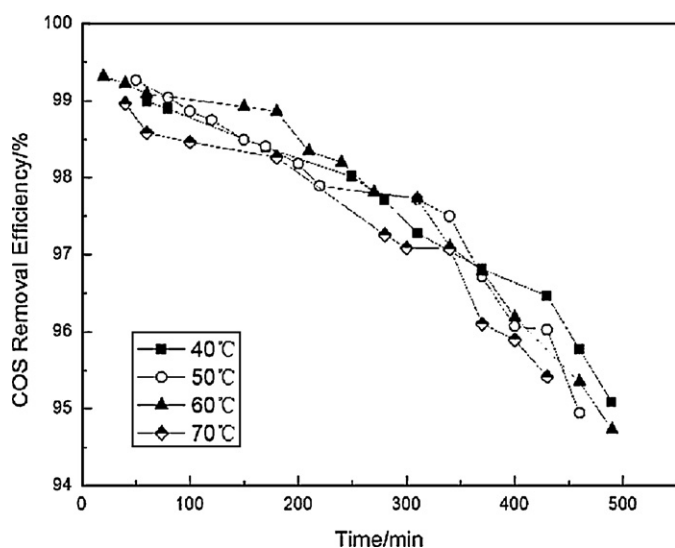


Fig. 9. Effect of temperature of the hydrothermal treatment on COS removal efficiency.

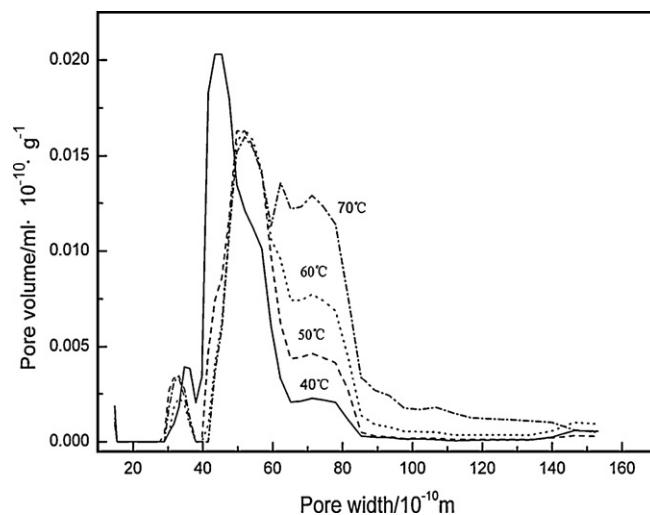


Fig. 10. Pore size distribution of catalysts at different temperatures of hydrothermal treatment.

and then increase with the temperature increasing. The maximum specific surface area and total pore volume of this series of catalysts reaches 260.2 m²/g and 0.6354 cm³/g when the temperature of hydrothermal treatment is 70 °C. However, the average pore diameter increases along with the temperature increasing. As seen in Fig. 10, in case of 40 °C, the volume of pore is obviously more than the other three samples at the range of 39.69–62.24 Å. The results can explain why it has the lowest average pore diameter. The difference 50 °C, 60 °C and 70 °C samples is the pore between 62.24 Å and 81.54 Å. With increasing the temperature, the volume of pore increased at the range of 62.24–81.54 Å. The trend is coincided with the total pore volume. Nitrogen adsorption-desorption isotherms of samples are displayed in Fig. 11. The results are the same as the synthetic temperature. All samples present type IV isotherms, which indicate they are mesoporous solids. The beginning of the isotherms was filled with microporous. Then capillary condensation occurs in the mesopore followed high partial pressure, which make isotherm continue upward, and adsorption amount increases. When the relative pressure is close to 1, the adsorption capacity reaches saturation.

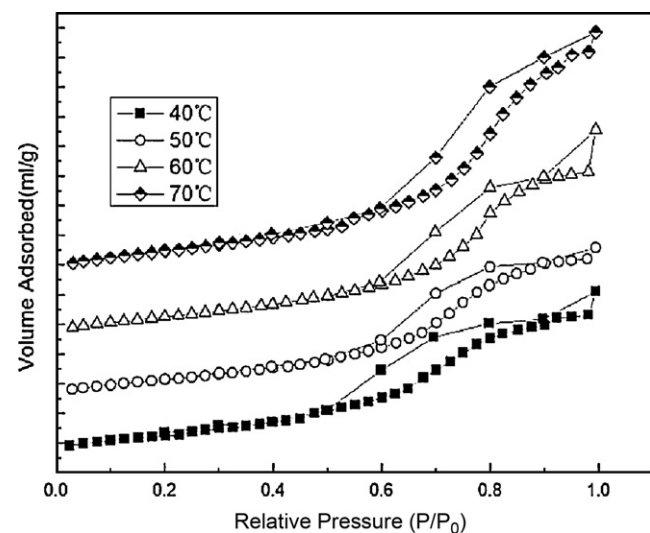


Fig. 11. N_2 adsorption-desorption isotherms of catalysts at different temperatures of hydrothermal treatment.

4. Conclusions

In this study, hydrolysis of COS on calcined hydrotalcite-like compounds was observed. The catalysts removed COS very effectively at a relatively low temperature of 50 °C. The results indicate that the pH values and synthetic temperature has influence on the hydrolysis. High synthetic temperature is not in favor of the reaction and the optimal temperature is 25 °C. There are three plateaus in the process of titrating the mixed salt solution with alkali solution. From the XRD, the precursors show the typical structure of HTLCs at different pH values, and the difference is little deviation of (003) peak, which may cause the difference of activity. The XRD characterization and catalytic activity indicates the alkaline is in favor of hydrolysis of COS and the basic sites are the active centers, which promotes the hydrolytic reaction. The change of conversion at different temperatures of hydrothermal treatment is not obvious, so the temperature range of the hydrothermal treatment in the study can meet the need of the reaction. The BET results show the adsorption and desorption isotherms of all samples present type IV isotherms according to IUPAC classification, which corresponds to mesoporous solids. Further studies aimed at improving the catalysts from hydrotalcite-like compounds are in progress.

Acknowledgments

The work was supported by National Natural Science Foundation (50908110), National High Technology Research and Development Program of China (2008AA062602), China Post-doctoral Science Foundation (20090451431) and Young and Middle-aged Academic and Technical Back-up Personnel Program of Yunnan Province (2007PY01-10).

References

- [1] P.D.N. Svoronos, T.J. Bruno, Carbonyl sulfide: a review of its chemistry and properties, *Ind. Eng. Chem. Res.* 41 (2002) 5321.
- [2] C. Rhodes, S.A. Riddel, J. West, et al., The low-temperature hydrolysis of carbonyl sulfide and carbon disulfide: a review, *Catal. Today* 59 (2000) 443–464.
- [3] J. Shangguan, C.-h. Li, H.-x. Guo, Disulfide over alumina based catalysts. I. Study on activities of COS and CS₂ hydrolysis, *J. Nat. Gas Chem.* 7 (1998) 16–23.
- [4] Y.-q. Zhang, Z.-b. Xiao, J.-x. Ma, Hydrolysis of carbonyl sulfide over rare earth oxysulfides, *Appl. Catal. B* 48 (2004) 57–63.
- [5] L.-t. Liang, The study on modified alumina based catalyst for high concentration carbonyl sulfide hydrolysis, D, Taiyuan University of Technology, Taiyuan, 2005.
- [6] H.-l. Fan, C.-h. Li, H.-x. Guo, A study on removal of organic sulfur compound with modified activated carbon, *J. Nat. Gas Chem.* 8 (2) (1999) 151–156.
- [7] K. Sakanishi, Z. Wu, A. Matsumura, et al., Simultaneous removal of H₂S and COS using activated carbons and their supported catalysts, *Catal. Today* 104 (2000) 94–100.
- [8] B. Peter Williams, N.C. Young, J. West, et al., Carbonyl sulphide hydrolysis using alumina catalysts, *Catal. Today* 49 (1999) 99–104.
- [9] D.E. Sparks, T. Morgan, P.M. Patterson, et al., New sulfur adsorbents derived from layered double hydroxides. I. Synthesis and COS adsorption, *Appl. Catal. B* 82 (2008) 58–66.
- [10] Y.-c. Liu, H.E. Hong, Y.-j. Mu, Heterogeneous reactivity of carbonyl sulfide on α -Al₂O₃ and γ -Al₂O₃, *Atmos. Environ.* 42 (2008) 960–969.
- [11] X.-x. Li, Y.-x. Liu, X.-h. Wei, Hydrolysis of carbonyl sulfide in binary mixture of diethylene glycol diethyl ether and water, *Chin. J. Chem. Eng.* 13 (2005) 234–238.
- [12] K.-H. Goh, T.-T. Lim, Z. Dong, Application of layered double hydroxides for removal of oxyanions: a review, *Water Res.* 42 (2008) 1343–1368.
- [13] L. Liang, L. Li, Adsorption behavior of calcined layered double hydroxides towards removal of iodide contaminants, *J. Radioanal. Nucl. Chem.* 273 (2007) 221–226.
- [14] Y.-F. Chao, P.-C. Chen, S.-L. Wang, Adsorption of 2,4-D on Mg/Al-NO₃ layered double hydroxides with varying layer charge density, *Appl. Clay Sci.* 40 (2008) 193–200.
- [15] P.C. Pavan, G.d.A. Gomes, J.B. Valim, Adsorption of sodium dodecyl sulfate on layered double hydroxides, *Micropor. Mesopor. Mater.* 21 (1998) 659–665.
- [16] J.S. Valente, J. Hernandez-Cortez, M.S. Cantu, et al., Calcined layered double hydroxides Mg-Me-Al(Me:Cu,Fe,Ni,Zn) as bifunctional catalysts, *Catal. Today* (2009), doi:10.1016/j.cattod.08.020.
- [17] W. Shi, M. Wei, L. Jin, et al., Calcined layered double hydroxides as a “biomolecular vessel” for bromelain: immobilization, storage and release, *J. Mol. Catal. B: Enzym.* 47 (2007) 58–65.
- [18] E. Laperdrix, I. Justin, G. Costentin, et al., Comparative study of CS₂ hydrolysis catalyzed by alumina and titania, *Appl. Catal. B* 17 (1998) 167–173.
- [19] B. Peter, W. Nvicola, C. Young, et al., Carbonyl sulphide hydrolysis using alumina catalysts, *Catal. Today* 49 (1999) 99–104.
- [20] P.D. Clark, N.I. Dowing, M. Huang, Conversion of CS₂ and COS over alumina and titania under Claus process condition: reaction with H₂O and SO₂, *Appl. Catal. B* 31 (2001) 107–112.
- [21] E. Laperdrix, I. Justin, G. Costentin, et al., Comparative study of CS₂ hydrolysis catalyzed by alumina and titania, *Appl. Catal. B* 17 (1998) 167–173.
- [22] J. Shangguan, H.-x. Guo, The surface basicity and catalysis over the alumina based catalysts for COS and CS₂ hydrolysis, *J. Mol. Catal. (China)* 11 (1997) 337–342.
- [23] C.-h. Li, H.-x. Guo, S.-s. Tan, Study on the alkalized γ -Al₂O₃ catalyst for its base strength distribution and catalytic activity, *J. Mol. Catal. (China)* 8 (1994) 305–311.
- [24] Y.-m. Shen, J. Wu, H. Zhang, et al., Study of condition for synthesizing Ni-Mg-Al hydrotalcite like compounds, *Mater. Rev.* 9 (2005) 131–133.
- [25] C. Ruby, M. Abdelmoula, R. Aissa, et al., Aluminium substitution in iron(II-III)-layered double hydroxides: formation and cationic order, *J. Solid State Chem.* 181 (2008) 2285–2291.
- [26] M.D. Donohue, G.L. Aranovich, Classification of Gibbs adsorption isotherms, *Adv. Colloid Interface Sci.* 76–77 (1998) 137–152.
- [27] J.S. Valente, F. Tzompantzi, J. Prince, et al., Adsorption and photocatalytic degradation of phenol and 2,4 dichlorophenoxyacetic acid by Mg-Zn-Al layered double hydroxides, *Appl. Catal. B* 90 (2009) 330–338.