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Preparation of Ti–Si mixed oxides by sol–gel one step hydrolysis

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Abstract

Ti–Si mixed oxides of various TiO_2 contents were prepared via sol–gel one step hydrolysis with economical $TiCl_4$ and tetraethoxy silane (TEOS) as the precursors and characterized by means of N_2-physisortion, FT-IR and XRD. The effects of TiO_2 content on the gelation time were studied. The influences of calcination temperature on the mixed oxide of 20 wt.% TiO_2 (20TiSi) were also studied. The results indicate that titanium is in four-fold coordination with oxygen in the SiO_4^{4-} structure and Ti–O–Si band is observed by FT-IR. The mixed oxides with large TiO_2 content exist on the pattern of amorphous material but not anatase. The composites have high specific surface areas, up to 681.5 m^2/g, and a narrow pore size distribution. The ratio of the micropore declines with the increase of TiO_2 content. 20TiSi has good thermal stability and still possesses 11 m^2/g after calcination at 1100 °C. Within the range of tested calcination temperature, Ti–O–Si band does not break. TiO_2 is well dispersed as the form of amorphous in 20TiSi calcined at 1100 °C.

Keywords: Ti–Si mixed oxides; Sol–gel one step hydrolysis; Gelation time

1. Introduction

Titania–silica mixed oxide materials have received much attention over recent years because of their physical properties and lend them to a number of technological uses. These materials have been used as ultra-low-thermal-expansion glasses [1], catalysts, catalyst support [2,3] and thin films with tailored refractive indices [4]. The properties of titania–silica binaries are strongly dependent on their chemical composition, homogeneity, and texture, which in turn depend on synthesis conditions. Homogeneity at atomic level is especially important. And there are many methods to prepare Ti–Si mixed oxides, such as conventional solid-state mixing, coprecipitation and sol–gel process. Among these methods, sol–gel process is an effective route. Sol–gel synthesis based on the hydrolysis and subsequent condensation of metal alkoxide precursors provides a low temperature route to materials with a high level of atomic mixing and a high degree of porosity. When the sol–gel process is used to prepare titania–silica mixed materials, the different rates of hydrolysis of the silicon and titanium alkoxides can cause phase separation, producing Ti- and Si-rich regions. In order to solve this problem, the researchers [5,6] took two kinds of routes. Firstly, the Si alkoxides partially hydrolyzed prior mixed with the Ti alkoxides. Secondly, Ti alkoxides reacted with acetylacetone in order to produce less reactive precursors which in turn react with prehydrolysed solution of Si alkoxides. The above measures complicate the procedure and titanium alkoxides make the cost increase. In this work we used a simple sol–gel method to prepare Ti–Si mixed oxides avoiding the prehydrolysis of silicon alkoxide and organic modification of titanium alkoxide.

Moreover, in a high temperature reactions, it is very important that the catalyst has good thermal stability. The study on the stability of catalysts becomes more and more important. For example, Yu et al. [7] studied the phase transformation under different calcination temperature, and Yan et al. [8] reviewed the effect of heat temperature on the Ti–Si composites.

In this paper, we used the cheap inorganic titanate—$TiCl_4$ as the starting material and prepared the Ti–Si mixed oxides by sol–gel one step hydrolysis process in the existence of acetic acid. The properties of the mixed oxides were studied by means of N_2-physisorption, XRD, FT-IR, etc. And the effects of calcination temperature on the Ti–Si mixed oxide of 20 wt.% TiO_2 were also investigated.

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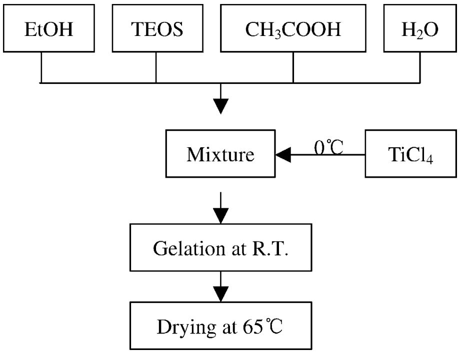

Fig. 1. The procedure for preparing Ti–Si mixed oxides.

2. Experimental

Ti–Si mixed oxides with different TiO_2 contents were prepared with the following precursors: tetraethyoxysilane (TEOS), $TiCl_4$, acetic acid (CH_3COOH) and distilled water. And ethanol was used as a mutual solvent. The procedure was shown in Fig. 1. The amounts of TEOS and $TiCl_4$ were varied to obtain mixed oxides with TiO_2 content from 0 to 100 wt.%, and the corresponding molar ratios of TEOS:$TiCl_4$:EtOH:H_2O:CH_3COOH were x:y:7($x + y$):10($x + y$):2($x + y$). Firstly, EtOH, TEOS, H_2O and CH_3COOH were mixed by stirring, then $TiCl_4$ was added to at 0 °C under vigorous stirring. The resulting sol was stirred for a few minutes before gelling at room temperature and drying at 65 °C. All samples were heated to 400 °C in atmosphere and marked with xTiSi, in which x displayed the normal TiO_2 content in weight percentage.

Moreover, the effects of varied calcination temperature were studied with 20TiSi. The specimen names were indicated as follows: 20TiSi-300, 20TiSi-400, 20TiSi-500, 20TiSi-700, 20TiSi-900, 20TiSi-1100. For comparison, 20TiSi-900 was prepared, in which SiO_2 and TiO_2 gained by sol–gel method were mixed by the weight ratio of 1:4 and were calcined at 900 °C in atmosphere.

3. Characterization of the Ti–Si mixed oxides

3.1. Determination of textural properties

The specific surface area of the mixed oxides with different TiO_2 weight content and 20TiSi calcined at different temperature were determined by nitrogen physisorption at 77 K using CE SORPTOMIC 1990 SERIES. The total pore volume (and the average diameter of pore, etc.) were obtained by the Barrett–Joyner–Halenda (BJH) method from adsorption/desorption curves of N_2 at 77 K.

3.2. X-ray powder diffraction study

X-ray powder diffraction (XRD) patterns were measured on a Rigaku D/max 2500 X-ray diffractometer. The diffractograms were recorded with Cu Kα radiation over a 2θ range of 10°–80°.

3.3. FT-IR study

FT-IR measurements were performed on a 1730 Infrared Fourier Transform Spectrometer (Perkin-Elmer) using the potassium bromide as the background.

4. Results and discussion

4.1. Experiment of gelation time

Table 1 shows the gelation time of the materials with different TiO_2 weight content. It is observed that the gelation time first decreases from 165 h (pure SiO_2) to 8 h (20TiSi), then prolongs from 8 h (20TiSi) to 60 h (80TiSi) with the increasing of TiO_2 content. Two factors determine the hydrolysis and condensation rates. First factor is the acetic acid, which promote the hydrolysis of TEOS; the second is the titanate formed by the chelate of acetic acid and titanium, which accelerate the condensation of TEOS [9]. With respect to acetic acid, it plays two roles in the system. One side, it acts as the catalyst to promote the hydrolysis of TEOS; on the other side, it chelate with titanium to form titanate, which accelerate the condensation of TEOS and retard the hydrolysis and condensation of $TiCl_4$. The acetic acid make these two hydrolysis and condensation processes compatible. When a lower TiO_2 is added to the system of TEOS, such as10TiSi, the gelation time dramatically decreased, which consent to that titanate can speed up condensation of TEOS [9]. While when TiO_2 content are increased further, more acetic acid is chelate with titanium than to catalyze the hydrolysis, which results in some extent the prolong of the gelation time. It is noticeable that TiO_2 prepared from $TiCl_4$ does not gelate. Generally, TiO_2 gelate when prepared from titanium alkoxide by sol–gel method. So far, as we know, no one has studied the gelation time of TiO_2 in the system of $TiCl_4$. We found that TiO_2 could not gelate at 30 °C but existed in the form of transparent sol. A lot of changes will happen along with the temperature rise and some precipitate will appear at 75 °C. But the same phenomenon did not appear when $TiCl_4$ was

Table 1
The effect of TiO_2 content on the gelation time of Ti–Si mixed oxides

Samples	Gelation (time/h)
SiO_2	165
10TiSi	18.5
20TiSi	8
40TiSi	31
60TiSi	39.5
80TiSi	60
TiO_2	∞

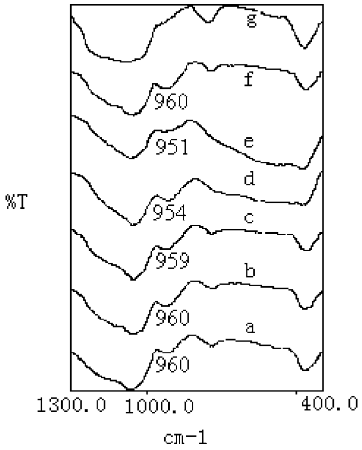

Fig. 2. The FT-IR of the mixed oxides. (a) SiO_2, (b) 20TiSi, (c) 40TiSi, (d) 60TiSi, (e) 80TiSi, (f) 20TiSi-1000, and (g) SiO_2-600.

replaced by Ti-alkoxide. From the above information, it can be concluded that the absence of TiO_2 gel is only because of the property of $TiCl_4$. In addition, the amount of acetic acid have a big effect on the gelation time. The gelation time of 20TiSi and 60TiSi decreased when the amount of acetic acid increased and 60TiSi decreased more rapidly than 20TiSi did. When the molar ratio of CH_3COOH:(TEOS + $TiCl_4$) reached 7, 20TiSi and 60TiSi became gel almost at the same time. The further mechanism is still under investigation.

4.2. Characterization bonds

Fig. 2 shows the FT-IR spectra of all the Ti–Si mixed oxides. The peaks in the spectra have been assigned according to the literature [6]. The spectra reveal three major absorption bands at about 1070, 950 and 460 cm^{-1} (Fig. 2b-e), which represent the characteristic bonds of Si–O–Si asymmetric stretching (near 1070 cm^{-1}), Ti–O–Si asymmetric stretching (around 950 cm^{-1}) and Ti–O stretching (near 460 cm^{-1}), respectively. The absorption band observed at about 950 cm^{-1} is associated with titanium in four-fold coordination with oxygen in the SiO_4^{4-} structure. SiO_2 also gives a 950 cm^{-1} peak in the FT-IR spectrum, which is attributed to Si–OH band. However, this band disappeared after heat treatment at 600 °C (Fig. 2g). In addition, the 950 cm^{-1} absorption band is still observed on the 20TiSi, which has been thermally treated at 1000 °C (Fig. 2f). Accordingly, the 950 cm^{-1} peak of Ti–O–Si mixed oxides should not be attributed to Si–OH band, but associated with Si–O–Ti band. Particularly, the characteristic bond was still existed when the content of TiO_2 is up to 80 wt.%. From the results, we could reach an important conclusion that titanium is in four-fold coordination with oxygen in the SiO_4^{4-} structure, and each component in the materials is mixed on an atomic scale.

4.3. Nitrogen physisorption results

4.3.1. Specific surface areas and pore volumes

The results of the sorption measurements are listed in Table 2. Note that these mixed materials have high specific surface area, can reach to 549.3 m^2/g (10TiSi), which is higher than the Ref. [5].

The specific surface area of the samples decreased from 549.3 m^2/g (10TiSi) to 194.0 m^2/g (80TiSi) when TiO_2 weight content increased and it is not dramatically decreased when TiO_2 content is not more than 20%, and the reason is that a little content of TiO_2 cannot result in the change of SiO_2 structure, which is consistent well with the XRD analysis. The decrease in surface area with TiO_2 content increasing can be partly explained by the higher atomic weight of Ti, but the loss of the most surface area must be attributed to an increased contribution of the pure titania character in the high-titania materials. According to the results shown in Table 2, pore specific volume (V_p) of the specimen first decrease and then increase with along the rise of the TiO_2 content, and reach to the maxima at 20TiSi. It can be explained that the hydrolysis rate of TEOS and $TiCl_4$ is well compactable just as shown in the experiment of gelation time.

4.3.2. Pore structure

Fig. 3 shows the nitrogen adsorption isothermal curves at 77.15 K for the samples prepared by sol–gel one step hydrolysis method. The isothermal adsorption of TiO_2 is type

Table 2
Physisorption results of mixed oxides

Samples	Surface area BET (m^2/g)	V_p (cm^3/g)	Micropore (%)	Pore-size[a] diameter maxima (nm)	Pore-size diameter range (nm)
SiO_2	582.04	3.45	65.95	0.66	0.55–4.5
10TiSi	549.3	0.29	66.32	0.85	0.62–4.5
20TiSi	511.5	0.39	57.77	0.94	0.58–5.5
40TiSi	219.6	0.19	32.38	1.2	0.76–18.9
60TiSi	292.0	0.21	37.77	1.1	0.65–18.9
60TiSi[b]	63.8	0.10	23.62	1.2	0.87–40.6
80TiSi	194.0	0.18	19.86	1.3	0.82–16.0
TiO_2	59.5	0.27	13.91		

[a] Maximum of pore size distribution.
[b] 60TiSi preparing with lower acetic acid-amount.

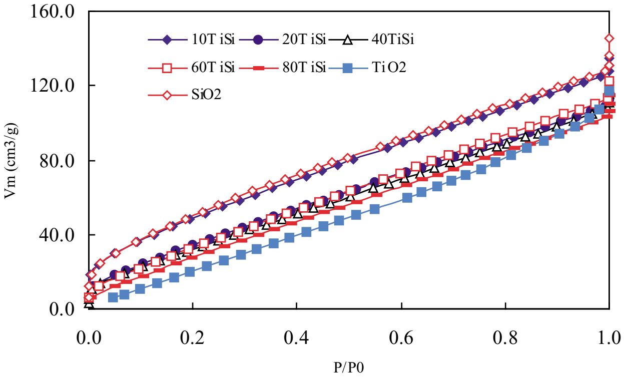

Fig. 3. N_2 physisorption isotherm of the mixed oxides.

III of the IUPAC isothermal classifications, indicating that TiO_2 contained both mesopores and macropores. The adsorption curves of SiO_2 and other mixed oxides are between types I and II isotherms, indicating that these specimens are composed of micropores, mesopores and macropores. Depending on the titania content, the tested materials reveal pore-size maxima between 0.85 and 1.3 nm (Table 2). No clear correlation is found between titania content and pore-size, but the pore distribution tends to be broad. The change of micropore ratios are in good agreement with those obtained from analysis of isothermal adsorption curves.

4.4. Phase analysis

The XRD analysis results are given in Fig. 4. When the titania content is less than 80 wt.%, there is a weak and broad peak around $2\theta = 25^\circ$, which represented that these specimens prepared by sol–gel one step hydrolysis method and obtained after being thermally treated at 400 °C were all noncrystalline. These results suggest that the low titania materials are mixed on an atomic scale, which prevented the materials from phase separation and crystallization even at high content of TiO_2. When the titania content reaches 80 wt.% the broad diffraction lines are located in 25.5°, 38.1°, 48.2°, 53.9°, 55.4° and 62.8° (2θ). They are characteristic lines of anatase TiO_2. However, it is broader than pure TiO_2, which proves that the size of anatase crystal in 80TiSi is very small. The absence of large sharp diffraction peak in TiO_2 rich samples indicated that the titanium in the samples did not exist as crystals of sufficient size to be detected by XRD and the relatively small proportion of silica is highly dispersed through the titania network homogeneously. The SiO_2 does restrain the crystallization of TiO_2 in the mixed oxides while this strong retarding has been often ascribed to a good chemical homogeneity of the starting gels, i.e., to a high degree of Si–O–Ti bonding, titania oxide species are dispersed in amorphous structures of SiO_2 matrices.

4.5. Effect of calcination temperature

Fig. 5 shows the nitrogen adsorption curves at 77.15 K for 20TiSi calcined at from 300 to 1100 °C. The isothermal adsorption of 20TiSi calcined below 500 °C are between types I and II of IUPAC classification, indicating that these materials are composed of micrpore, mesopore and macropore. When 20TiSi is calcined at 700, 900 °C, the adsorption are type III, showing that 20TiSi-700 and 20TiSi-900 have many macropore. The isotherm of 20TiSi-1100 is a beeline, which indicates that it is a kind of nonpore material.

It can be learned from physisorption results (Table 3) that with the elevation of temperature the specific surface area first increase, reach to the maxima at 400 °C, and then decrease. V_p and micropore volume have the same trend. This trend can be explained as follows: one hand, at lower temperature the samples will contain unreacted alkoxide groups, solvent molecules and hydroxyl group, and these groups will be decomposed when the temperature rising, which result in the increase of specific surface, V_p and micropore volume; on the other hand, with the elevation of the temperature, calcinations cause shrinkage of the structural pore. Further-

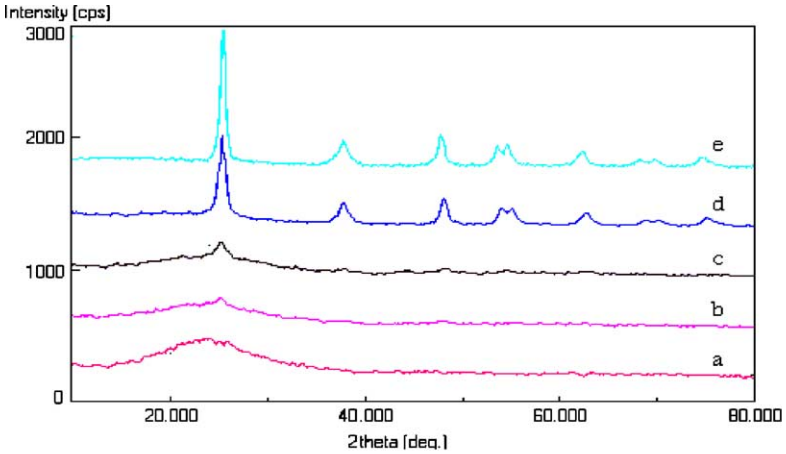

Fig. 4. XRD patterns of the mixed oxides. (a) 20TiSi, (b) 40TiSi, (c) 60TiSi, (d) 80TiSi, and (e) TiO_2.

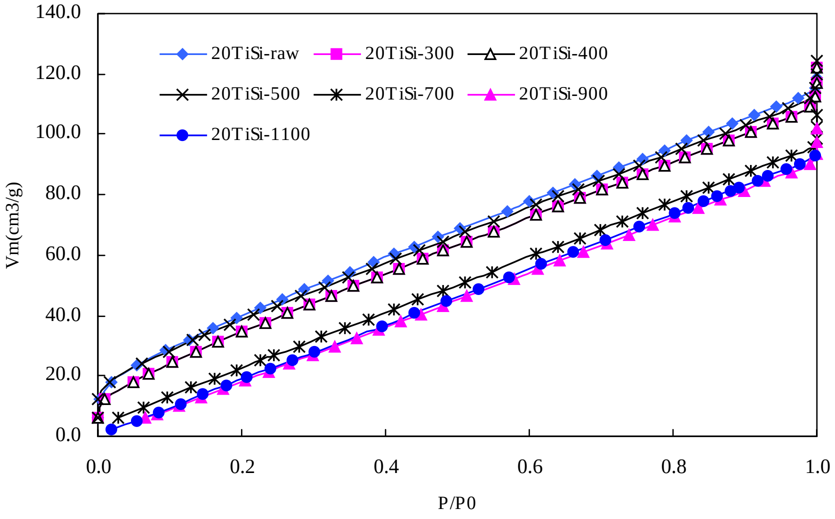

Fig. 5. N_2 physisorption isotherm of the mixed oxides.

Table 3
Physisorption results

Samples	Surface area BET (m^2/g)	V_p BET (cm^3/g)	Micropore volume (Dobinin) (cm^3/g)
20TiSi-300	422.9	0.26	0.19
20TiSi-400	511.5	0.39	0.24
20TiSi-500	293.2	0.21	0.15
20TiSi-700	90.5	0.10	0.04
20TiSi-900	66.4	0.11	0
20TiSi-1100	11	0.22	0

more, compared with the Ref. [10], 20TiSi has high specific surface area after calcination at 1100 °C.

The effect of the calcination temperature on the structure of TiO_2–SiO_2, revealed by XRD, is illustrated in Fig. 6. When 20TiSi is calcined at from 300 to 1100 °C, it is shown that there are only weak and broad diffraction around $2\theta = 25°$, which is characteristic of amorphous silica. This suggests that TiO_2 in the composite is highly dispersed. To compare with TiSi material the TiO_2–SiO_2 mixed material were also calcined at 900 °C. Shown as (f), SiO_2 and TiO_2 in 20TiSi-900 appear in the pattern of amorphous and anatase respectively. Yu et al. [7] prepared Ti–Si composite particles which existed in the form of anatase at 473 °C and transformed into rutile at 1100 °C. Yan et al. [8] gained TiO_2–SiO_2 mixed materials in which anatase appeared at 400 °C. Accordingly, it is suggested that TiO_2 and SiO_2 are mixed uniformly on an atomic scale in the sol–gel one step hydrolysis preparation. This atomic scale mixing retards the phase separation and crystallization even at elevated temperatures. Although the calcination may break the Ti–O–Si band [6], the mobility of the constitutional elements in the structure are not sufficiently high, so that the materials obtained at 1100 °C are still not crystal.

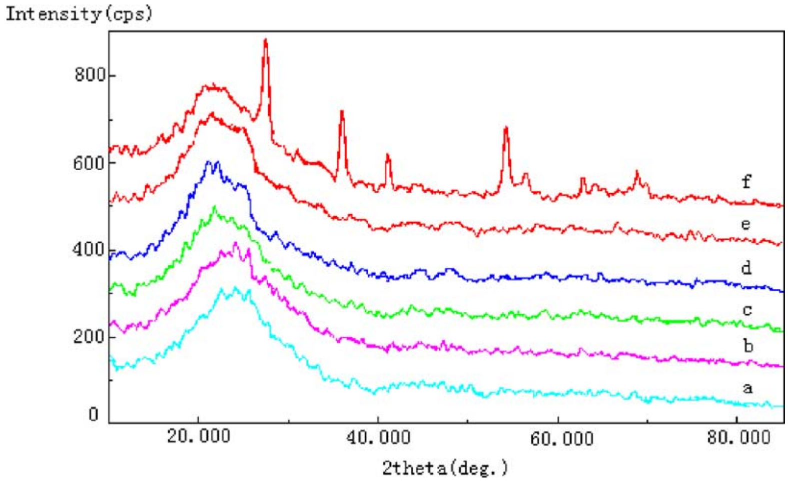

Fig. 6. XRD patterns of 20TiSi calcined at different temperature. (a) 20TiSi-300, (b) 20TiSi-500, (c) 20TiSi-700, (d) 20TiSi-900, (e) 20TiSi-1100, and (f) 20TiSi-900.

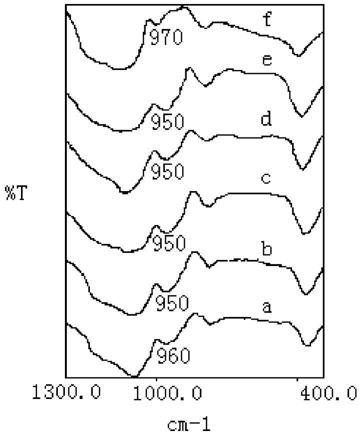

Fig. 7. FT-IR spectra of 20TiSi calcined at different temperature. (a) 20TiSi-300, (b) 20TiSi-500, (c) 20TiSi-700, (d) 20TiSi-900, (e) 20TiSi-1100, and (f) 20TiSi-900.

FT-IR of 20TiSi calcined at different temperature is shown in Fig. 7. The results indicate that the characteristic bond of 950 cm^{-1} cannot vary in intensity and position when the calcination temperature increases, and calcination at 1100 °C does not cause the break of Ti–O–Si. However, there is not the adsorption band of 950 cm^{-1} but 970 cm^{-1} in 20TiSi-900. Accordingly, it can be concluded that 20TiSi prepared by sol–gel one step hydrolysis method has good thermal stability, and calcination at 1100 °C does not result in the break of Ti–O–Si.

5. Conclusion

Ti–Si composite materials are mixed on an atomic scale, and Ti–O–Si band appears in the all samples with different TiO_2 content

1. The specimens have high specific surface area, up to 549.3 m^2/g, and the adsorption isotherm of the mixed oxides are between types I and II.
2. The mixed oxides mainly remain amorpouse pattern. Anatase appears when the TiO_2 content is more than 80 wt.%, comparing with the intension of pure TiO_2, it is very tiny.
3. 20TiSi has good thermal stability. It still possesses 11.8 m^2/g after calcination at 1100 °C. Calcination on the large scale of temperature does not cause the break of Ti–O–Si band. TiO_2 is well dispersed in 20TiSi calcined at 1100 °C, and still existed in the form of amorphous.

Acknowledgements

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