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The preparation and characteristics of cobalt blue mica coated titania pearlescent pigment

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Abstract

This paper studies the experimental method that uses the liquid phase method to prepare cobalt blue mica coated titania pearlescent pigment with urea as precipitant. The optimum technology parameters and the chemical composition of resulting pigment are introduced. The coating principle of cobalt blue mica coated titania is analyzed by infrared spectral analysis and tested by scanning electron microscopy (SEM). Then the activation energy of the cobalt blue mica coated titania precursor in the later reaction stage of the dehydrating process is computed using the variations of the sample's specific surface area under different calcining temperatures and time. Furthermore, the model of the reaction kinetics is put forward in the paper. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Cobalt blue mica coated titania; Spectral reflectance; Activation energy; Model of reaction kinetics

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1. Introduction

As a colorful pearlescent pigment, cobalt blue mica coated titania pearlescent pigment uses fine mica titania flakes as substrate and is prepared by coating a particle layer with a blue-hued spinel cobalt aluminate structure on its surface. Due to its absorption and reflection to the light, this pigment has both a color and a pearlescent effect. Japan patent 60-184570 has introduced the method to prepare blue pearlescent pigment, i.e. in the environment of N_2, reduces the TiO_2 that is on the surface of mica titania to TiO_2 particle with low-valence state using NH_3, then blue color will appear. American patent 3951679 has introduced the method of coating mica titania using iron blue. However, the former technology is complicated and needs a very high requirement for devices; while using the latter, the product's heat-resistance and alkali-resistance are not ideal.

The cobalt blue used in this paper uses urea as precipitant, and the precipitate of Al and Co hydroxide are formed to be coated on the surface of mica titania substrate. Then calcining it in 1173–1273 K, we can get the bright-colored blue pearlescent pigment with excellent dispersivity and luster. The pigment is not poisonous, and it has not only excellent light-resistance, heat-resistance and chemical-resistance, but also has coloring ability, covering ability and a flickering pearlescent effect. Thus, it is widely used in many fields

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such as paint, printing ink, plastic, rubber, craft ceramics, enamel and cosmetics etc. This paper will discuss the preparation method of the pigment, the choice of optimal technology parameter, the coating principle of cobalt blue coated mica titania and the model of sintering reaction kinetics of precursor in later stage of dehydrating process.

2. Experiment

2.1. Raw materials and chemical reagents

$Co(NO_3)_2 \cdot 6H_2O$ chemically pure, $Al(NO_3)_3 \cdot 9H_2O$ chemically pure, urea C P, dehydrate Na_2SO_4 chemically pure, mica titania (10–40 μm) self-made.

2.2. The characteristics analysis

The spectral reflectance of the pigment is measured by color-measuring apparatus $JFY\text{-}AB_1$, and the specific surface area is measured by specific surface area measuring apparatus CHEM-BET-3000, so the model of sintering reaction kinetics of precursor in later stage of dehydrating process can be studied. The particle surface appearance is observed by environment scanning electronic microscope XL30; the chemical composite of the pigment is measured by energy-spectrum apparatus EDAX-9100; the zeta potential on the surface of mica titania is measured using DPM-II zeta potential measuring apparatus.

2.3. The preparation method

We put mixed liquid with a mole ratio of Co^{2+}: $Al^{3+} = 1:2$, urea and a small amount of Na_2SO_4 solid into the reactor, then stirred them and raised the temperature to 358–363 K while keeping the urea consistency as 2.0 mol l^{-1}. The urea hydrolyzes gradually under this temperature. When there appears $Al(OH)_3$ microscopic particle, we add mica titania substrate with solid:liquid (1:30) to coat. If there is no more precipitate generated when adding 2.0 mol l^{-1} NaOH liquid in supernatant, the reaction is finished. Continue stirring while keeping the temperature for 1 h, we filter and wash until the filtered liquid is neutral. Dry the filter cake in 383 K in temperature-constant drying box, then calcine it in 1173–1273 K for 1 h, we will get the cobalt blue coated mica titania pearlescent pigment.

3. Conclusion and discussion

3.1. The composite of pigment

The composite of pigment is measured by energy-spectrum apparatus EDAX-9100. From the measured atom composition in percentage (at.%), we can find its weight composition in percentage (wt.%). The result is shown in Table 1.

3.2. The choice of optimum technology parameter

Color pigment is resulted from its selectively absorbing and reflecting to different wavelengths in optical spectrum. The visible spectrum reflectance is expressed as the selectivity of color to the light wave. The higher the reflectance, then the higher the saturation degree and the stronger the brightness [1]. The hue of the pigment is resulted from the difference of reflectance to the wavelength of visible light spectrum. If the reflectance is larger in some wavelength, then the color in this range will appear. So different spectral reflectance will result in different hue. Therefore, the main basis for choosing optimum technology parameter is the reflectance of the sample to visible light spectrum.

3.2.1. The mole ratio of CoO to Al_2O_3

With other experimental conditions fixed, we change the mole ratio of $Co(NO_3)_3$ to $Al(NO_3)_3$ (computed by the finally generated CoO and Al_2O_3). The experiment finds that, when CoO: $Al_2O_3 > 1$, the pigment color is mainly green. When

Table 1
The composite of pigment

Composition	O	Mg	Al	Si	K	Ti	Co
At.%	55.72	0.02	14.73	12.13	4.47	11.19	1.74
Wt.%	36.51	0.02	16.28	13.90	7.15	21.93	4.20

$CoO:Al_2O_3 = 1–2$, the spectral reflectance curve of the pigment is shown in Fig. 1.

From Fig. 1, it is shown that the sample with mole ratio as 1:1 will get the largest reflectance in the range of blue wavelength of 400–500 nm. With large reflectance, the pigment will have higher saturation degree, higher brightness and an ideal pearlescent effect. So we take $CoO:Al_2O_3 = 1:1$.

3.2.2. $CoAl_2O_4$ coating ratio

The quantity of coated $CoAl_2O_4$ on mica titania substrate will affect the hue and the brightness of the pigment. The ratio of weight of coated $CoAl_2O_4$ to the weight of pigment after coating is called coating ratio. For the convenience of computing, we use the coating ratio of CoO to express. With other experimental conditions fixed and provided that $CoO:Al_2O_3 = 1:1$, we change the added quantity of Co^{2+} and Al^{3+} and measure the spectral reflectance of the sample. The result is shown in Fig. 2.

From Fig. 2 it can be seen that the sample has a high reflectance in the range of blue wavelength of 400–500 nm, and the saturation degree and brightness is excellent, so we take deposition quantity of CoO as 4.0%. The largest reflectance of a and c will move to red, so the purity of color will become worse.

3.2.3. The reaction temperature

With other experimental conditions fixed, we change the reaction temperature, then we get the sample's spectral reflectance curves shown in Fig. 3.

From Fig. 3 it can be seen that with the increase of reaction temperature, the sample's maximum reflectance decreases, the saturation degree and brightness of the color also decrease, in turn, the pearlescent effect becomes worse. The reason is that the hydrolysis of urea is heat-absorbing reaction, the degree of hydrolysis increases with the temperature increasing. Then the concentration of OH^- ion increases and the supersaturating degree

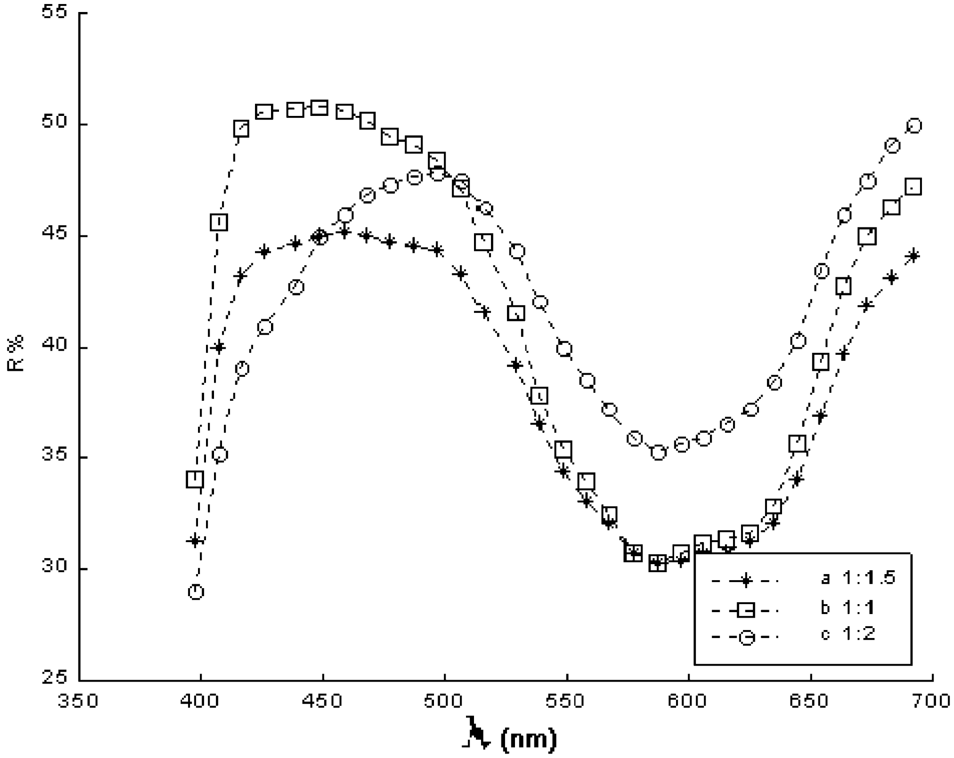

Fig. 1. The sample's reflectance curves with different mole ratio of $CoO:Al_2O_3$.

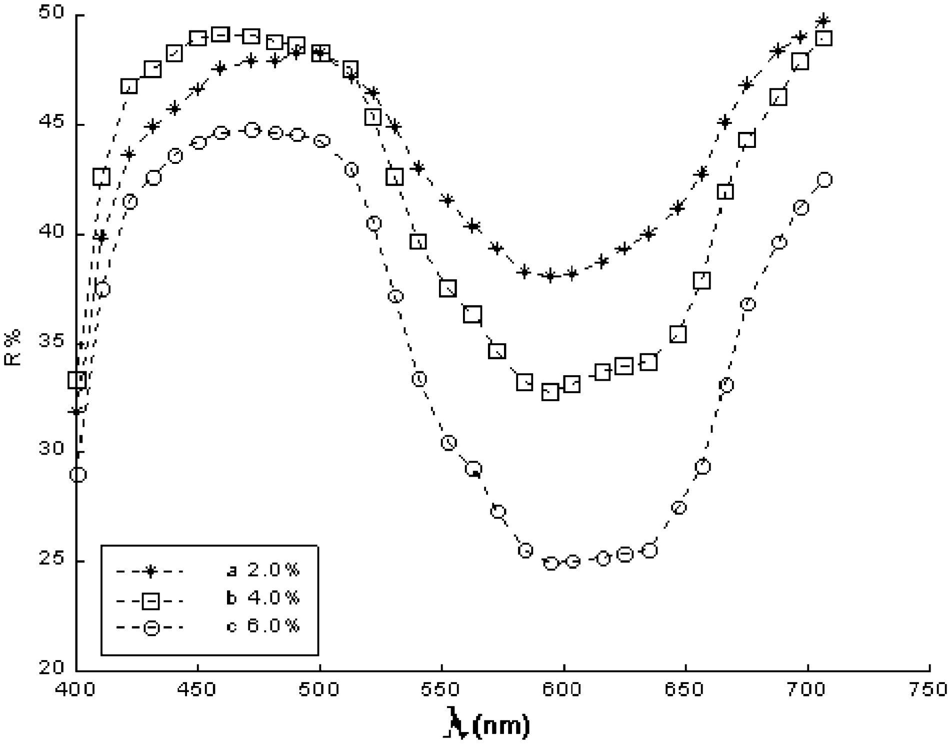

Fig. 2. The sample's spectral reflectance curves with different coating ratio of CoO.

increases. So there will appear plenty of crystal nuclei in a very short moment. With not enough time to adhere to the surface of mica titania, the crystal nuclei are free. This results in the scattering to the light and the decrease of reflectance. On the other hand, if the temperature is too low, then the reaction time will be too long, so it is not easy to be completely precipitated. Therefore, we take the temperature as 358–363 K.

3.2.4. The method of feeding raw materials

The method of feeding raw materials refers to the time to feed mica titania substrate. With other experimental conditions fixed, we observe the effect of the feeding time to the sample's spectral reflectance. The result is shown in Table 2.

From Table 2 we can see that although the reaction time of three different feeding methods has no big difference, their average reflectance are greatly different. Among them, the third method is the best, i.e. feeding mica titanium when $Al(OH)_3$ precipitate just appears. This is because if we feed mica titanium too early, TiO_2 particles coated on mica will partially come off since they are affected by the effect of shear force over a long period, and they will be free in the liquid. In this way, the new-formed particles will coat on the surface of these free particles. So there will be some foreign substance in the pigment, and the reflectance will decrease. Therefore, we choose the third method.

3.3. The discussion of principle of cobalt blue mica coated titania

3.3.1. The surface electric characteristics of mica titania substrate

The structure of TiO_2 layer on the surface of mica titania is mainly of rutile type. From the angle of crystal structure of TiO_2, rutile type and anatase type both belong to cubic system [2]. The ligand number of Ti atom is 6, and six oxygen atoms form an octahedron structure around the Ti atom by covalent bond. Two neighboring octahedra are connected using common horizontal edge, so in

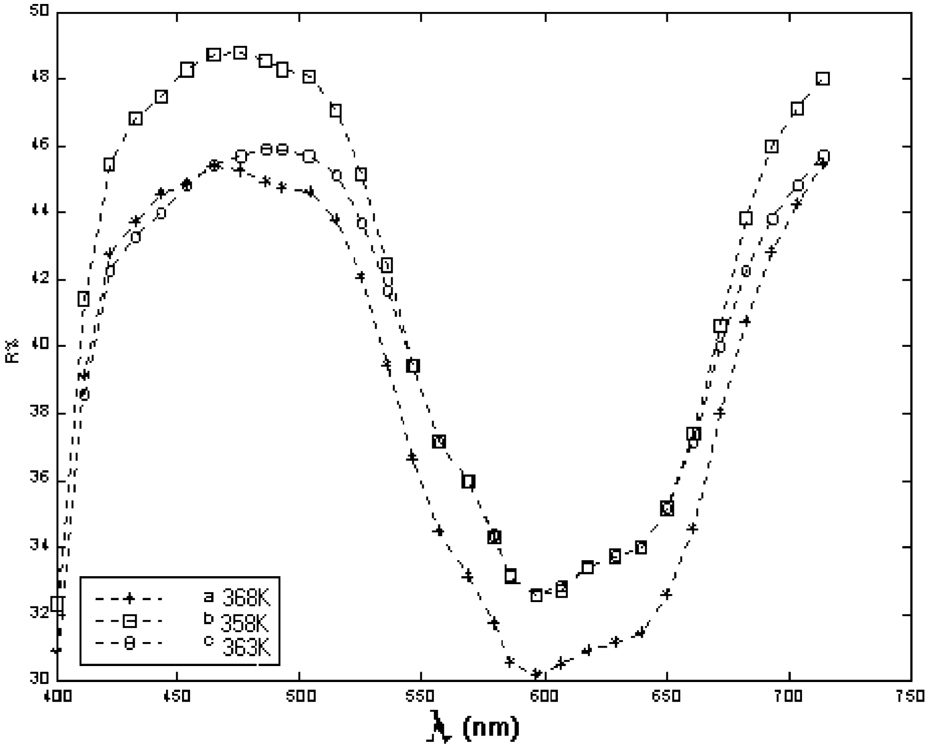

Fig. 3. The sample's reflectance curves with different temperatures.

the horizontal direction, the density of O^{2-} is larger than that in other direction, and this direction will be electronegative. The zeta potential on the surface of mica titania is measured using DPM-II zeta potential measuring apparatus as −5.84 mv.

3.3.2. *The characteristics of ion in the solution*

In the beginning of the reaction, there mainly exist ions with positive electric charge in the solution such as hydrate $[Co(H_2O)_4]^{2+}$, $[Co(H_2O)_3\ (OH)]^+$, $[Al(H_2O)_6]^{3+}$, $[Al(H_2O)_5(OH)]^{2+}$, $[Al(H_2O)_4\ (OH)_2]^+$, etc. When we feed in mica titania, the negative electric charge of substrate will be surrounded by the positive ions in the system through electrostatic force, and one layer of positive electric charge with some bond force is formed on the surface of substrate. With OH^- ions are slowly released by urea, the quantity of positive electric charge decreases. In some certain supersaturating degree of the solution, the ion on the surface of positive electric charge layer will form nucleus with OH^-, then the nucleus will grow into membrane particle, then they deposit to form membrane layer. Finally, there will be a state of adherence balance and deposition balance, and we can get coated mica titanium precursor.

Table 2
The relation between methods of feeding raw materials and the sample's average reflectance

Method of feeding	Average reflectance	Reaction time (h)
In the beginning	39.24	12.0
Before $Al(OH)_3$ precipitate	39.60	10.6
When $AL(OH)_3$ begin precipitate	42.08	11.9

The reaction time refers to the period from beginning feed the raw material to the end of the reaction.

3.3.3. *The infrared spectrum of substrate and cobalt blue mica coated titania*

The infrared spectrum of mica titania and cobalt blue mica coated titania is shown in Fig. 4.

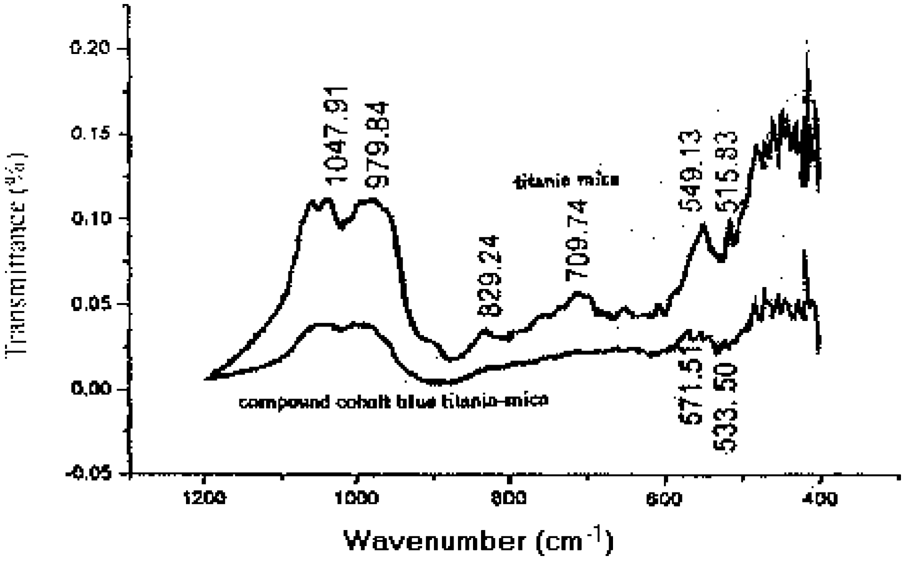

Fig. 4. The infrared spectrum of titania-mica and compound cobalt blue titania-mica.

From Fig. 4 we can see that there are large differences between titania-mica and compound cobalt blue titania-mica. The absorbing peaks of the mica titania at 1047.9 and 979.8 cm^{-1} are weakened obviously in the mica coated titania, while the absorbing peaks at 829.2 and 709.2 cm^{-1} in the former are disappeared. On the other hand, there appears a new absorbing peak at 571.5 cm^{-1}. Looking up in infrared spectrum graph handbook [3], we can find that this new peak is resulted from the superposing of Co–O bond and Al–O bond vibrating absorbing peaks. This shows the formation of spinel cobalt aluminate. Moreover, the Ti–O vibrating absorbing peak of anatase type TiO_2 at 515.8 cm^{-1} in mica titanium disappears, and the Ti–O vibrating absorbing peak of rutile type TiO_2 at 549.1 cm^{-1} moves to 533.5 cm^{-1}. This is because that, after calcining the precursor under 1173–1273 K, some TiO_2 of anatase type almost transform to rutile type. Due to the existence of Co–O bond and Al–O bond and calcining under high temperature, the crystal structure will distort and the bonds' positions will change. This states that when we coated Co or Al complex oxide to the surface of mica titania, its surface appearance changed greatly.

3.3.4. *The appearance analysis by SEM*

The process of coating hydroxide of cobalt and aluminum on the surface of mica titania substrate mentioned above is that the hydrate M^{n+} ion adhere to the surface of substrate at first by electrostatic force, then the surface ion is combined with OH^- to form nucleus. The nucleuses grow up as membrane particle, and they deposit repeatedly to form membrane layer. Testing using scanning electric microscope, the result is shown below.

From Fig. 5 we can see that there is no crack after calcining the precursor, but it's a well-distributed layer. This proves the coating principle again.

3.4. *The model of sinter reaction kinetics of precursor in later stage of dehydrating process*

3.4.1. *Principle*

In sinter process, the substances on the surface of micro-grain and inside the micro-grain diffuse. The acceleration of the sinter reaction is the decrease of free energy on the surface of particles [4]. For two contacted particles, each has its own great surface energy. When heating to the temperature below their melting point, the substances inside the particle move and the surface energy decrease. If the two particles melt together, their total specific surface area will decrease, in turn, the surface energy will also decrease. German and Munir have put forward the below model of sinter reaction kinetics [5],

$$[\Delta S/S_0]^{\gamma} = \beta[\exp(-E_a/RT)]t \tag{1}$$

where ΔS is the difference of the sample's surface areas (m^2/g) before and after the sinter reaction, i.e. $\Delta S = S_0 - S_t$. S_0 is specific surface area before sinter, while S_t is that after sinter. β is the parameter to reflect particle characteristics; E_a is activation energy (kJ mol^{-1}); T is calcine temperature (K); t is calcine time(s), γ is determined by sinter principle. Assume the temperature is fixed. We can get Eq. (2) from Eq. (1),

$$\ln(\Delta S/S_0) = 1/\gamma \cdot \ln(t) + \text{constant} \tag{2}$$

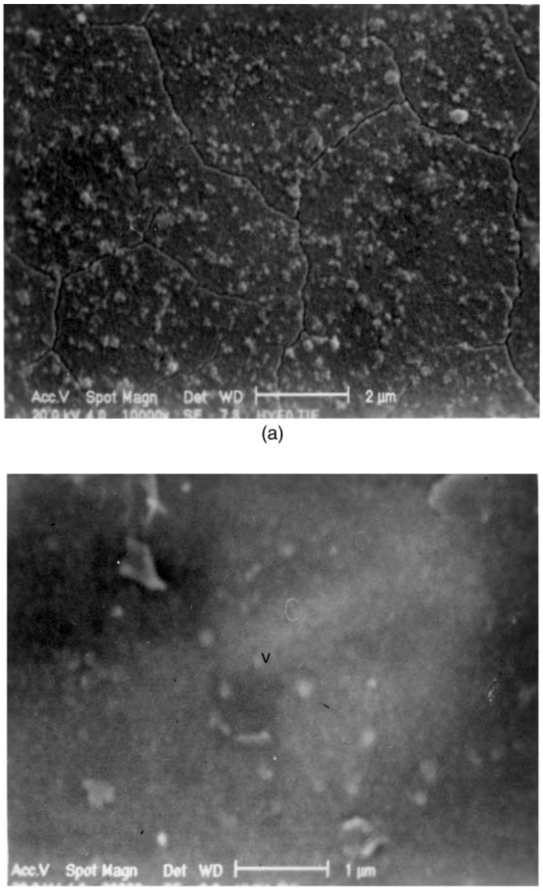

Fig. 5. The scanning result using SEM: (a) mica titania; (b) compound cobalt blue titania-mica.

According to experimental data, we draw the figure of $\ln(\Delta S/S_0)$ versus $\ln(t)$ and compute the slope $J_1 = 1/\gamma$, then we can get the principle parameter γ. Assume the increasing temperature rate $\phi = dT/dt$ and calcine time is fixed, and assume that the sinter principle is same in different temperatures, we can measure the surface area under different temperatures and get

$$\ln(\Delta S/S_0) = -E_a/(\gamma \cdot RT) + \text{ constant} \tag{3}$$

According to experimental data, we draw the figure of $\ln(\Delta S/S_0)$ versus $1/T$. Then we get the slope $J2 = -E_a/(\gamma \cdot RT)$. Furthermore, the activation energy will be found.

3.4.2. Experimental data

We prepare the cobalt blue mica coated titania using optimum conditions which are got using the method mentioned above. Increasing the precursor's temperature as 293 K/min to some temperature and calcine it 1800, 3600 and 5400 s h, respectively, while keeping the temperature. Let it cool naturally to room temperature, then we take the sample to measure its specific surface area. The data and measured results are shown in Tables 3–5.

Drawing the figures using the data in Tables 4 and 5, we can get 2 straight lines. The lines are:

$\gamma_1 = -4.03 + 0.45X_1$ slope is 0.45,
$\gamma_2 = 13.01 - 1.67X_2$ slope is 0.37.

Table 3
The measured results of the sample's specific surface area under different conditions

Calcine temperature (K)	Time of keeping temperature (s)	Surface area (m^2 g)
1073	3600	33.60
1173	3600	20.14
1273	1800	17.19
1273	3600	8.63
1273	5400	5.50

The sample's surface area before calcine $S_0 = 36.08$ m^2/g.

Table 4
The relation of $\ln(\Delta S/S_0)$ and $\ln(t)$ under different calcine time period in 1273 K

Calcine time (s)	lnt (s)	ΔS (m^2/g)	$\ln(\Delta S/S_0)$
1800	7.5	18.89	−0.647
3600	8.19	27.45	−0.273
5400	8.59	30.58	−0.165

Table 5
The relation of $\ln(\Delta S/S_0)$ and T^{-1} under different calcine temperatures for 3600 s

Calcine temperature (K)	T^{-1} ($\times 10^{-4}$ K^{-1})	ΔS (m^2/g)	$\ln(\Delta S/S_0)$
1073	9.32	2.48	−2.677
1173	8.53	15.94	−0.817
1273	7.86	27.45	−0.273

So γ is 2.22, then we can compute the sinter activation energy of precursor in later stage of dehydrating process is $E_a = 30.8$ kJ mol^{-1}, and the model of reaction kinetics is

$$(\Delta S/S_0)^{2.22} = \beta\cdot[\exp(-30.8/RT)]\cdot t.$$

4. Conclusion

We used a liquid phase method to prepare cobalt blue mica coated titania precursor with urea as precipitant, and the optimum technology parameters are shown below: the mole ratio of CoO to Al_2O_3 is 1:1; the coating ratio is 4.0% (computed from CoO); the reaction temperature is 358–363 K; the stirring rate is 160–200 r/min; the method of feeding raw materials is to add mica titania when there just appears $Al(OH)_3$ precipitate in the solution, and solid:liquid (1:30). The principle of coated mica titania is that: hydrate metal ions with different valence states adhere to the surface of substrate at first, then they react with the OH^- ions to generate nucleus through surface ions; the nucleus grow to membrane particle and deposit gradually to form the fine and close membrane layer. The model of sintering reaction kinetics of precursor in later stage of dehydrating process is:

$$(\Delta S/S_0)^{2.22} = \beta\cdot[\exp(-30.8/RT)]\cdot t.$$

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