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Synthesis of sulphur-modified bifunctional hydrotalcites and study of their surface characteristics by

inverse gas chromatography

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ABSTRACT:

In this study, various sulphur-modified hydrotalcite catalysts were prepared, and the influence of calcined temperature on acid-base properties was investigated. The structural characterization of catalysts was studied using X-ray powder diffraction, Scanning electron microscopy, N₂ physisorption, Element analysis and Fourier transform infrared spectroscopy. The structural characterization indicated that all catalysts remained layer structure but the specific surface areas were enlarged. Inverse gas chromatography technique was used to quantitatively determine the catalysts' acid-base properties by calculating thermodynamic parameters, including dispersive surface free energy, adsorption free energy, adsorption enthalpy, and acid-base interaction constants. Results showed that the strength and content of acid and alkaline sites were enhanced with the increasing of calcined temperature. Moreover, several typical aldol condensation reactions were selected to study the catalytic activity of developed catalysts. Results showed the sulphur-modified hydrotalcite catalyst possesses high activity and good regenerability for typical aldol condensation reactions.

Key words: Hydrotalcite; Ammonium persulfate; Inverse gas chromatography; Aldol condensation reaction **1. Introduction**

The aldol condensation reaction is one of the most powerful and popular C-C bond-forming methods.¹ In the past decades, many homogeneous and heterogeneous catalysts have been developed to catalyze the reaction. Because of the great advantages of heterogeneous catalysts, there have been more interests in designing and developing high reactive multifunctional heterogeneous catalysts for aldol condensation reactions.^{2, 3} In some studies, these catalysts showed superior catalytic activity than traditional monofunctional catalysts, which contain only acidic sites or alkaline sites.⁴ Multifunctional heterogeneous catalysts, such as hydrotalcite like compounds (HTLcs) and its derivatives, can provide more than two types of active centers in reaction system, which can co-activate the substrates and promote the reactions.

Layered double hydroxides (LDHs) or hydrotalcite like compounds are widely applied clay materials with typical 2D nanostructure.⁵⁻⁸ The specific layered structure of LDHs could be destroyed and form Mg-Al complex oxides (LDO) when the calcined temperature is over 473 K. LDO and its reconstructed product have superior catalytic activity on various reactions,^{9,10} Yamaguchi et al prepared LDHs with Mg/Al ratios from 3 to 8 and calcined them at various temperatures from 673 K to 1273 K.¹¹ Under different calcinated temperatures, the formed catalyst may have various acid-base properties and can provide diverse catalytic performance. The above alkaline materials can also combine with other functional materials, i.e. Al-containing mesoporous silica¹², amberlyst¹³ and rubber nanocomposites¹⁴, to create new multifunctional catalysts. In many studies, sulfate and persulfate are applied to enhance the acidity of catalysts. Tanabe reported that the addition of SO_4^{2-} anions to ZrO₂ could enhance the acidity of catalyst, and calcined temperature may affect the catalytic behavior.¹⁵ Yang et al prepared SO₄²⁻/TiO₂-SiO₂ catalyst by the way of impregnation and calcination.^{16, 17} Meanwhile, the acidity measurements showed that the acid strength of catalyst could reach to -12.70. So, using sulfate and persulfate to modify hydrotalcite may enhance catalyst's acidity and obtain various acid-base bifunctional catalysts. By altering calcined temperature, the acid-base properties of catalysts could be optimized and provide better catalytic activity. As mentioned, HTLcs is the material with typical layer structure, and high temperature may destroy the layer structure (Fig.S1), which may influence the material's primordial acid-base properties. An appropriate testing technique, such as inverse gas

chromatography (IGC) technique, is crucial in characterizing the developed catalysts by determining the surface properties.

IGC is a popular tool with advantages of convenience, high efficiency and mild conditions. This technique has been applied in the characterizing many materials with heat-sensitivity or weak acid-base properties.^{18, 19} IGC technique could determine the properties of HTLcs materials under mild conditions and it just needs a small amount of experimental data and simple thermodynamic calculation. Therefore, we used IGC technique as an effective tool to analyze the acid-base properties of prepared catalysts.

In this study, sulfate was used to adjust the acidity and alkalinity of catalyst. A series of acid-base bifunctional catalysts were developed after the processes of calcination and self-assembly. IGC technique, Pyridine-IR (Py-IR) analysis and Hammett indicators were used to investigate the acid-base properties of these developed catalysts. The catalytic activity of the catalysts for typical aldol reactions and the interaction mechanism between acidity, alkalinity, and catalytic activity are also investigated.

2. Experimental section

2.1 Materials

All chemicals were purchased from Sinopharm Reagent Co. (Shanghai, China). Magnesium nitrate Mg(NO₃)₂·6H₂O, aluminum nitrate Al(NO₃)₃·9H₂O, urea CO(NH₂)₂, ammonium persulfate (NH₄)₂S₂O₈ and other reagents were used as obtained without further purification.

2.2 Hydrotalcite preparation

A certain weight of $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and urea were dissolved in 250 mL deionized water to yield a solution containing 0.15 mol $Mg(NO_3)_2 \cdot 6H_2O$, 0.05 mol $Al(NO_3)_3 \cdot 9H_2O$ and 0.9 mol urea. Then, this solution was transferred to an autoclave placed in an oven with constant 453 K to react for 24 h. After cooling to room temperature, the precipitate formed was filtered and washed with deionized water until the pH=7. The solid was dried at 373 K for 24 h to yield the as-synthesized layered double hydroxide (LDH).

2.3 Modification of hydrotalcites

LDH was calcined at 723 K for 8 h in muffle to obtain LDO. The calcined temperature was raised at a heating rate of 5 K·min⁻¹. Then, an amount of 1.0 g LDO was suspended in 100 mL of 0.05 g aqueous ammonium persulfate solution and stirred at 298 K for 24 h. The suspension was evaporated at 343 K for 1 h using a rotary evaporator and the obtained solid was ground into powder. The following treating conditions are similar to the process as described above; the powder was calcined at 673 K (or 723 K, 773 K, 823 K, 873 K) for 8 h and treated with 100 mL water again. Finally, the suspension was dried and the obtained powder was named S/LDH-673 (or S/LDH-723, S/LDH-823, S/LDH-873) catalyst.

2.4 Catalyst characterization

XRD analysis was conducted on Bruker D8 Advance powder X-Ray diffractometer, using Cu K α radiation (λ =0.154 nm) at 40 kV, 200 mA, a scanning rate of 20°/min, and a 2 θ angle ranging from 5° to 80°. N₂ physical adsorption-desorption measurements were carried out on an ASAP2000 surface analyser (Micromeritics Co., USA) at 77 K. Before the measurement, the catalysts were degased at 473 K for 4 h. The textural properties of the samples were calculated by BET method. The contents of Mg and Al in samples were determined using inductively coupled plasma atomic emission spectroscopy on a Perkin Elmer ICP-OES Optima 3000 instrument using solutions prepared by dissolving samples in dilute HNO₃. The contents of non-metallic element in the samples were measured using an elemental analysis instrument (Elementar, vario Micro cube, Germany). The morphologies of catalysts were observed by SEM, using HITCHI S-4800 instruments. X-ray photoelectron spectra (XPS) were measured with a Kratos Axis HSi photoelectron spectrometer equipped with an Al K α radiation (*hv*=1486.6 eV). A powder of 250 W and a pass energy of 37.5 eV were used during the experiment. The base pressure of the chamber was better than 3×10⁻⁹ Torr. FT-IR spectra were obtained using a Nexus 870 FTIR

spectrometer in the range of 4000 to 400 cm⁻¹. Py-IR spectra were recorded using a Perkin Elmer Spectrum One FT-IR spectrometer. The solid sample was pretreated under vacuum at 423 K for 24 h. Then solid sample (about 20 mg) was pressed into a self-supporting wafer of 13 mm diameter and treated under vacuum at 423 K for 2 h. The background spectrum was recorded first after the sample cooling to room temperature. The pyridine was then introduced to the sample for 5 min, and then consequently desorbed at 423 K. Finally, the spectrum was recorded with a 4 cm⁻¹ resolution in the range of 1600-1400 cm⁻¹. The basic strength and alkali number were determined by Hammett indicators. The number of alkaline sites was estimated by titration using benzoic acid. IGC was used to measure the acid-base interaction constants K_a and K_b. A conventional gas chromatography (Kechuang, GC-910, China) with a thermal conductivity detector was used for the measurements. A loading between 0.5 and 0.6 g of catalysts was placed into a 15-cm length 304 stainless steel column with 3 mm inside diameter. All columns were packed with mechanical vibration, and the two ends were plugged with deactivated glass wool. The columns were pretreated in the GC system at 403 K overnight with a nitrogen flow rate of 20 mL/min. Measurements were carried out in the temperature range from 333 to 363 K. High purity nitrogen was used as carrier gas, and flow rates were measured using a soap bubble flowmeter. In order to meet the requirement of adsorption at infinite dilution, the probes injected were in the range from 0.2 to 0.3 µL. The procedures and thermodynamic concepts which link the net retention volume of the IGC experiment with the dispersive surface free energy of the catalyst, γ_{a}^{d} , and its acid and base interaction constants, K_{a} and K_{b} , have been fully described elsewhere²⁰⁻²⁴. The properties of probes used for IGC technique as shown in Table S1. All calculations and results of IGC measurements were summarized in Table S2 to Table S23.

2.5 Catalytic testing

In a typical experiment, 1.0 g of *p*-nitrobenzaldehyde, 5.0 g of acetone, and 0.05 g of catalyst were mixed in a 50 ml round-bottomed flask. The reaction was carried out with reflux and nitrogen protection at 333 K for a required time. The conversion of *p*-nitrobenzaldehyde was determined using a high performance liquid chromatograph (HPLC, SHIMADZU, Japan) equipped with a C-18 column (4.6×250 mm, 5µm). The UV detection wavelength and the volume ratio of mobile phase were based on the reaction.

3. Results and discussion

3.1 Structural characterization

There are seven typical hydrotalcite diffraction peaks ([003], [006], [009], [015], [018], [110], [113]) on the XRD patterns (Fig.S2), which showed that all modified catalysts retain the layer structure. The XRD patterns of S/LDH and LDH-823 revealed broader and lower peaks than LDH, indicating a lower crystallinity, which may attribute to the vigorous mechanical stirring during the rehydration process.^{25, 26} This process can break and exfoliate the platelets of LDH to increase the surface area of catalysts.²⁵ When calcined temperature is 973 K, there are three spinel peaks exhibited on the patterns, which revealed that this part of metal oxides is unrecoverable.²⁶ However, when calcined temperature was below 873 K, there is no obvious spinel peaks exhibited on patterns. So, 873 K was selected as the highest calcined temperature in this research.

Fig.S3 is the SEM images of LDH and S/LDH-823. The morphology of LDH is obvious layered solid (Fig.S3a), which indicates a well-developed layer structure. However, the morphology of S/LDH-823 is irregular particles (Fig.S3b) and obvious layer structure can be observed on it (Fig.S3c). These generated smaller particles may due to vigorous mechanical stirring in reconstruction procedure. The generated small plates may agglomerate into larger particles with the presence of small amount of absorbed water. The SEM-EDS spectrum graph in Fig.S3d demonstrates the existence of sulfur element on the surface of S/LDH-823. The molar ratio of Mg to Al is 3.07 (14.53/4.73), which is consistent with the molar ratio of Mg(NO₃)₂·6H₂O to Al(NO₃)₃·9H₂O in experimental section.

Thysicoencinear properties of catalysis									
Catalyst	▲ [a]	$V_{T}^{\left[b\right] }$	Alkali number ^[c]			Mass fra	action/%	ICP	
	ABET		≥ 7.2	≥ 9.3	Total	Н	S	n(Mg):n(Al)	
LDH	77	0.13	0.32	0.00	0.32	1.00	0.00	2.98: 1	
LDH-823	197	0.65	2.74	1.89	2.74	4.28	0.00	3.17:1	
S/LDH-673	128	0.38	1.69	1.28	1.69	3.81	0.39	3.13:1	
S/LDH-723	144	0.42	1.82	1.39	1.82	3.87	0.37	3.17:1	
S/LDH-773	158	0.49	2.13	1.73	2.13	3.87	0.36	3.16: 1	
S/LDH-823	165	0.54	2.21	1.80	2.21	3.86	0.36	3.13:1	
S/LDH-873	155	0.52	2.05	1.67	2.05	3.83	0.35	3.15:1	
S/LDH-873-5	-	-	-	-	-	3.86	0.36	-	

Physicochemical	properties	of catalysts

Table 1

[a] BET method, $m^2 \cdot g^{-1}$. [b] Total pore volume (P/P₀=0.990), $cm^3 \cdot g^{-1}$. [c] Hammett titration method, bromothymol blue and phenolphthalein as indicator, mmol $\cdot g^{-1}$.

Table 1 shows the physicochemical properties of catalysts. The surface area of the modified catalyst is larger than LDH, which may be caused by the vigorous mechanical stirring.²⁵ The stirring process could exfoliate the smaller particles to form very thin plates. The thinner plates and higher surface area may provide more active sites, such as more surface hydroxyl groups and defects of layer.²⁷ Under the same treatment conditions (room temperature, 700 rmp, 24 h), the pore volume of S/LDH-823 is smaller than LDH-823. This phenomenon may attributed to internal sulfate blocked the pore of S/LDH catalysts. Many researches demonstrated that LDHs could obtain strong alkaline sites under appropriate calcined temperature.²⁸⁻³⁰ Similarly, the results of Hammett indicators indicated that the alkaline content of catalysts increased along with the calcined temperature. S/LDH-773, S/LDH-823 and S/LDH-873 catalysts revealed similar total alkaline content. It could be concluded that when calcined temperature is over 773 K, the alkalinity of catalysts increase slightly after modification, which may attribute to several times calcination and reconstruction processes. These processes may result in the removal of aluminum element.





The FT-IR spectra of the catalysts are presented in Fig.1a. The absorption bands at 3470 cm⁻¹ and 1640 cm⁻¹ observed in the spectra for these samples are attributed to stretching modes of adsorbed water and hydroxyl groups.³¹ The absorption band at 870 cm⁻¹ is characteristic for the out-of-plane deformation of carbonate, whereas the in-plane bending is located at 667 cm⁻¹.²⁵ The vibration of the carbonates appears at 1370 cm⁻¹ could be assigned to interlayer carbonates. The absorption bands at 450 cm⁻¹ and 554 cm⁻¹ are attributed to the vibrations of the MgO and Al₂O₃. The bands are observed at 1120 cm⁻¹ and 955 cm⁻¹ correspond to the asymmetric and symmetric stretching frequencies of S=O and S-O bonds respectively, which indicate the configuration of acidic sites is chelating bidentate.³² The spectrum of S *2p* for S/LDH-823 is shown in Fig.1b. The binding energy of S *2p* is 169.6 eV, which can suggest the presence of S⁶⁺ (SO₄²⁻).^{33, 34} Fig.1c shows the Py-IR spectra of LDH-823 and S/LDH-823 catalysts. It is observed that two catalysts exhibit bands at 1544 cm⁻¹ assigned to pyridine bound to Brönsted acidic sites and at 1448 cm⁻¹ assigned to pyridine bound to Lewis acid sites. In terms of the area of adsorption bands, the acidic content of S/LDH-823 catalyst is more than LDH-823 catalyst. Meanwhile, the

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content of S/LDH-823 catalyst's Lewis acidic sites is increased greatly, which may attribute to the interaction of metal oxides with sulfate. As a result of the strong attracting electrons from metal ions by way of two covalent S=O bonds, the center metal atom lacks electrons severely, thus the strong Lewis acidic site is generated.³² When a Lewis acidic site absorbs water, it may transform into a Brönsted acidic site.





Fig.2 (a) Plot γ_s^d vs column temperature (b) Energy of adsorption $RTln(V_n)$ vs $2aN(\gamma_s^d)^{0.5}$ of n-alkanes and polar probes on the surface of S/LDH-823, at T=333 K (c)Plot of $-\Delta G^{sp}/T$ as function of 1/T for DCM on S/LDH-823 (d) Plot of $\Delta H_a^s/AN^*$ as function of AN*/DN on S/LDH-823

In general, the retention time is converted into a net retention volume, V_n , which can be obtained by Eq. (1)^{22,23}:

$$V_n = F \cdot \frac{P_0 - P_w}{P_0} \cdot (t_r - t_0) \cdot J \cdot \frac{T}{T_c} - (1)$$

Here, F is carrier gas flow rate in mL/s. P_w is vapor pressure of water in the flow rate. P_0 is atmospheric pressure at room temperature. t_r and t_0 are retention time of probe and methane, respectively. J is the well-known James-Martin correction factor for gas compressibility. T_c and T are the temperature at column and flow meter. When retention volume are available, the disperse component of surface free energy (γ_s^d) can be obtained from a plot of the logarithm of retention volume of a series of alkane probe molecules versus the product of liquid tension and molecular area. The γ_s^d can be calculated from the slope according to Eq. (2)^{22, 23}: RTln(V_n)=(γ_s^d)^{0.5}·2aN(γ_1^d)^{0.5}+C-(2)

The plots of γ_s^d values versus column temperature are shown in Fig.2a, which showed good linear fit. The γ_s^d values decreased with the increasing of column temperature, which indicated that the interaction of catalysts with probes decreased. When calcined temperature is above 823 K, the γ_s^d values of S/LDH-823 and S/LDH-873 are similar, which may attribute to these two samples have similar energy spots on the surface.

The contribution of Lewis acid-base interactions to the adsorption free energy of polar probes $(-\Delta G_a^s)$ was marked on Fig.2b. The straight line shows the dispersive interactions of stationary phase, while the polar probes lie above this line, indicating that acid-base interactions are present. The $-\Delta G_a^s$ values of all acidic, alkaline, and amphoteric probes are relatively high. It can be concluded that all types of active sites are present on the surface of S/LDH-823 catalyst. When $-\Delta G_a^s$ are available, the adsorption enthalpy values of polar probes can be obtained from a plot of the $\Delta G_a^s/T_c$ versus the $1/T_c$, a straight line should be obtained, its slope, $-\Delta H_a^s$, reflecting the acid-base interactions, as shown in Fig.2c. The results of calculation are summarized in Table 2.

Table 2

Specific components of adsorption enthalpy of polar probes on the surface of catalysts (KJ	∫∙mol⁻	1)
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Probe	LDH	LDH-823	S/LDH-673	S/LDH-723	S/LDH-773	S/LDH-823	S/LDH-873
DCM	7.9726	37.4520	22.1723	26.6000	29.8810	32.3101	30.8445
TCM	9.3247	43.9359	28.1398	32.4984	39.5418	40.4524	39.7836
DEE	2.9666	16.0085	15.7577	20.6286	30.7334	36.1386	33.4512
Acet	4.7289	17.7204	18.4871	24.2871	37.3122	37.7271	40.8128
THF	3.0660	8.6862	12.7577	17.4809	28.8744	35.6832	32.2674

Here, we can estimate the acid-base properties of catalysts based on the adsorption enthalpy values. From Table 2, the $-\Delta H_a^s$ values of LDH, LDH-823, S/LDH-673, and S/LDH-723 are acid probes > neutral probes > base probes, which indicated that these four samples have stronger interaction with acid probes and the acid-base properties of catalysts are more alkaline. Moreover, when increased calcined temperature, the base probes' enthalpy values of S/LDH catalysts increased obviously, which indicated that the acidity of these catalysts has been further enhanced. Compared to LDH-823 catalyst, the S/LDH-823 catalyst's enthalpy values of THF, DEE, and Acet are obviously greater, but the enthalpy values of DCM and TCM are smaller. It indicates that modification process could introduce acidic sites in hydrotalcite materials, but some alkaline sites would be quenched. Here, S/LDH-823 catalyst has the maximum $-\Delta H_a^s$ value of THF that means it may have the strongest acidity.

Table 3

The acid-base properties of catalysts

Sample	K _a	K _b	$K_a + K_b$	K _a / K _b
LDH	0.0255	0.4955	0.5210	0.0515
LDH-823	0.0508	2.1227	2.1735	0.0239
S/LDH-673	0.1195	1.3123	1.4318	0.0911
S/LDH-723	0.1696	1.5590	1.7286	0.1088
S/LDH-773	0.3107	1.7619	2.0726	0.1734
S/LDH-823	0.3774	1.8747	2.2521	0.2013
S/LDH-873	0.3381	1.8519	2.1900	0.1826

When enthalpy data are available, the empirical relationship given by Eq. $(3)^{22, 23}$ can be used to establish the acid-base parameters of the catalysts. As shown in Fig.2d, when $-\Delta H_a^s/AN^*$ is plotted versus DN/AN^{*} of a set of polar probes, a straight line could be regressed. The slope, K_a, designates the acidity of sample, and the intercept, K_b, reflects its electron donor ability. According to the electronic theory of acid and alkali, the determination of K_a and K_b values enables a quantitative basis to correlate acid-base character of surface to composite strength.²¹ $-\Delta H_a^s = K_a \cdot DN + K_b \cdot AN^*$ -(3)

Results in Table 3 shows that the S/LDH-823 catalyst is the most active catalyst (maximum $K_a + K_b$ value) and LDH catalyst is the least active catalyst. The huge difference between LDH and LDH-823 catalysts may attribute to the rehydration process. This process could enhance the surface of catalysts and expose more Brönsted alkaline sites (surface hydroxyl groups and defects of layer) in the interlayer spaces.³⁵ The acidity of sulphur-modified catalysts increased with the increasing of calcined temperature. When calcined temperature is up to 823 K, the acidity of S/LDH catalyst reaches the highest value. The K_a value of S/LDH-823 catalyst (0.3774) is greater than LDH-823 catalyst (0.0508), which means the acidity of the former is stronger than the later. The K_b value of S/LDH-823 catalyst is lesser than LDH-823 catalyst. Moreover, the LDH-823 catalyst has the highest K_b value (2.1227) that means the strongest alkalinity. These results are consistent with the results of Py-IR and Hammett indicator. The values of K_a/K_b are all greater than 1, which indicated that the alkalinity of all catalysts stronger than acidity. So, the S/LDH catalysts are

amphoteric and predominantly alkaline materials.

3.3 Catalytic performance

Table 4

Direct asymmetric aldol condensation reactions of aldehydes with ketones catalyzed by S/LDH-823 catalyst

	+ R3 R4			3 2 0 R4	+ н ^{_0} ́н				
Enter D1		ЪĴ	D2 D/	D 4	LDH-823		S/LDH-823		
Ениу	K1	K2	K3	K4	Yield	Selectivity	Yield	Selectivity	
1 ^{a,d}	4-NO ₂ Ph	Н	-(CH	2)3-	69.5	98.2	95.5	96.7	
2 ^{a,d}	Ph	Η	-(CH ₂) ₃ -		34.2	97.5	69.2	95.2	
3 ^{a,e}	2-Furanyl	Н	-(CH ₂) ₃ -		44.9	95.8	78.4	93.6	
4 ^{a,e}	$(CH_3)_2CH$	Η	-(CH ₂) ₃ -		11.9	99.3	11.9	99.3	
5 ^{b,d}	4-NO ₂ Ph	Η	-(CH ₂) ₂ -		75.8	99.5	98.7	94.5	
6 ^{b,d}	Ph	Η	-(CH ₂) ₂ -		55.1	96.2	83.0	96.2	
7 ^{b,e}	2-Furanyl	Η	-(CH ₂) ₂ -		41.7	95.4	90.2	95.8	
8 ^{b,e}	$(CH_3)_2CH$	Н	-(CH ₂) ₂ -		10.9	99.5	23.1	97.8	
9 ^{c,d}	Ph	Н	Η	Н	82.5	98.6	95.7	95.3	
10 ^{c,e}	2-Furanyl	Н	Η	Н	45.1	94.2	72.5	98.1	
11 ^{c, e}	$(CH_3)_2CH$	Η	Η	Н	3.8	98.8	14.4	94.7	
12 ^{a,e}	-(CH ₂) ₅ -		-(CH ₂) ₃ -		<0.1%		5.7	97.1	
13 ^{a,e}	-(CH ₂) ₄ -		-(CH ₂) ₂ -		<0.1%		8.4	98.5	

a)Reaction conditions: 373 K, 12 h; b)Reaction conditions: 353 K, 8 h; c)Reaction conditions: 333 K, 4 h; d)Yield and selectivity were based on the aldehyde and were determined by HPLC using area normalization method; e)Yield and selectivity were based on the aldehyde and were determined by gas chromatography using area normalization method.

Various typical aldol condensation reactions were selected to compare the catalytic activity of S/LDH-823 catalyst with LDH-823 catalyst. The experimental results (Table 4) showed that S/LDH-823 catalyst has higher catalytic activities than LDH-823 catalyst, especially in the self-condensation reaction of cyclohexanone. Moreover, when the aldehyde contains aromatic ring, the S/LDH-823 catalyst displays excellent performance for the reaction. The aldol condensation reaction of acetone and *p*-nitrobenzaldehyde was selected as probe to check the catalytic performance of catalysts, as shown in Fig.3a. When the calcined temperature is over 773 K, the catalysts showed high activity with 90%~ yield of *p*-nitrobenzaldehyde after 2 h. However, the LDH-823 catalyst showed 55.3% yield of *p*-nitrobenzaldehyde under the same reaction condition. The experimental results indicated that S/LDH-823 catalyst showed higher catalytic activities than LDH-823 and other catalysts.

The used S/LDH-823 catalyst was washed with acetone several times, followed by same calcination and reconstruction processes described previously. Then the aldol condensation reaction of *p*-nitrobenzaldehyde with acetone was used as probe to determine the regeneration performance of S/LDH-823 catalyst. The results of regeneration experiment are show in Fig.3b. After 5 times regeneration, there are no obvious changes in the catalytic activity and products selectivity of S/LDH-823 catalyst.



Fig.3 (a)The catalytic performance of five samples. (b)The regeneration performance of S/LDH-823 catalyst. Reaction conditions: *p*-nitrobenzaldehyde, 1.0 g; acetone, 5.0 g; catalyst dosage, 0.05 g; reaction temperature, 333 K; reaction time, 2 h. Product: A—4-hydroxy-4-(nitrophenyl)-2-butanone, B—*p*-nitrobenzylideneacetone.



Fig.4 Possible acid-base cooperative mechanism in aldol condensation reaction

Zeidan *et al* described a possible reaction mechanism when they studied multi-functional modified SBA-15 catalysts.³⁶ They believed that the acidic sites and alkaline sites could synergistic activate acetone forming stable enol. Then, the nucleophilic reaction of enol and *p*-nitrobenzaldehyde occured. Moreover, Climent *et al* also reported a potential reaction mechanism when they studied using bifunctional amorphous aluminophosphate catalysts to catalyze the aldol condensation of heptaldehyde and benzaldehyde.³⁷ They thought that the acidic sites could activate the carbonyl of benzaldehyde and strengthen the polarization of C=O double bond, which enhance the electropositivity of carbonyl carbon atom. This process is conductive to the nucleophilic reaction of benzaldehyde and enol.

Considering above two reaction mechanism, we proposed a probable reaction mechanism as show in Fig.4. Firstly, Brönsted acidic site attacks the carbonyl oxygen atom of aldehyde, which will cause the electron of C=O covalent bond transfer to oxygen atom and strengthen the electrophilicity of aldehyde. The activated hydroxyl of LDHs and Brönsted acidic sites synergistic activate acetone to generate enol. Finally, activated aldehyde reacts with enol to gain product A directly or further generate product B after dehydration. In reaction system, the roles of Brönsted acidic sites not only strengthen the electrophilicity of aldehyde but also activate the acetone to generate enol. The key role of activated surface hydroxyl is dominant the proceeding of aldol reactions.

4. Conclusion

In this study, acid-base bifunctional heterogeneous sulphur-modified catalysts were prepared using hydrotalcite, characterized, and were applied successfully in aldol condensation reactions. The advantages of S/LDH catalyst are low price, easy preparation, high catalytic activity and better regenerability. IGC technique was introduced successfully to analyze the acid-base properties of catalysts. The results of IGC technique are consistent with

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Hammett indicator and Py-IR analysis. The acidity of S/LDH catalyst was enhanced as calcined temperature increased. Meanwhile, the S/LDH catalyst with strongest acidity can be obtained when calcined temperature is up to 823 K. The experimental results show that S/LDH-823 catalyst has higher catalytic activity for aldol reactions than LDH-823 catalyst. It can be explained that the introduced acidic sites cooperate with alkaline sites to activate aldehyde and acetone molecules simultaneously, which could reduce the difficulty of nucleophilic addition reaction significantly. The acid-base characteristic indicates that S/LDH-823 catalyst is amphoteric and predominantly alkaline material. This catalyst is different from many reported acid-base bifunctional catalysts which are amphoteric and predominantly acidic materials.

Acknowledgements

This work was supported by the National High Technology Research and Development Program of China (2011AA02A203, 2014AA021205) and Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

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Graphical Abstract



The prepared S/LDH catalyst possesses both alkaline sites and acidic sites, and exhibited obvious acid-base complementary effect with good catalytic performance for aldol reaction.