碱土金属修饰 NaY 分子筛催化乳酸脱水制丙烯酸: 碱性位对催化活性的影响

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摘要: 采用碱土金属 (Mg, Ca, Sr, Ba) 对 NaY 分子筛进行改性, 并采用氮气物理吸附、X 射线衍射、氨气及二氧化碳程序升温脱附等技术对样品进行了表征, 考察了阳离子物种对 NaY 结构、表面酸碱分布等的影响, 以进一步甄别影响催化剂活性的关键因素。结果表明, 阳离子物种所引入的碱性位尤其是中强碱性位控制着丙烯酸的生成, 而表面酸性位则影响乙醛的生成。当以钡含量为 2% 的 NaY 分子筛为催化剂, 在乳酸进料浓度为 38%, 进料空速为 3 h⁻¹ 及 325 °C 反应条件下, 丙烯酸收率最高, 为 44.6%。这归结于该催化剂表面具有最多的中强碱性位, 且表面 Ba²⁺ 簇具有合适的 Ba–O 键长及碱度。

关键词: 碱土金属; 碱性位; NaY 分子筛; 乳酸; 脱水; 丙烯酸

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Alkaline Earth Metal Modified NaY for Lactic Acid Dehydration to Acrylic Acid: Effect of Basic Sites on the Catalytic Performance

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Abstract: Various NaY zeolites modified by alkaline earth metals (Mg, Ca, Sr, and Ba) were synthesized and used as catalysts for the dehydration of lactic acid to acrylic acid to investigate the effects of cationic species on the structure and surface acid/base distribution of the NaY zeolites. The important factors that affect their catalytic performance were also identified. The catalysts were characterized by N₂ physical adsorption/desorption, X-ray diffraction, temperature-programmed desorption of NH₃, and temperature-programmed desorption of CO₂. The results show that the basic sites that are induced by modified metallic species, particularly the medium basic sites, are mainly responsible for the formation of acrylic acid. The generation of acetaldehyde was affected by the acidic sites. Among the catalysts, 2% Ba/NaY showed the highest yield of acrylic acid at up to 44.6% (38% solution, LHSV = 3 h⁻¹, 325 °C) because it contained the most medium basic sites and a suitable Ba²⁺ cluster character.

Key words: alkaline earth; basic site; NaY zeolite; lactic acid; dehydration; acrylic acid

Acrylic acid (AA) and its esters are mainly produced by a two-step gas-phase oxidation of propylene in the petrochemical industry [1] and are widely used as raw materials for polymers, drugs, and other products [2,3]. With the increasing shortage of petroleum resources the synthesis of AA by the dehydration of bio-lactic acid (bio-LA) is considered to be a sustainable alternative route. Catalysis is a

promising process for the production of AA from bio-LA and it is similar to other transformation processes of bio-renewable resources to hydrogen, liquid fuel, and plastic precursors [4–6]. Since 1958, typical inorganic salt catalysts have been the focus of research into the conversion of LA [7–11] such as phosphates, silicates, carbonates, nitrates, and sulfates. Nonetheless, the research and development of

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suitable catalysts for the prospective industrialization of acrylic acid production by the lactic acid dehydration route is still important.

Recently, NaY based catalysts with unique acid/base characteristics and with broad application in industrial processes [12,13] have been investigated and used in the dehydration of lactate/LA to AA [14,15]. It has been found that the introduction of alkaline or rare earth metal species to NaY zeolites could effectively improve catalytic performance. Generally, dehydration over zeolites has always been considered to be a process catalyzed by acidic sites, which could be modified by surface cations. Experimental and theoretical studies [16,17] have shown that the structure and location of the surface cation species are important for the adsorption of reactants, which will eventually affect the reaction pathway. However, the influence of surface basic sites on the surface of solid acidic material-NaY zeolites on the catalytic performance during LA dehydration has not received enough attention.

We thus modified NaY zeolites using various alkaline earth metals to prepare AA from LA, and Ba-modified NaY zeolites with different amounts of Ba were also prepared, characterized, and used for this catalytic dehydration. We used N_2 physical adsorption/desorption, X-ray diffraction (XRD), temperature-programmed desorption of ammonia (NH_3 -TPD), and temperature-programmed desorption of carbon dioxide (CO_2 -TPD) to obtain information about structures and surface properties. The main purpose of this paper is to investigate the effects of alkaline earth species on the structure and surface acid/base distribution of NaY zeolites and to further identify the important factors that affect their catalytic performance. The relationship between surface species, basic sites, and performance for the dehydration of LA to AA is discussed.

1 Experimental

1.1 Catalyst preparation

NaY zeolites (Si/Al = 4.5, Shanghai Hengye Molecular Sieve Co. Ltd., China) were pretreated with a 1 mol/L aqueous solution of $NaNO_3$. Alkaline earth metal (Sino-pharm Chemical Reagent Co. Ltd., China) modified zeolites were prepared by the incipient wetness impregnation of NaY with the appropriate amount of nitrate, which was calculated to yield the desired content of oxides. The volume of solution used was 21 ml per 10 g of zeolite powder. This mixture was continuously stirred at 80 °C for 4 h and dried at 120 °C for 4 h. The dried samples were calcined from 120 to 550 °C at a heating rate of 10 °C/min and held for 5 h at 550 °C. The samples were then cooled to room temperature under ambient conditions.

1.2 Catalytic reaction

The dehydration of LA to AA over the catalysts was carried out in a fixed-bed quartz reactor with an 8 mm inner diameter. The catalyst (1.5 g, 30–50 mesh) was placed in the middle of the reactor and quartz wool was placed in both ends. Before catalytic evaluation the catalyst was pretreated at the required reaction temperature (325 °C) for 0.5 h under high purity N_2 (0.1 MPa, 30 ml/min). The feedstock (38% solution of LA) was then pumped into the preheating zone (LHSV = 3 h^{-1}) and driven through the catalyst bed by nitrogen. The liquid products were condensed and analyzed off-line using an Agilent 6890 gas chromatograph with a FFAP capillary column connected to an FID. Quantitative analysis of the products was carried out by the internal standard method using *n*-butanol as the internal standard.

1.3 Catalyst characterization

XRD analysis was carried out with a Bruker D8 ADVANCE X-ray diffractometer using $Cu K_\alpha$ radiation, operated at 40 kV and 30 mA. The intensity data were collected at 25 °C in a 2θ range from 5° to 50° with a scanning speed of 5°/min.

N_2 physical adsorption/desorption measurements were carried out on an ASAP 2020 instrument from Micromeritics. Before the measurements, the catalysts were placed in a vacuum for 10 h and 4 h at 300 °C and 325 °C, respectively. The BET surface area was determined from the nitrogen isotherms and the pore volume was estimated by the *t*-plot method.

NH_3 -TPD and CO_2 -TPD were performed using a BEL-CAT-B-82 instrument connected to a thermal conductivity detector. The sample (0.12 g) in the quartz reactor was heated in a flow of helium to 600 °C at a rate of 20 °C/min and maintained at this temperature for 30 min. The NH_3 (or CO_2) was adsorbed at 100 °C for 30 min and the sample was then flushed with a flow of helium at 100 °C for 15 min. The TPD of NH_3 (or CO_2) was performed with a helium flow of 30 ml/min and a heating rate of 10 °C/min from 100 to 600 °C. The amount of acid (or base) was determined by integrating the TPD curve over the studied temperature range.

2 Results and discussion

2.1 Catalytic performance

To study the influence of cation species on the catalytic performance, NaY zeolites modified with various alkaline earth metals (2%) were synthesized and used as catalysts for the reaction. The respective results are shown in Table 1. By

Table 1 Catalytic performance of the modified NaY zeolites for dehydration of LA

Catalyst	Conversion (%)	Selectivity (mol%)			
		AA	AD	Propanoic acid	2,3-pentadione
NaY	99.2	21.6	23.1	1.4	0.0
2%Mg/NaY	98.8	12.2	7.1	0.0	0.0
2%Ca/NaY	99.6	31.1	18.9	0.0	0.0
2%Sr/NaY	99.7	43.7	13.6	0.8	0.0
2%Ba/NaY	99.9	44.6	26.3	0.8	4.2
0.5%Ba/NaY	99.5	37.7	33.7	0.0	3.3
1%Ba/NaY	99.4	33.5	30.9	0.0	0.0
5%Ba/NaY	98.9	33.8	18.0	0.0	0.0

Reaction conditions: 38% solution of LA, LHSV = 3 h⁻¹, 325 °C.

comparison with the parent NaY, the modified zeolites except for 2%Mg/NaY all showed better dehydration performance and higher selectivity for AA. Although the conversion of LA over 2%Mg/NaY reached 98.8% its selectivity for AA was the lowest at 12.2%. The dehydration of LA over 2%Ba/NaY was much more efficient than that of the other modified zeolites. From Table 1, the yield of AA over the modified NaY zeolites is shown to increase according to atomic number, i.e., Mg < Ca < Sr < Ba.

To investigate the influence of the amount of Ba on the reaction, NaY zeolites were modified with various amounts of Ba and the catalytic results obtained are also shown in Table 1. Compared with the NaY zeolite, the catalysts modified by Ba all gave higher AA selectivities. However, the yield of AA was not dependent on the increase in Ba content. 2%Ba/NaY had the highest AA selectivity of 44.6% among the Ba/NaY zeolites. The yield of acetaldehyde (AD) obtained over the Ba/NaY zeolites decreased gradually with an increase in Ba content. We conclude that the introduction of Ba enhances the production of AA and too much Ba could inhibit the formation of AD.

2.2 Characterization

2.2.1 XRD

Figure 1 shows XRD patterns of the modified NaY zeolites by various alkaline earth metals. As shown in Fig. 1, all the XRD patterns were similar. This means that the structure of the modified zeolites was retained after impregnation and calcination. However, there are slight differences in these XRD patterns. Compared with the parent NaY the characteristic peak strength of the (111) crystal face at $2\theta = 6.2^\circ$ for the catalysts all increased except for 2%Ba/NaY, while the peak intensity of (331), (642), and (555) changed slightly. The diffraction peaks of 2%Ba/NaY moved to a higher angle, which is due to the slight distortion of the zeolite crystal cells. We conclude that the introduction of

Fig. 1. XRD patterns of the catalysts modified by various alkaline earth metals. (1) NaY; (2) 2%Mg/NaY; (3) 2%Ca/NaY; (4) 2%Sr/NaY; (5) 2%Ba/NaY.

alkaline earth metals slightly affects the structure of the NaY zeolite.

The XRD patterns of the NaY zeolites that were modified by various amounts of barium are shown in Fig. 2. The structure of the modified zeolites with different Ba content was retained after impregnation and calcination. The diffraction peak intensities of (331), (642), and (555) for the modified zeolites all increased compared with those of the NaY parent zeolite. To some extent, the changes in zeolite structure depended on the amount of Ba loading. In addition, no obvious diffraction peaks corresponding to crystallized Ba_xO_y were observed even though the amount of Ba loading reached 5%. This suggests good dispersion of Ba on the surface and limited segregation of Ba_xO_y nanoparticles [18].

Fig. 2. XRD patterns of the NaY catalysts modified with different amounts of Ba. (1) NaY; (2) 0.5%Ba/NaY; (3) 1%Ba/NaY; (4) 2%Ba/NaY; (5) 5%Ba/NaY.

2.2.2 Surface area and pore volume

The BET surface areas and total pore volumes of the series of catalysts modified by alkaline earth metals were also determined and the results are shown in Table 2. Compared with the parent NaY, the surface areas and pore volumes of the modified NaY zeolites were all reduced. This might result from the packing of cationic species in the micro-channel after the modification with alkaline earth metals. Moreover, the surface area and pore volume of the 2%Mg/NaY decreased most obviously, which might explain why it had the lowest AA yield. Table 2 also lists the surface areas and pore volumes of the modified zeolites with different amounts of barium. Compared with the parent NaY, the surface areas and pore volumes of the Ba/NaY zeolites were all lower, particularly the 5%Ba/NaY. XRD results show that the structures of the modified zeolites were well retained but slight changes did occur. Therefore, the reduction in surface areas and pore volumes might be attributed to the blocking of some microchannels of zeolites by surface species.

Table 2 Surface areas and pore volumes of the modified NaY zeolites

Catalyst	$A_{\text{BET}}/(\text{m}^2/\text{g})$	$V_{\text{micro}}/(\text{cm}^3/\text{g})$
NaY	577	0.34
2%Mg/NaY	472	0.29
2%Ca/NaY	514	0.31
2%Sr/NaY	518	0.32
2%Ba/NaY	524	0.33
0.5%Ba/NaY	519	0.33
1%Ba/NaY	515	0.33
5%Ba/NaY	460	0.29

2.2.3 Acidity and basicity

NH_3 -TPD is a popular method to determine the amount of acid sites and their strength in solid catalysts [19,20]. It is used to obtain information about acid sites in the catalysts modified by various alkaline earth metals. The catalyst profiles are shown in Fig. 3. The NH_3 desorption curves of the zeolites modified by the alkaline earth metals are similar to each other. This shows that there are few differences in the acid sites between the zeolites. Zeolite desorption peaks appeared between 100–600 °C and the curves are always

Fig. 3. NH_3 -TPD profiles of the NaY modified by alkaline earth metals. (1) NaY; (2) 2%Mg/NaY; (3) 2%Ca/NaY; (4) 2%Sr/NaY; (5) 2%Ba/NaY.

divided into three temperature ranges when determining the acid site distribution.

Quantitative analysis results of the desorbed NH_3 using the Gauss distribution method are shown in Table 3. As shown in Table 3, the total amount of acid sites in the zeolites modified by the alkaline earth metals was less than that of the parent NaY zeolite. The amount of medium acid sites in these catalysts decreased as follows: 2%Ba/NaY > NaY > 2%Mg/NaY > 2%Ca/NaY > 2%Sr/NaY. This is mostly consistent with the decrease in AD yield: 2%Ba/NaY > NaY > 2%Ca/NaY > 2%Sr/NaY > 2%Mg/NaY. The amount of strong acid sites in the modified zeolites all decreased while the AA yield over these zeolites, except for 2%Mg/NaY (see Table 1), increased. It seems that the generation of AD is partly controlled by the medium acidic sites but there is no clear tendency between the AA yield and the NH_3 -TPD results. We speculate that other factors such as the basic sites affect the yield of AA.

CO_2 -TPD technology was used to obtain information about the basic sites of the catalysts modified by various alkaline earth metals and the profiles are shown in Fig. 4. The curves consist of three temperature ranges [15,21] and quantitative analysis results of the desorbed amounts of CO_2

Table 3 NH_3 -TPD results of the NaY zeolites modified by various alkaline earth metals

Catalyst	Acidity amount ($\mu\text{mol/g}$)			Total acid amount ($\mu\text{mol/g}$)	Acidic site density ($\mu\text{mol/m}^2$)
	Weak (100–200 °C)	Medium (200–400 °C)	Strong (400–600 °C)		
NaY	837	664	34	1535	2.7
2%Ba/NaY	735	715	11	1461	2.8
2%Sr/NaY	867	551	13	1431	2.8
2%Ca/NaY	713	591	18	1322	2.6
2%Mg/NaY	774	599	17	1390	2.9

Fig. 4. CO₂-TPD profiles of the NaY modified by alkaline earth metals. (1) NaY; (2) 2%Mg/NaY; (3) 2%Ca/NaY; (4) 2%Sr/NaY; (5) 2%Ba/NaY.

using the Gauss distribution method are shown in Table 4.

As shown in Fig. 4, some differences exist in the zeolite profiles suggesting different distributions of basic sites over the zeolites. The total amount of basic sites in the modified zeolites was more than that in the parent NaY zeolite (see Table 4). 2%Ba/NaY had a higher ratio of medium basic sites than the other zeolites, which might be the reason for the higher yield of AA over it. 2%Sr/NaY and 2%Ca/NaY had the same total amount of basic sites and the same density, while there were more medium basic sites on the 2%Sr/NaY. 2%Sr/NaY gave a higher AA yield than 2%Ca/NaY. Therefore, the medium basic sites might be the main active sites for AA generation. In addition, 2%Mg/NaY has a high ratio of medium basic sites and medium acidic sites but it gives lower yields of AA and AD. This might be because of the nature of the Mg species.

To obtain more information about the effects of basic sites on the catalytic performance the NaY zeolites were modified with various amounts of Ba. The CO₂-TPD profiles and relative results are shown in Fig. 5 and Table 4,

Fig. 5. CO₂-TPD profiles of the NaY catalysts modified with various amounts of Ba. (1) 0.5%Ba/NaY; (2) 1%Ba/NaY; (3) 2%Ba/NaY; (4) 5%Ba/NaY.

respectively. The amount of medium basic sites in 2%Ba/NaY, in addition to the total amount of basic sites, is higher than that in the other catalysts (see Table 4). Moreover, the amount of medium basic sites in the zeolites increased as follows: 0.5%Ba/NaY < 1%Ba/NaY < 2%Ba/NaY. At a Ba load of 5% (5%Ba/NaY), an increase in the weak basic sites and a decrease in the medium basic sites was observed according to the CO₂-TPD results (see Table 4).

2.3 Discussion

The basic sites that were induced by the alkaline earth species play a positive role in the formation of AA. HY with the same Si/Al was also used to investigate the effect of basic sites, and we obtained a 99.6% conversion of LA with 46.1% selectivity for AD and just 0.7% selectivity for AA. The cations are the preferred adsorption sites and are particularly important for the interaction with polar or easily polarizable molecules [22]. The extent or strength of mo-

Table 4 CO₂-TPD results of NaY zeolites modified by various alkaline earth metals

Catalyst	Basicity amount (μmol/g)			Total base amount (μmol/g)	Basic site density (μmol/m ²)
	Weak (100–200 °C)	Medium (200–400 °C)	Strong (400–600 °C)		
NaY	4.6	31.7	8.4	44.7	0.08
2%Mg/NaY	7.2	36.1	10.6	53.8	0.11
2%Ca/NaY	4.7	26.1	14.9	45.8	0.09
2%Sr/NaY	7.4	29.4	8.9	45.8	0.09
2%Ba/NaY	5.0	40.5	8.6	54.1	0.10
0.5%Ba/NaY	3.8	27.5	8.0	39.3	0.08
1%Ba/NaY	5.4	27.7	7.6	40.6	0.08
5%Ba/NaY	6.9	27.0	9.5	43.4	0.09

lecular adsorption in the zeolite pores are dominated by the interaction of the adsorbate (such as CO_2) with the electric field induced by the cations [22,23]. The CO_2 adsorption sites are always defined as basic sites. LA and AA contain a carbonyl group and can also be considered to be adsorbates, similar to CO_2 , during the catalytic dehydration of LA to AA. However, the adsorption behavior of the reactants and products during LA dehydration are different to that of CO_2 because of their molecular sizes and nature.

The adsorption of LA onto the catalyst surface and bonding to the active sites is important to obtain a high yield of AA from LA. Strong adsorption might enhance the secondary AA reaction leading to more by-products while weak adsorption might effectively reduce the conversion of LA to

AA. The high catalytic performance obtained over 2%Ba/NaY, which contained more medium basic sites than the other modified catalysts, suggests that medium basic sites might be the main but not the only active sites that participate in the formation of AA. The surface basicity induced by cations has always been explained using the trimer cluster model. The cations are sorted as trimer cationic clusters and interact with the zeolite framework oxygen [24,25] (see Fig. 6). The framework oxygen nearest the cation provides a basic site. The basicity and cation-oxygen distance increases with ionic radius, i.e., $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$. In addition, the basicity of the Na^+ cluster is stronger than that of the alkaline earth cationic clusters at higher S_k^-/S_k^+ values [25].

Fig. 6. Geometry of the trimer cluster model. (a) X^+ = alkali cations; (b) X^{2+} = alkaline earth metal cations.

Among the clusters of alkaline earth metallic ions the Ba^{2+} cluster seems more suitable for the formation of AA. The bond strength and steric effect of the cluster are important factors that control the interaction of LA with the cluster [26–28]. The long distance and suitable strength for Ba–O bond might reduce the inner stereospecific blockade for the adsorption of LA upon surface bonding to the Ba^{2+} clusters. This finally leads to high catalytic performance over 2%Ba/NaY. Moreover, the yield of AA over the NaY zeolites modified by the alkaline earth metals increases with the atomic number, i.e., $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$, which can be partly attributed to the different characteristics of the X^{2+} clusters.

The diffusion efficiency of the reactants in the conversion of LA to AA is also an important factor that affects the reaction in addition to the characteristics of the surface cation clusters mentioned above. The diffusion resistance for LA and AA depends on the channel size (super cage < sodalite cage < hexagonal prism) and the location of the cations over the zeolites. Frising et al. [29] summarized the extra framework cation distribution in X and Y faujasite zeolites. An diagram of the different cation sites in the faujasite structure is shown in Fig. 7.

The catalytic performance depends on the amount of active cation clusters in a suitable location, which is affected by the amount of surface species loading. Over the Ba/NaY

zeolites, sites II and I' were the preferred locations for the Ba cations during the catalytic dehydration of LA to AA with water at 325 °C. Site II, site I, and site I' were the main locations for the Ba cations in the Ba^{2+} clusters [30] while the cations migrate out of site I towards the super cage when hydrated [29]. Based on this, the catalytic results over the Ba/NaY zeolites can be explained. The higher AA yield over 2%Ba/NaY compared to 0.5%Ba/NaY and 1%Ba/NaY can be attributed to the larger number of Ba^{2+} clusters. According to the XRD results and other reports [18,31], the lower AA yield over 5%Ba/NaY compared to 2%Ba/NaY can be attributed to the coverage of active clusters by the species in a specific phase.

Fig. 7. The different cation sites in the faujasite structure.

3 Conclusions

Differently substituted zeolites were investigated and the yields of acrylic acid were found to increase as follows: 2%Mg/NaY < 2%Ca/NaY < 2%Sr/NaY < 2%Ba/NaY. This order is consistent with the basicity of the respective cation clusters and the amount of medium basic sites on the catalysts. The yield of acetaldehyde gave the following sequence: 2%Ba/NaY > NaY > 2%Ca/NaY > 2%Sr/NaY > 2%Mg/NaY. This is similar to the amount of medium acidic sites on the catalysts. Moreover, the sequence for the yields of acrylic acid over the Ba/NaY zeolites containing various amounts of Ba was similar to that of the amount of medium basic sites. The higher amount of Ba can inhibit the formation of acetaldehyde. Among the studied catalysts, 2%Ba/NaY gave the highest yield of acrylic acid at up to 44.6% because it contained the most medium basic sites and a suitable Ba²⁺ cluster character. The results discussed above reveal that the basic sites that were induced by the modified metallic species and particularly the medium basic sites are mainly responsible for the formation of acrylic acid. The generation of acetaldehyde can be affected by the acidic sites. Our research reveals a new method to obtain more effective catalysts for AA production by adjusting the natural alkalinity of the surface species and also by creating more basic solid materials for use as supports instead of NaY zeolites.

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