

## BASIC PROPERTIES OF POTASSIUM OXIDE SUPPORTED ON ZEOLITE Y STUDIED BY PYRROLE-TPD AND CATALYTIC CONVERSION OF METHYLBUTYNOL

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We report on the basic properties of zeolite NaY and potassium supported on NaY (K/NaY) assessed by pyrrole-TPD and MBOH transformation. Pyrrole-TPD revealed that impregnation of zeolite NaY with potassium promoted additional adsorption sites for pyrrole compared to parent zeolite. For zeolite with various potassium loadings, pyrrole adsorbed on K/NaY decreased with increased potassium loading. Reduction in pyrrole adsorption could be due to potassium hindering intrinsic basic sites (lattice oxygen), to oxide of potassium occluding in zeolite cavities restricting access for pyrrole, or to  $K_2O$  reacting with pyrrole to form nondesorbed pyrrolate anions. On MBOH transformation, potassium almost completely suppressed NaY acid sites while K/NaY basicity increased with potassium loading.

Keywords: potassium on zeolite Y; pyrrole adsorption; MBOH.

### INTRODUCTION

We recently reported a preparation of base heterogeneous catalysts containing potassium supported on zeolite NaY ( $xK/NaY$  where  $x = 4, 8$  and 12%wt loading of K) by impregnation of a solution of potassium on the zeolite.<sup>1</sup> This method prevented collapse of the zeolite structure and the catalysts obtained were effective for transesterification of *Jatropha* seed oil to produce biodiesel. Catalytic performance increased with potassium loading and complete conversion was observed on 12K/NaY. The addition of potassium proved able to change the basic properties of the zeolite. Thus, we further investigated the basicity of the NaY and  $xK/NaY$  catalysts.

Typically, oxygen atoms in the framework of zeolites are intrinsic Lewis basic sites which form acid-base pairs with the charge compensating cations.<sup>2</sup> The basicity of zeolite can be further increased by impregnating it with a solution of alkali metal salt which can be decomposed to form oxides. The occlusion of alkali metal oxide clusters in the zeolite cages results in a further increase in basicity.<sup>3</sup>

A technique widely used to study the basic properties of solids is temperature programmed desorption of carbon dioxide ( $CO_2$ -TPD) in which the desorption temperatures reflect the strength of  $CO_2$  adsorption whereas the amount of desorbed  $CO_2$  correlates with the quantity of basic sites. Noiroj *et al.*<sup>4</sup> used  $CO_2$ -TPD to study the basic properties of NaY and NaY loaded with 10 wt% KOH.  $CO_2$  desorption on NaY occurred in the 100-300 °C range reaching a maximum at around 200 °C corresponding to adsorption on weak basic sites. Desorption on KOH/NaY was observed in the 230-370 °C temperature range corresponding to adsorption on medium strength basic sites which were responsible for the catalytic activity for transesterification. Ramos *et al.*<sup>5</sup> also used  $CO_2$ -TPD to study basicity of catalysts prepared by loading sodium acetate solution on three different zeolites (mordenite, beta and X) to determine the influence of the zeolite type on biodiesel production. The modified zeolite X provided greater activity than the others because it contained a higher concentration

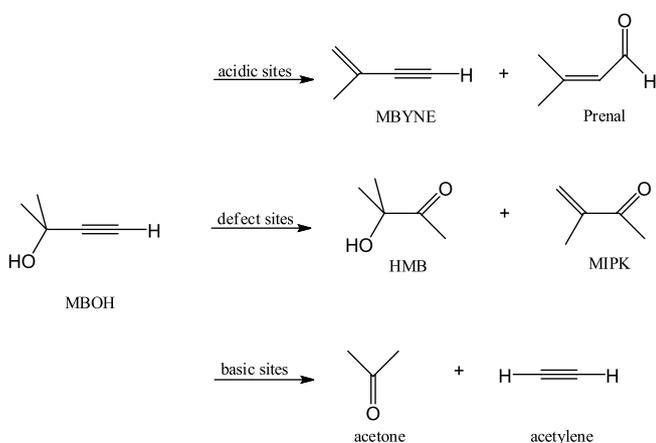
of occluded sodium oxide species which acted as super basic sites.

However, the main drawback of  $CO_2$ -TPD is the strong interaction of  $CO_2$  with basic sites, data for which may not reflect the correct number of basic sites.<sup>2</sup> Consequently, pyrrole ( $C_4H_4NH$ ), a five-membered ring heterocyclic aromatic compound may be used as an alternative probe molecule to characterize zeolite basicity.<sup>2,6,7</sup> Pyrrole is an amphoteric molecule which can either interact with the Lewis basic oxygen of zeolite via the NH group by hydrogen bonding or with the Lewis acidic cation via the aromatic  $\pi$ -electrons interaction.<sup>7</sup> Pyrrole can be used as a probe molecule in TPD for the characterization of basic sites because it can be adsorbed reversibly due to its weak acidity.<sup>3,7</sup> In the present work, we applied pyrrole-TPD to study the basicity of NaY and K/NaY.

Furthermore, the basic properties of the K/NaY catalysts were correlated with the catalytic activity on transformation of 2-methyl-3-buten-2-ol (MBOH). Products from different reaction pathways can be used to distinguish acidic and basic sites of a catalyst.<sup>8-10</sup> The overall reaction pathways of MBOH are shown in Scheme 1. In the presence of weak acidic sites, 3-methyl-3-buten-1-yne (MBYNE) is produced via dehydration of MBOH. In the presence of strong acidic sites, 3-methyl-2-buten-1-al (prenal) is formed via isomerization of MBOH. On the other hand, the coordinatively unsaturated (defect) sites lead to the formation of 3-hydroxy-3-methyl-2-butanone (HMB) and 3-methyl-3-buten-2-one (MIPK). Over the basic sites, acetone and acetylene are produced from the decomposition of MBOH. The MBOH reaction has been used to test for the basic zeolite catalyst. For instance, Meyer and Hoelderich<sup>11</sup> investigated the basic properties of various basic NaX zeolite catalysts prepared by ion exchange or impregnation with aqueous solution of cesium acetate and methanolic solution of sodium azide. The basic sites were generated in the zeolite after loading alkali metal cations and alkaline metal oxides by ion exchange and the impregnation method, respectively. The authors observed that both conversion of MBOH and selectivity for basic products correlated with the amount of cesium acetate decomposed on zeolite NaX.

The aim of the present work was to investigate the basic properties of NaY and K/NaY by pyrrole-TPD and transformation of MBOH.

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**Scheme 1.** Reaction pathways of MBOH

## EXPERIMENTAL

### Catalyst preparation

The catalysts studied in this work were prepared by impregnating NaY with a solution containing a mixture of  $\text{CH}_3\text{COOK}/\text{CH}_3\text{COOH}$  to give potassium loadings of 4, 8 and 12 wt%. The samples were dried in an oven at 30 °C for 4 h and at 80 °C overnight before calcination at 400 °C for 3 h. The resultant samples were 4K/NaY, 8K/NaY and 12K/NaY.

### Pyrrole-TPD

Pyrrole-TPD analysis was performed on an apparatus manufactured by Raczek Analysen Technik GmbH, Hannover (Germany).<sup>12</sup> A 0.1 g sample with a particle size of 200–315  $\mu\text{m}$  was placed into a plug flow quartz reactor which was coupled to a thermal conductivity detector (TCD). The prepared catalysts were then conditioned under a helium flow (45 mL/min) to 350 °C at a heating rate of 10 °C/min with the final temperature held for 1 h. Subsequently, a helium flow saturated with pyrrole at 20 °C was fed at a flow rate of 59.3 mL/min over the conditioned catalyst at 55 °C for 45 min. The physically adsorbed pyrrole was removed by flushing with helium at a flow rate of 45 mL/min at 100 °C for 2 h. Temperature programmed desorption (TPD) of the chemically adsorbed pyrrole was studied in the temperature range to 600 °C with a heating rate of 10 °C/min using helium as a carrier gas. Gaussian deconvolution of the TPD curve was performed using the Origin 6.0 program to identify peak positions and to integrate the peak area. To determine the amount of pyrrole, a calibration curve was constructed based on peak area versus number of moles of pyrrole corresponding to 0.5, 0.8 and 1.0  $\mu\text{L}$  of pyrrole directly injected into the quartz reactor. The TCD signals were recorded isothermally at 110 °C. The amount of injected pyrrole in mol was calculated using Equation 1.

$$n_{\text{pyr}} = \frac{\rho_{\text{pyr}} V_{\text{pyr}}}{M_{\text{pyr}}} \quad (1)$$

where  $\rho_{\text{pyr}}$ ,  $V_{\text{pyr}}$  and  $M_{\text{pyr}}$  represent the density (0.966 g  $\text{cm}^{-3}$ ), volume ( $\mu\text{L}$ ) and molecular weight (67.09 g  $\text{mol}^{-1}$ ) of pyrrole, respectively.

### Transformation of MBOH

The transformation of MBOH was conducted in a fixed bed reactor controlled by an automated bench unit.<sup>12</sup> MBOH and toluene with a purity of 99% were obtained from Fluka and used without further

purification. A catalyst weight of 20 mg with a particle size of 200–315  $\mu\text{m}$  placed in the central section of a quartz tubular reactor was heated to 350 °C at a rate of 8 °C/min and kept at this temperature for 4 h under nitrogen flow (13.7 mL/min) to remove any adsorbed compounds from the surface. After catalyst activation, the reactor temperature was lowered to 120 °C. A solution mixture of MBOH (95 vol%) and toluene (5 vol%, as an internal standard) placed and cooled in a storage vessel at 13 °C was fed into an evaporator. The vapor produced was passed through a capillary in which a static nitrogen pressure of 2 bars was applied to obtain a gas flow rate of 0.02 mL/min. The gas stream was flowed over the catalyst in the reactor where the temperature was maintained at 120 °C. The outlet gas was analyzed on-line using a HP 8090 Series II gas chromatograph with a 60 m Optima Wax capillary column. The MBOH conversion ( $X_{\text{MBOH}}$ ), yield (Y) and selectivity (S) of each product from the transformation of MBOH were calculated by Equation 2–4, respectively.

$$X_{\text{MBOH}} (\%) = \frac{n_{\text{MBOH, in}} - n_{\text{MBOH, out}}}{n_{\text{MBOH, in}}} \times 100 \quad (2)$$

$$Y_p (\%) = \frac{A_p R_p / M_p}{\sum_k A_k R_k / M_k} \times 100 \quad (3)$$

$$S_p (\%) = \frac{Y_p}{X_{\text{MBOH}}} \times 100 \quad (4)$$

where  $A_p$ ,  $R_p$ ,  $M_p$ ,  $S_p$  and  $Y_p$  represent the area, response factor, mass, selectivity and yield of product P, respectively.  $A_k$ ,  $R_k$  and  $M_k$  represent the area, response factor and mass of all components.

## RESULTS AND DISCUSSION

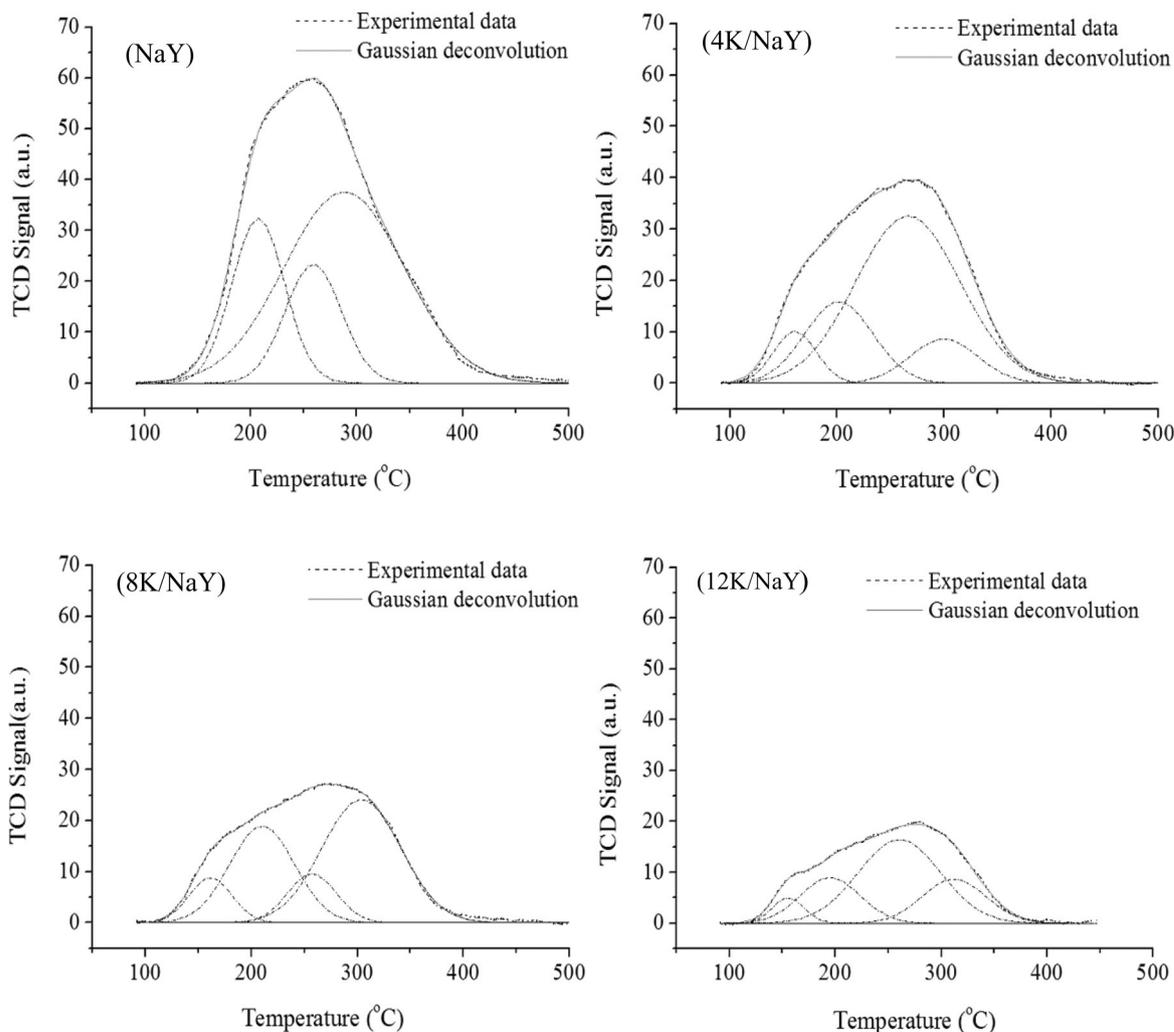
### Pyrrole-TPD

The pyrrole-TPD profiles of NaY and xK/NaY are shown in Figure 1. Using a similar procedure for each sample, NaY yielded the most intense TCD signal. For the K/NaY samples, curve intensity decreased as the potassium loading was increased. The total peak area of each curve and the corresponding amount of pyrrole per gram of the catalyst, calculated from the calibration curve, are listed in Table 1. It was reported that the surface area of K/NaY decreases linearly as the potassium loading is increased.<sup>1</sup> In the present case, the adsorbed amount of pyrrole also decreased linearly with increased potassium loading ( $R^2 = 0.9898$ ). Thus, the amount of adsorbed pyrrole was related directly to the surface area. The specific amount of pyrrole (mmol per surface area) on all catalysts was similar, at approximately 0.02 mmol/ $\text{m}^2$ . It was likely that the oxide of potassium occluded in the zeolite cavities, rendering them smaller and less accessible for pyrrole molecules.<sup>13,14</sup> By comparing the TPD profiles of the K/NaY samples with that of NaY, an additional shoulder was observed at around 150 °C suggesting that loading the zeolite with potassium generated additional adsorption sites. According to Doskocil *et al.* and Lavalley, potassium can generate species such as  $\text{K}_2\text{O}$  which act as the strong base and can generate pyrrolate anion ( $\text{C}_4\text{H}_4\text{N}^-$ ).<sup>3,15</sup> The pyrrolate anion interacted with surface hydroxyl groups which are less basic and thus, the pyrrole desorption occurred at a lower temperature.<sup>3,15</sup> Furthermore, this model could explain the decrease in the desorbed amount of pyrrole with increasing potassium content, since the formed pyrrolate cannot desorb under the given conditions.

The pyrrole molecule interacts with zeolite via a hydrogen bond between the NH group and lattice oxygen which acts as the Lewis basic sites and interaction of pyrrole aromatic electrons with the

**Table 1.** Results from pyrrole-TPD

Sample	Total peak area (area/g)	Amount of pyrrole (mmol/g)	Amount of pyrrole per surface area (mmol/m <sup>2</sup> )	Peak of desorption temperature (°C) from deconvolution and corresponding peak area (%)			
NaY	89,133	19.9	0.0213	207 (22.6%)	259 (17.4%)	288 (59.9%)	
4K/NaY	64,498	14.4	0.0198	160 (7.8%)	210 (19.7%)	266 (61.7%)	299 (10.6%)
8K/NaY	47,108	10.5	0.0208	161 (9.5%)	210 (30.8%)	257 (11.7%)	303 (47.8%)
12K/NaY	30,750	6.8	0.0192	155 (6.0%)	195 (20.6%)	260 (52.0%)	312 (21.2%)

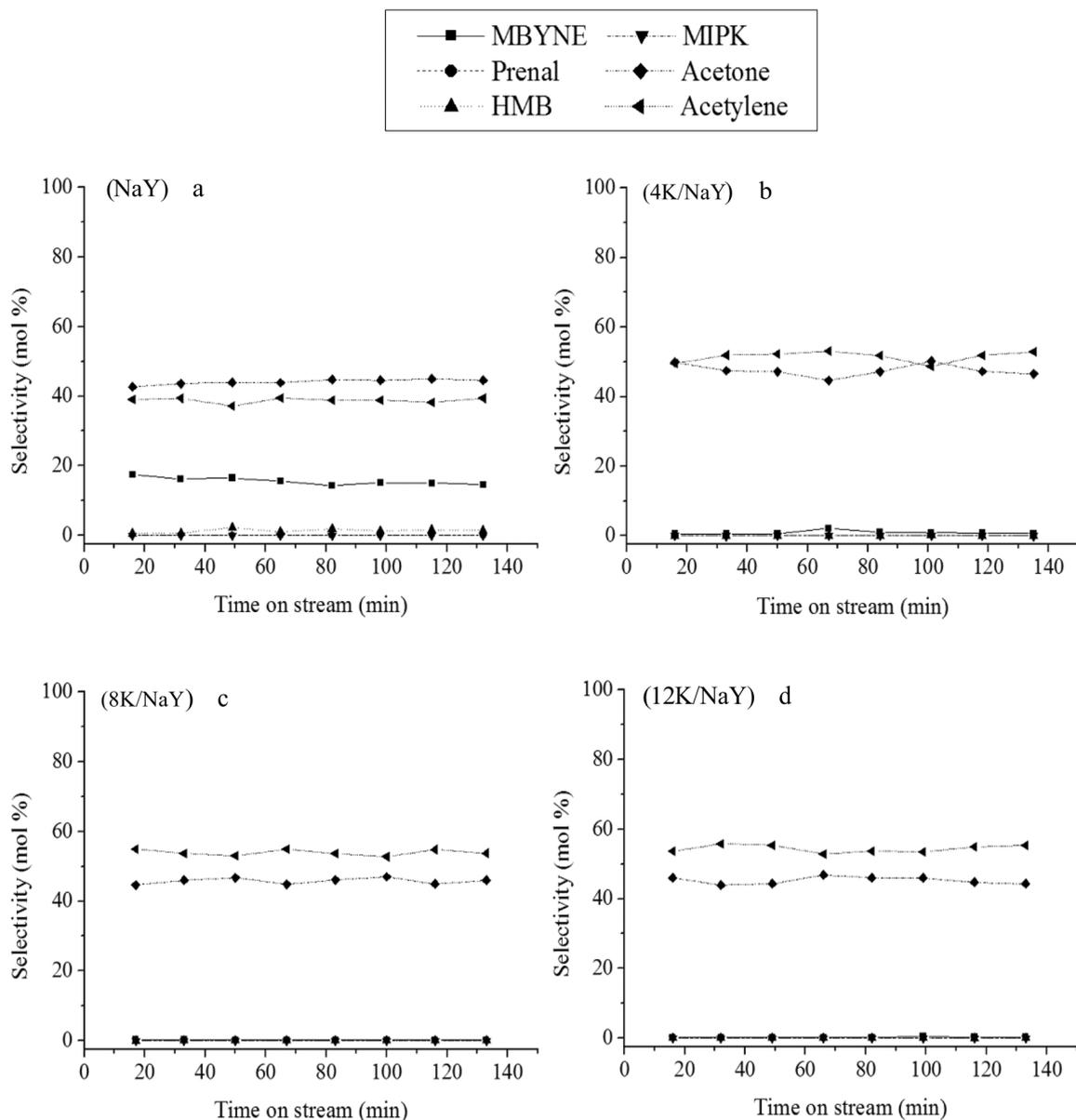
**Figure 1.** Experimental and deconvolution of TPD peaks of pyrrole on NaY, 4K/NaY, 8K/NaY and 12K/NaY

cations (Na ions) which are Lewis acidic sites. With potassium loading by impregnation, the cations were able to interact with the Lewis basic sites, hinder adsorption of pyrrole and result in less hydrogen bonding. The potassium ions also interacted with the aromatic electrons. Moreover, in the event that some potassium cations exchanged with the Na cations, the basicity can be enhanced according to the difference in cationic size.<sup>7,13,14</sup>

Because the peak positions in all samples were not clearly resolved, deconvolutions of the TPD profiles were generated (Figure 1). There were three peaks for NaY and four peaks for the K/NaY samples. The additional peak in the profiles of the K/NaY samples can be assigned to the additional adsorption sites, potassium ions, which interacted with pyrrole. The difference in the cationic size of potassium and sodium resulted in different adsorption strength.

### Transformation of MBOH

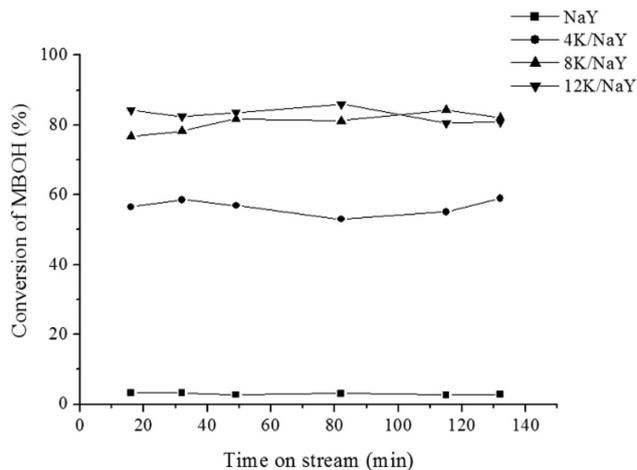
Because the test reaction of MBOH transformation was able to distinguish between acidic, basic and coordinatively unsaturated active sites, the change in basicity can be compared directly from the product selectivity. Selectivity over the NaY and K/NaY samples are shown in Figure 2. The reaction over the NaY zeolite catalyst generated main products from basic pathway (acetone and acetylene) with a significant amount of MBYNE which is a product from the acidic pathway (Figure 2a). Thus, the surface of the NaY zeolite contained predominantly basic sites and a moderate number of acidic sites. This observation was in strong agreement with reports in the literature.<sup>16</sup> The products from the amphoteric pathway (HMB and MIPK) were not significant in all catalysts. In contrast, all the K/NaY samples



**Figure 2.** Selectivity of the product of MBOH test reaction over NaY, 4K/NaY, 8K/NaY, and 12K/NaY catalyst, reaction temperature, 120 °C; amount of catalyst, 0.020 g

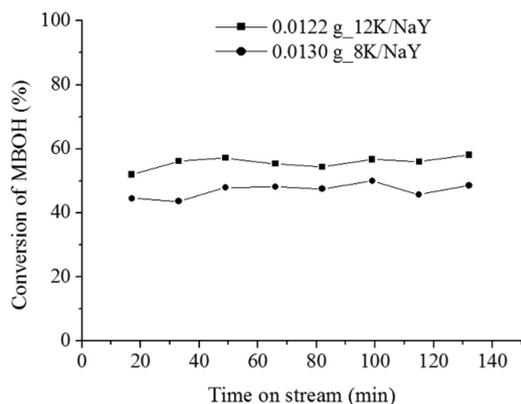
generated acetone and acetylene as the major products (Figure 2b-d) confirming their basicity. The amount of MBYNE was less than 0.9% for 4K/NaY and less than 0.3% for 8K/NaY and 12K/NaY. These results indicated that impregnation with potassium suppressed the acidic sites of NaY zeolite by solid state ion exchange and that all the prepared catalysts were basic in nature. The molar ratio between acetone and acetylene (0.93, 0.90 and 0.85 of 4K/NaY, 8K/NaY and 12K/NaY, respectively) was less than the theoretical value, 1.00, probably because of aldol condensation of acetone producing condensation products which adsorbed strongly on the surface.<sup>17,18</sup>

The conversions of MBOH over the NaY and K/NaY samples are shown in Figure 3. The conversion on NaY was significantly lower than those of the K/NaY samples indicating that impregnation with potassium increased the active sites. In the first 80 min, conversion on K/NaY increased with potassium loading but after that the conversion on 12K/NaY was similar to that on 8K/NaY. The absence of any difference was probably caused by the high degree of conversion which does not allow differentiation between the two samples. To confirm this hypothesis, the amount of the two catalysts (8K/NaY and



**Figure 3.** Conversion of MBOH test reaction over the parent NaY and xK/NaY catalysts with 4, 8 and 12 wt% loading, reaction temperature, 120 °C; amount of catalyst, 0.020 g

12K/NaY) for the MBOH test reaction was decreased from 0.02 to 0.01 g and the conversions compared again (Figure 4). The products from the basic pathway were still predominant in both catalysts (not shown). The conversion on 12K/NaY was higher than that on 8K/NaY confirming the assumption that the strength of basic sites of K/NaY increased with potassium loading. The information on basicity of these catalysts were in good agreement with their catalytic performance on transesterification of *Jatropha* seed oil in which conversion and biodiesel yield increased with potassium loading.<sup>1</sup>



**Figure 4.** Conversion of MBOH test reaction over the 8K/NaY and 12K/NaY catalysts, reaction temperature, 120 °C; amount of catalyst, 0.01 g

## CONCLUSION

The basic properties of K/NaY were studied by pyrrole-TPD and the MBOH test reaction. Pyrrole-TPD indicated at decrease in adsorption sites after impregnation of potassium on NaY in accordance with the decrease in surface area. The nature of pyrrole adsorption on the K/NaY samples was different to that on NaY because potassium ions can hinder the intrinsic basic site (lattice oxygen) and possibly occluded in the zeolite cavities preventing the access of pyrrole. The potassium ions can also interact with the aromatic electrons of pyrrole. The difference in cation size between impregnated potassium and original sodium on the zeolite resulted in additional adsorption sites.

Further study by MBOH test reaction revealed that impregnation of potassium almost completely suppressed the acidic sites of NaY while the basicity of K/NaY samples increased with potassium loading.

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## REFERENCES

- Supamathanon, N.; Wittayakun, J.; Prayoonpokharach, S.; *J. Ind. Eng. Chem.* **2011**, *17*, 182.
- Barthomeuf, D.; *Catal. Rev.: Sci. Eng.* **1996**, *38*, 512.
- Doskocil, E. J.; Bordawekar, S.; Davis, R. J. In *Catalysis*; Spivey, J. J., ed.; Royal Society of Chemistry: Cambridge, 2000, vol. 15, chap. 2.
- Noiroj, K.; Intarapong, P.; Luengnaruemitchai, A.; Jai-In, S.; *Renew. Energ.* **2009**, *34*, 1145.
- Ramos, M. J.; Casas, A.; Rodríguez, L.; Romero, R.; Pérez, A.; *Appl. Catal., A* **2008**, *346*, 79.
- Hattori, H.; *Chem. Rev.* **1995**, *95*, 537.
- Förster, H.; Fuess, H.; Geidel, E.; Hunger, B.; Jobic, H.; Kirschhock, C.; Klepel, O.; Krause, K.; *Phys. Chem. Chem. Phys.* **1999**, *1*, 593.
- Lauron-Pernot, H.; Luck, F.; Popa, J. M.; *Appl. Catal.* **1991**, *78*, 213.
- Handa, H.; Fu, Y.; Baba, T.; Ono, Y.; *Catal. Lett.* **1999**, *59*, 195.
- Brei, V. V.; *Theor. Exp. Chem.* **2008**, *44*, 320.
- Meyer, U.; Hoelderich, W. F.; *J. Mol. Catal. A: Chem.* **1999**, *142*, 213.
- Kuśtrowski, P.; Chmielarz, L.; Božek, E.; Sawalha, M.; Roessner, F.; *Mater. Res. Bull.* **2004**, *39*, 263.
- Sánchez, M. S.; Blasco, T.; *J. Am. Chem. Soc.* **2002**, *124*, 3443.
- Heidler, R.; Janssens, G. O. A.; Mortier, W. J.; Schoonheydt, R. A.; *Microporous Mater.* **1997**, *12*, 1.
- Lavalley, J. C.; *Catal. Today* **1996**, *27*, 377.
- Huang, M.; Kaliaguine, S.; *Catal. Lett.* **1993**, *18*, 373.
- Corma, A.; Iborra, S.; *Adv. Catal.* **2006**, *49*, 239.
- Aramendía, M. A.; Boráu, V.; García, I. M.; Jiménez, C.; Marinas, A.; Marinas, J. M.; Porras, A.; Urbano, F. J.; *Appl. Catal., A* **1999**, *184*, 115.