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

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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 K₂O 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 sodium azide. 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. 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.

A technique widely used to study the basic properties of solids is temperature programmed desorption of carbon dioxide (CO₂-TPD) in which the desorption temperatures reflect the strength of CO₂ adsorption whereas the amount of desorbed CO₂ correlates with the quantity of basic sites. Noiroj et al. used CO₂-TPD to study the basic properties of NaY and NaY loaded with 10 wt% KOH. CO₂ 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. also used CO₂-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 CO₂-TPD is the strong interaction of CO₂ with basic sites, data for which may not reflect the correct number of basic sites. Consequently, pyrrole (C₅H₅NH), a five-membered ring heterocyclic aromatic compound may be used as an alternative probe molecule to characterize zeolite basicity. 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 π-electrons interaction. 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. 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. 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-ol (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-butanol (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 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.
purification. A catalyst weight of 20 mg with a particle size of 200-
315 μm 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
clear 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_{MBOH}),
yield (Y) and selectivity (S) of each product from the transformation
of MBOH were calculated by Equation 2-4, respectively.

\[
X_{\text{MBOH}}(\%) = \frac{n_{\text{MBOH}} - n_{\text{MBOH ad}}}{n_{\text{MBOH in}}} \times 100
\]

\[
Y_k(\%) = \frac{A_k R_k}{\sum_k A_k R_k / M_k} \times 100
\]

\[
S_k(\%) = \frac{Y_k}{X_{\text{MBOH}}} \times 100
\]

where \(A_k, R_k, M_k, S_k\), and \(Y_k\) represent the area, response factor, mass,
selectivity and yield of product \(P_k\) respectively. \(A_k, R_k\) and \(M_k\) repre-
sent the area, response factor and mass of all components.

RESULTS AND DISCUSSION
Pyrolye-TPD

The pyrolye-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 inte-
density 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.1 In
the present case, the adsorbed amount of pyrrole also decreased linearly
with increased potassium loading (R² = 0.9898). Thus, the amount
of adsorbed pyrrole was related directly to the surface area. The spe-
cific amount of pyrrole (mmol per surface area) on all catalysts
was similar, at approximately 0.02 mmol/m². It was likely that the
oxide of potassium occluded in the zeolite cavities, rendering them
smaller and less accessible for pyrrole molecules.13,14 By comparing
the TPD profiles of the K/NaY samples with that of NaY, an addi-
tional shoulder was observed at around 150 °C suggesting that loading
the zeolite with potassium generated additional adsorption sites.
According to Doskoci1 and Lavalley, potassium can generate
species such as K2O which act as the strong base and can generate
pyrrole anion (C3H4N2-).13,14 The pyrrole anion interacted with
surface hydroxyl groups which are less basic and thus, the pyrrole
desorption occurred at a lower temperature.15 Furthermore, this model
could explain the decrease in the desorbed amount of pyrrole
with increasing potassium content, since the formed pyrrole 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

EXPERIMENTAL
Catalyst preparation

The catalysts studied in this work were prepared by impregnating
NaY with a solution containing a mixture of CH3COOK/CH3COOH
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 cal-
cination at 400 °C for 3 h. The resultant samples were 4K/NaY , 8K/
NaY and 12K/NaY .

Pyrole-TPD analysis was performed on an apparatus manufac-
tured by Raczek Analysen Technik GmbH, Hannover (Germany).15
A 0.1 g sample with a particle size of 200-315 μm was placed into a
plug flow quartz reactor which was coupled to a thermal conductivity
detector (TCD). The prepared catalysts was 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 μL 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.

\[
n_{\text{pyr}} = \frac{\rho_{\text{pyr}} V_{\text{pyr}}}{M_{\text{pyr}}}
\]

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

Transformation of MBOH

The transformation of MBOH was conducted in a fixed bed reac-
tor controlled by an automated bench unit.12 MBOH and toluene with
a purity of 99% were obtained from Fluka and used without further
Basic properties of potassium oxide supported on zeolite Y studied by pyrrole-TPD

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.

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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total peak area (area/g)</th>
<th>Amount of pyrrole (mmol/g)</th>
<th>Amount of pyrrole per surface area (mmol/m²)</th>
<th>Peak of desorption temperature (°C) from deconvolution and corresponding peak area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaY</td>
<td>89,133</td>
<td>19.9</td>
<td>0.0213</td>
<td>207 (22.6%) 259 (17.4%) 288 (59.9%)</td>
</tr>
<tr>
<td>4K/NaY</td>
<td>64,498</td>
<td>14.4</td>
<td>0.0198</td>
<td>160 (7.8%) 210 (19.7%) 266 (61.7%) 299 (10.6%)</td>
</tr>
<tr>
<td>8K/NaY</td>
<td>47,108</td>
<td>10.5</td>
<td>0.0208</td>
<td>161 (9.5%) 210 (30.8%) 257 (11.7%) 303 (47.8%)</td>
</tr>
<tr>
<td>12K/NaY</td>
<td>30,750</td>
<td>6.8</td>
<td>0.0192</td>
<td>155 (6.0%) 195 (20.6%) 260 (52.0%) 312 (21.2%)</td>
</tr>
</tbody>
</table>

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

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

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. The products from the amphoteric pathway (HMB and MIPK) were not significant in all catalysts. In contrast, all the K/NaY samples
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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

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

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 4KNaY, 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.17,18

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
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.¹

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**CONCLUSION**

The basic properties of K/NaY were studied by pyrrole-TPD and the MBOH test reaction. Pyrrole-TPD indicated a 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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**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