Oxidative dehydrogenation of ethane with oxygen catalyzed by K–Y zeolite supported first-row transition metals

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A B S T R A C T
Fe, Co, Ni, and Cu oxide loaded K–Y zeolites were synthesized using a two-step method, in which transition metals in the zeolite framework reacted with the anions in solution to form an insoluble salt which, when calcined, is expected to form an oxide that is anchored to the inner and/or outer zeolite surface(s). The catalytic properties of these zeolites, for the oxidative dehydrogenation of ethane (ODHE) to ethylene were then investigated. An ethylene selectivity of close to 80%, at an ethane conversion of >20% was achieved on a nickel oxide loaded K–Y catalyst. This is a higher ethylene selectivity, at higher ethane conversion, than was achieved using a previously reported Ni/RY catalyst. The effects of both reaction temperature and the O₂/C₂H₆ ratio on the catalytic performance were examined. The apparent energy of activation for the ODHE reaction on the nickel oxide loaded K–Y catalyst was 51.5 ± 0.7 kJ/mol. The C₂H₄ selectivity at zero conversion (S₀) on nickel oxide loaded K–Y was estimated for various O₂/C₂H₆ ratios at a number of temperatures. The implications for the reaction mechanism of the S₀ values, with regard to the relative values of critical rate constants are discussed.

1. Introduction

Over 100 million metric tons of ethylene are produced annually [1], with steam cracking of longer chain hydrocarbons being the primary method for ethylene production [2]. Oxidative dehydrogenation (ODH) of ethane (ODHE) is potentially a lower energy and less capital intensive method for the production of ethylene. Petroleum is currently the main feedstock for the steam cracking. Since petroleum is expected to be exhausted many years before natural gas, a source of short chain alkanes, it is desirable to develop chemical processes that employ small alkanes to yield more chemically useful olefins.

Although a large body of ODHE research has been reported, no ODHE process is currently a clear candidate to replace steam cracking [3]. This is primarily because catalysts are not available that give high conversions of alkanes along with high selectivity for alkenes. In the literature ODH catalysts can be divided into three categories [4]: catalysts based on (i) reducible metal oxides, (ii) noble metal-based catalysts, primarily Pt-based catalysts, and (iii) catalysts that generate radicals to initiate homogenous reactions in the gas phase (these typically contain alkali earth oxides and oxides of rare earth metals). For the first type of catalysts, vanadium and molybdenum oxide-based catalysts have been studied most extensively [3,5–8]. In contrast, there has been less work with the first-row group VIII metals for ODH catalysis [9–11]. However, since these metals are plentiful and relatively inexpensive they would be highly desirable as catalysts. Additionally, reports on ODHE reactions using zeolite supports, especially microporous zeolites, are relatively sparse [12,13]. In previous work [13] we have shown that Ni loaded acid Y zeolites exhibited an ethylene productivity of up to 1.08 S₀ C₂H₄/(g cat h) with a selectivity of ~75%. Extended X-ray absorption fine structure (EXAFS) showed that the active Ni catalysts contain both Ni–Ni and Ni–O bonds. In the synthetic method employed in Ref. [13], Ni ions are initially incorporated into the zeolite framework and are subsequently reduced by H₂ to neutral Ni, which then anchors to the inner and outer zeolite surface(s).

Zeolite supported transition metal compounds can be prepared in a variety of ways, and the method of preparation can greatly affect the catalytic property of a catalyst as a result of changes in particle size and shape, and oxidation states, etc. For example, Sun and Sachthler [14] have reported three methods of preparation of Mn loaded MFI zeolites (wet-ion-exchange, chemical vapor deposition and solid state ion-exchange), where wet-ion-exchange leads to the highest activity for NO reduction with alkanes.

In this paper we explore a synthetic method for metal (M = Fe, Co, Ni, and Cu) loaded zeolites catalysts for ODHE reactions that differs from what was employed in Ref. [13], and we investigate the catalytic performance of these zeolites and the mechanistic implications of changes in yields as a function of reaction parameters. In the present study, as in Ref [13], the transition metal ions were initially incorporated into the zeolite cationic sites by ion-exchange. They then reacted with the anions in solution (OH− and...
possibly a small amount of PO$_4^{3-}$ to form an insoluble salt that, when calcined, is expected to form an oxide that is anchored to the inner and/or outer zeolite surface(s). All catalysts examined in the present work employ a basic zeolitic support with the exchanged ion being K$^+$. 

An ethylene selectivity of close to 80% at ethane conversions of >20% was obtained on K–Y supported Ni catalyst. Compared to the Ni/K–Y catalyst, where the Ni component was anchored using H$_2$-treatment [13] (13.7% conversion with 72.9% ethylene selectivity was reported for 100 mg Ni/K–Y) the Ni catalyst reported in this paper gives a higher selectivity for ethylene at a higher conversion rate at atmospheric pressure. The weight of catalyst was varied in the range of >20% was obtained on K–Y supported Ni catalyst. Compared to the Ni/K–Y catalyst, where the Ni component was anchored using H$_2$-treatment [13] (13.7% conversion with 72.9% ethylene selectivity was reported for 100 mg Ni/K–Y) the Ni catalyst reported in this paper gives a higher selectivity for ethylene at a higher rate of 10 K/min from 50 to 700 °C. The effect of the ratio of O$_2$ to C$_2$H$_6$ in the flow on the yield of and selectivity for C$_2$H$_4$ was examined by varying the O$_2$ flow rate from 5.8 to 10.3 ml/min at a constant ethane and He flow rate. The reaction products were analyzed with a HP 5890 series II gas chromatograph equipped with a TCD. Different columns were used to separate CO$_2$, C$_2$H$_4$ and C$_2$H$_6$ (Porapak Q 80/100) and O$_2$ and CO (molecular sieve 5A). The was no observable conversion of ethane at 550 °C in either a homogenous gas phase reaction or a reaction over quartz, and there was less than 0.5% conversion of ethane at 600 °C for these reactions. The conversion of C$_2$H$_6$(X$_{C2H6}$) and the selectivity (S$_{C2H4}$) of C$_2$H$_4$ and carbon oxides (S$_{CO}$, CO$_2$ = CO or CO$_2$) are based on the carbon mass balance, which was between 95 and 100%, and was calculated using the following equations:

$$X_{C2H6} = \frac{[CO]+[CO2]+2[C2H4]}{2[C2H6]_{reactant}} \times 100\%,$$

$$S_{C2H4} = \frac{2[C2H4]}{[CO]+[CO2]+2[C2H4]} \times 100\%,$$

$$S_{CO} = \frac{[CO]}{[CO]+[CO2]+2[C2H4]} \times 100\%.$$ 

### 3. Results and discussions

#### 3.1. Catalyst characterization

Table 1 lists the chemical compositions of the M–Y and M/K–Y type II zeolites determined from ICP-AES. Based on the M/Al and Na/Al values the transition metal ions replace ~2/3 of the exchanged ions in the original Na–Y zeolite. However, the metal loading (i.e. M/Al ratio) does not change (for example, Ni/Al = 0.36 for Ni/K–Y type II and Ni–Y) after treatment using K$_3$PO$_4$ solutions as evidenced by the fact that ([K]+[Na])/[Al] is ~1.0 for all the M/K–Y type II zeolites. These data show that effectively all the transition metal ions in M–Y zeolites were replaced by the alkali ions after the treatment with K$_3$PO$_4$ solution. The replaced M ions remained on the zeolitic support as transition metal oxides or hydroxides. Small amounts of P were detected in the M/K–Y type II samples as indicated in the last column of Table 1. The XRD data for the transition metal–loaded Y zeolites, in Fig. 1, show that the as-prepared M/K–Y type II zeolites in Fig. 2 shows the H$_2$–TPR profiles of the M/K–Y type II and M–Y zeolites. When the Ni and Co loaded zeolites are treated with K$_3$PO$_4$ solution, H$_2$-reduction occurs at a lower temperature for M/K–Y

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>M/Al</th>
<th>Na/Al</th>
<th>K/Al</th>
<th>P/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/K–Y type II</td>
<td>0.36</td>
<td>0.06</td>
<td>0.93</td>
<td>0.01</td>
</tr>
<tr>
<td>Co/K–Y type II</td>
<td>0.33</td>
<td>0.06</td>
<td>0.95</td>
<td>0.01</td>
</tr>
<tr>
<td>Cu/K–Y type II</td>
<td>0.36</td>
<td>0.06</td>
<td>0.95</td>
<td>0.05</td>
</tr>
<tr>
<td>Fe/K–Y type II</td>
<td>0.37</td>
<td>0.06</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>Ni–Y</td>
<td>0.36</td>
<td>0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co–Y</td>
<td>0.34</td>
<td>0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu–Y</td>
<td>0.37</td>
<td>0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe–Y</td>
<td>0.37</td>
<td>0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na–Y</td>
<td>0.37</td>
<td>0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K–Y</td>
<td>0.06</td>
<td>0.96</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1. X-ray diffraction patterns of metal-loaded Y zeolites.

Type II relative to the untreated metal-loaded zeolites (M–Y). For instance, for Co–Y, no obvious H₂-uptake peak was observed in the TPR data (Fig. 2b, dotted line), whereas for Co/K–Y type II, a H₂ reduction peak starts at ∼550°C which extends to higher temperature with a maximum at T > 700°C. An H₂-uptake signal was observed starting at ∼350°C for both Ni–Y and Ni/K–Y type II zeolites. However, above ∼425°C the shape of the H₂-uptake curve differs markedly for the Ni/K–Y type II and Ni–Y zeolites. For the cases of Cu and Fe, treatment with K₃PO₄ solution leads to H₂-reduction taking place at a lower temperature for M/K–Y type II relative to the untreated metal-loaded zeolites (M–Y). A plausible explanation for these differences in reductive behavior relates to the bond energies for the metal–oxygen bonds for the different metals and different synthetic methods. Thus, the structures and/or morphologies of these two sets of zeolites are different.

3.2. ODHE reactions on M/K–Y type II catalysts

3.2.1. Effect of the metal

Table 2 presents the catalytic test results for the ODHE reactions at 600°C. All data in Table 2 were taken using the same O₂ and C₂H₆ flow rates and are the result of averaging GC data for two runs with a typical difference between runs of less than 2%. Only C₂H₄, CO, CO₂, and a very small amount of CH₄ were observed as reaction products. Because Na–Y and K–Y do not show significant catalytic activity for the ODHE reaction under these conditions, the catalytic conversion observed for the M/K–Y type II catalysts is a consequence of the metal loaded on these supports. From Table 2 it can be seen that the order of activity for these four ODHE catalysts is: Ni > Co > Cu > Fe, which is somewhat different than the order reported for the bulk transition metal oxides (Co > Ni > Fe)[9]. These differences between the unsupported and supported metal oxides could be a result of support effects and/or differences in shape and/or morphology of
Table 2
Reaction test result of ODHE on 500 mg M/K–Y type II catalysts listed in the Table. T=600 °C. Flow: 10.3 ml C2H6 + 10.3 ml/min O2 + 68.2 ml/min He.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion of C2H6 (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C2H4</td>
</tr>
<tr>
<td>Ni/K–Y type II</td>
<td>18.8</td>
<td>77.9</td>
</tr>
<tr>
<td>Ni–Y</td>
<td>9.4</td>
<td>77.7</td>
</tr>
<tr>
<td>Ni/IV</td>
<td>13.8</td>
<td>72.9</td>
</tr>
<tr>
<td>Co/K–Y type II</td>
<td>17.3</td>
<td>30.7</td>
</tr>
<tr>
<td>Cu/K–Y type II</td>
<td>17.0</td>
<td>23.6</td>
</tr>
<tr>
<td>Fe/K–Y type II</td>
<td>11.7</td>
<td>35.5</td>
</tr>
<tr>
<td>Na–Y</td>
<td>0.9</td>
<td>71.0</td>
</tr>
<tr>
<td>K–Y</td>
<td>1.2</td>
<td>74.6</td>
</tr>
</tbody>
</table>

* Data were taken from [13]. Weight of catalyst: 100 mg; T=600 °C; Flow: 9.7 ml C2H6 + 3.3 ml/min O2 + 62.2 ml/min He.

The metal/metal oxide particles. The selectivity for C2H4 was the highest on Ni/K–Y type II at ~78%, and the lowest on Cu/K–Y type II at ~24%.

Ni–Y is less active for ODHE than Ni/K–Y type II (first two rows of Table 2). This may be partly due to Ni2+ in Ni–Y being harder to reduce than in the Ni/K–Y type II zeolite, which is suggested by the large difference in their H2–TPR profiles (Fig. 2a) in the 425–700 °C temperature range. Compared to the Ni/K–Y catalyst reported previously [13], where the Ni component was anchored as a result of exposure to H2, the Ni/K–Y type II catalysts reported in this paper gives a higher selectivity for ethylene at a higher C2H6 conversion.

3.2.2. Effects of temperature

According to the generally accepted reaction scheme (Scheme 1) for ODHE reactions the initial selectivity (at low conversion of ethane) to C2H4 depends on the k1/k2 ratio, while at higher conversions of ethane, the observed selectivity for production of C2H4 is associated with the ratio k1/(k2 + k3) [16,17]. In the following sections the mechanistic implications of our data will be discussed in the context of Scheme 1 above, and Scheme 2, which is discussed in Section 3.3.

Fig. 3 shows the conversion and selectivity for the ODHE reactions at 550 and 600 °C for each metal-loaded zeolite. For all systems, both the conversion of C2H6 and the observed selectivity for C2H4 are greater at 600 °C than at 550 °C. That higher temperature favors increased C2H4 selectivity suggests that these catalysts have similar ODHE reaction mechanisms. Thus for all the M/K–Y type II catalysts examined in this work, the major primary product of oxidation of ethane is C2H4, since the selectivity and thus the ratio k1/(k2 + k3) increases with temperature.

Fig. 4 shows the temperature dependence for C2H6 conversion and C2H4 selectivity over 500 mg of Ni/K–Y type II catalyst. The C2H4 selectivity remains at ~80% as the conversion increases up to over 23% as the temperature is increased from 500 to 620 °C at constant flow rate. The activation energy for a chemical reaction can be obtained by plotting the log of the rate of reaction versus 1/T. However, unless the reaction is elementary this activation energy should be viewed as a phenomenological activation energy that characterizes the temperature dependence of the overall mechanism (or the rate limiting step) for conversion of reactant to product. The data in Fig. 5 allow for the calculation of the phenomenological activation energy for the ODHE reaction on Ni/K–Y type II catalyst of 51.5 ± 0.7 kJ/mol.

3.2.3. Effect of the ratio of O2 and C2H6 flow rates (F_O2/F_C2H6) on conversion and selectivity

For all M/K–Y type II catalysts investigated in this study, the increasing F_O2/F_C2H6 increases the C2H6 conversion and lowers the C2H4 selectivity (see Fig. 6). The decrease in selectivity is relatively small for Ni (9.9%), but significant for Co (33.7%), Cu (25.4%) and

![Scheme 1](image1.png)

Scheme 1. Schematic diagram of a mechanism for catalytic ODHE reactions.

![Scheme 2](image2.png)

Scheme 2. Schematic diagram of a mechanism for catalytic ODHE reactions.

[Fig. 3](image3.png) A comparison of the conversion (a) and the selectivity towards C2H4 (b) for ODHE reactions at 550 and 600 °C catalyzed by 500 mg M/K–Y type II. Flow: 10.3 ml C2H6 + 10.3 ml/min O2 + 68.2 ml/min He.

[Fig. 4](image4.png) Shows the temperature dependence for C2H6 conversion and C2H4 selectivity over 500 mg of Ni/K–Y type II catalyst. The C2H4 selectivity remains at ~80% as the conversion increases up to over 23% as the temperature is increased from 500 to 620 °C at constant flow rate.
Fig. 4. Temperature dependence of the C2H6 conversion and the C2H4 selectivity for ODHE reactions catalyzed by 500 mg Ni/K–Y type II catalyst. The flow was: 10.3 ml C2H6 + 10.3 ml/min O2 + 68.2 ml/min He.

Fe (25.6%). These data suggest that over-oxidation of the desired product (C2H4) may be relatively more facile for Co, Cu and Fe loaded zeolites than for Ni loaded K–Y zeolites. The k3/k1 ratio increases more rapidly as a function of O2 concentration for Co, Cu and Fe than for Ni. To further characterize the slow decrease in C2H4 selectivity with increasing F O2/F C2H6 ratio, more data points, were obtained and are shown in Fig. 7. Due to their mitigating effect on the production of carbonaceous deposits, which can lead to catalyst deactivation, O2 rich flows are desirable during ODH catalysis because they would be expected to enhance catalyst durability. However, an increase in relative concentration of O2 can lead to more over-oxidation and thus less selectivity for ethylene production.

3.3. The C2H4 selectivity at zero conversion (S0) for Ni/K–Y type II and their mechanistic implications

From Scheme 1 it can be seen that at very low conversions of ethane the selectivity depends on the ratio k1/k2. Thus, the k1/k2 ratio can be estimated from the selectivity in the limit of zero conversion, which we will designate as S0, where S0 is obtained by extrapolating the ethane conversion to zero as discussed in Section 3.2.2.

Fig. 5. A plot of ln(conversion) of ethane versus 1/T yields the apparent energy of activation for the Ni/K–Y type II catalyzed ODHE reaction. Flow: 10.3 ml C2H6 + 10.3 ml/min O2 + 68.2 ml/min He.

Fig. 6. The effect of F O2/F C2H6 (the number in the figure correspond to the ratio F O2/F C2H6 ) on the C2H6 conversion (left) and C2H4 selectivity for the ODHE reactions. Weight of catalyst: 500 mg. Temperature: 600 °C.

Fig. 7. F O2/F C2H6 dependence of the C2H6 conversion and C2H4 selectivity of the ODHE reaction on 500 mg Ni/K–Y type II at 600 °C.
Kung [18] suggests that the first step for ODH reactions is activation of a C–H bond to form a metal alkyl or metal alkoxide. For the specific case of transition metal oxides, our previous work [13] on the Ni/H–Y catalyzed ODHE reaction allowed us to conclude that the mechanism depicted in Scheme 2, in which the first step of the ODHE reaction is to activate C–H bond in C2H6 to form a metal ethoxide, is consistent with our data. The metal ethoxide could subsequently undergo α-H abstraction to produce an aldehyde or β-H abstraction to produce ethylene. In Scheme 2, k_β/k_α is functionally equivalent to k_1/k_2, although k_1 is not identical to k_0 since the rate determining step involves conversion of C2H6 to the ethoxide. Therefore, the C2H4 selectivity at zero conversion (S_0) is controlled by k_β/k_α and this ratio can be estimated from S_0.

We now focus on the Ni/K–Y type II catalyst. S_0 for Ni/K–Y type II catalyzed ODHE can be estimated by extrapolation of the curve for C2H4 selectivity versus C2H6 conversion (see Figs. 8 and 9). From Fig. 8, S_0 at 550 °C is ~87%, which increase to ~91% at 600 °C. It is not clear that the difference in S_0 is greater than the error limits on S_0, given that we have a limited number of data points and the curves are generated from a spline fit. However, we have consistently observed an increase in both the yield and selectivity for a given quantity of catalyst when the temperature is increased from 550 to 600 °C. This is compatible with an increase in S_0. This behavior indicates that in the context of the model in Scheme 2, increased temperature favors β-H abstraction over α-H abstraction [i.e. k_β/k_α (550) < k_β/k_α (600)]. Fig. 9 demonstrates that for all O2/C2H6 ratios investigated the S_0 values were between ~91 and ~96% (this corresponds to k_β/k_α in the range of ~10–20). That is, at the temperature of 600 °C, over 90% of C2H6 molecules are converted to C2H4 even in a relatively O2 rich flow (“O2 rich” is with respect to the stoichiometric equation for ODHE: C2H6 + 1/2O2 = C2H4 + H2O). We note that the O2 consumption never reached 100% and though small amounts of CH4 were observed above 600 °C, hydrogen was not observed, indicating that there was minimal non-oxidative dehydrogenation. Additionally, no acetic acid or acetone was observed in the reaction products. However, a small amount of coke was observed on the catalyst after catalytic testing. As such, a CO2 peak could be observed when this catalyst was exposed to a flow of O2 in He. This result indicates that a small amount of non-oxidative dehydrogenation processes does take place above 600 °C.

The observed change in selectivity and yield of the two sets of catalysts, prepared via different methods (see Section 3.1.1), would typically be rationalized as due to a change in size, composition, and/or morphology of the catalyst particles. However, the fact that the selectivity at low S_0 is associated with the ratio k_β/k_α indicates that the relative magnitudes of these rate constants change for the different catalysts. Thus, the changes in selectivity cannot be due to simply a surface area resulting from a change in particle size: There must be either a change in particle morphology, most likely leading to preferential exposure of different crystal planes, and/or a change in the steady state proportion of oxide and/or metal.

With the advances in density functional theory (DFT) it has become feasible to attempt to calculate structures and other parameters for reactions on surfaces, including oxide surfaces [19]. Calculations of k_β and k_α for metal-loaded zeolites are a potential challenge for such DFT methods. The data obtained in this study could provide a calibration for such calculations, whereas the calculations could provide additional insights into the details of the mechanism for ODHE and why specific metal oxide catalysts exhibit higher yields and selectivities than others.

4. Conclusion

(1) Four first-row transition metal (Fe, Co, Ni and Cu) oxide loaded K–Y zeolites were synthesized and characterized, and their catalytic performance for ODHE was examined. At 600 °C, for equal concentration of O2 and C2H6, the ODHE activity follows the order: Ni ≈ Cu ≈ Fe and the C2H4 selectivity is: Ni ≈ Cu ≈ Fe. The Ni/K–Y type II catalyst can give a higher selectivity for ethylene at higher C2H6 conversions than previously reported for a Ni/K–Y catalyst prepared via a different method.

(2) Increasing reaction temperature leads to a modest increase in selectivity for all M/K–Y type II systems. The apparent energy of activation for the reaction of ethane on Ni/K–Y type II is 51.5 ± 0.7 kJ/mol.

(3) Increasing the concentration of O2 (F_{O2}) relative to C2H6 (F_{C2H6}) in the reactant flow leads to an increase in the conversion of
C$_2$H$_6$, but a decrease in the C$_2$H$_4$ selectivity. The influence of \( F_{O_2}/F_{C_2H_6} \) on the C$_2$H$_4$ selectivity is relatively small for Ni/K–Y type II, but more significant for the other M/K–Y type II zeolites. (4) The C$_2$H$_4$ selectivity at zero conversion (\( S_0 \)) on Ni/K–Y type II was obtained by extrapolation of the yield to zero. The values for \( S_0 \) are consistent with the rate of \( \beta-H \) abstraction being at least 10 times that of the rate of \( \alpha-H \) abstraction from a metal ethoxide formed from ethane via an ethyl radical intermediate.

Acknowledgments

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