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Boosting NiO Catalytic Activity by x wt % F-ions and K₂O for the Production of Methyl Ethyl Ketone (MEK) via Catalytic Dehydrogenation of 2-Butanol

Samih A. Halawy,* Ahmed I. Osman,* Adel Abdelkader, [a] and Haiping Yang [c]

Herein, the synthesis of pure and modified mesoporous nano-crystalline NiO is reported. The catalyst was modified with different wt % F-ions or K₂O to produce Methyl ethyl Ketone (MEK) as a potential fuel/solvent. XRD analysis of the promoted catalysts confirmed the formation of Ni-metal covered by the host oxide, compared with pure NiO, especially for the promoted catalysts with x wt % F-ions. CO₂-TPD results demonstrated the existence of different basic sites over these catalysts with varying strength. The catalytic conversion of sec-butanol (SB) into MEK over the parent NiO catalyst showed 52% and 76.8% conversion of SB at 250 and 275 °C, respectively, with higher selectivity to MEK > 96%. Among the promoted catalysts, NiO-10 wt % F- and NiO-1 wt % K₂O catalysts showed 99 and 95% conversion, respectively, with retaining the MEK selectivity of ≥ 96%. The catalytic activity, of the most active catalysts, was correlated with the presence of Ni/NiO interfaces, different types of basic sites, especially strong basic sites, and the surface area and porosity measurements.

1. Introduction

Methyl ethyl ketone (MEK) as a promising fuel alternative can be produced in the main commercial route via the catalytic dehydrogenation reaction of sec-butanol (SB). Two different methods were applied in the dehydrogenation of SB, i.e. gas-phase dehydrogenation and liquid-phase dehydrogenation for MEK production. Also, MEK can be produced biotechnologically from biomass-derived sugars by a fermentation process, using various microorganisms, followed by dehydration of the produced 2,3-butanediol. Worldwide production of MEK will exceed 1.7 million tons by 2020. The global market of MEK was valued at approximately 2.6 billion USD in 2015 and is expected to reach 4.0 billion USD by 2024. MEK has commercial, technical, and medical applications such as a solvent in adhesives, printing inks and lube oil dewaxing processes and its utilisation have significantly increased during COVID-19 (Corona Virus Disease 2019 caused by SARS-CoV-2) in the medical sector. Other applications of MEK include sterilisation of surgical instruments and vegetable oil extraction. It has prospective applications as a fuel substitute in direct injection spark ignition engines. Dagle et al. investigated the conversion of MEK into olefins using Zn₂Zr₂O₇ catalyst. Ordomsky et al. used the MEK a building block to synthesise various chemicals such as aldehydes.

Diverse experimental techniques and conditions have been applied to prepare NiO nanorods using Ni(NO₃)₂ and Aloe vera leaf extract solution, or a mesoporous NiO in the form of nanorods as a selective gas sensor for ammonia. Additionally, Xu et al. applied a soft templates method to produce mesoporous high surface area NiO for deep oxidation of CH₄. Various publications have reported the green and biosynthesis of NiO nanoparticles by the aid of several biomaterials, such as Solanum trilobatum extract, Ananas comosus leaf extract, Cactus plant extract, Okra plant extract and Phoenix dactylifera extract. Also, NiO nanoparticles successfully were synthesised using the sonocrystallisation technique. Some articles dealt with the preparation and use of porous Ni/NiO as an excellent catalyst for urea electro-oxidation, efficient alkaline hydrogen evolution, selective hydrogenation of biomass-derivative as well as its uses in Li-ion batteries due to its electrochemical performance as anodes. Also, promotion of catalysts by other elements to increase its catalytic activity and change the morphological characterisation of such catalysts is considered a new trend nowadays. Addition of F-ions or alkali promoters, i.e., K₂O has been found to play an important role as promoters for different catalysts. The main goal of the present study is to examine the promotional effect of both F- ions and K₂O on the catalytic activities of nanocrystalline mesoporous NiO that has been prepared from oxalate precursor, during the catalytic decomposition of sec-butanol into MEK along with the catalytic stability.
The novelty herein is in the simple and facile promotion by F-ions or K₂O over NiO catalyst that led to the formation of Ni/ NiO interfaces & the variety of basic sites and applying these catalysts during the production of MEK by catalytic dehydrogenation of SB at low reaction temperatures.

2. Results and discussions

2.1. Characterisation results

2.1.1. Thermal analyses

The thermal analyses were utilised herein to understand the effect of (x %-wt/wt) additions of both F-ions and K₂O, as NH₄HF₂ (AHDF) and KOH, during the thermal decomposition of pure NiC₂O₄·2H₂O (NiOxal). Thermal analyses, TG and DSC, curves obtained upon heating all samples at a heating rate of 10 °C.min⁻¹ under oxygen with a flow rate of 40 ml.min⁻¹ are shown in Figure 1. There are two clearly distinct and separate mass loss steps[25] in all TG curves (a1&b1) that corresponding to pure NiOxal and its mixtures with (AHDF) and with KOH, respectively. The first mass loss step (step-1) occurs in the temperature range of 50–250 °C, in case of pure NiOxal, due to its dehydration to give anhydrous NiC₂O₄[25] as shown in Equation [1]:

\[ \text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{NiC}_2\text{O}_4 + 2 \text{H}_2\text{O} \]  

(1)

Addition of 1 or 5 wt % of either F⁻ or K⁺ did not alter the temperature range of step-1 significantly. Increasing the additions to 10 wt % of both F⁻ and K⁺ has led to a notable delay of this step to 270 °C, in case of NiOxal+ 10 % F⁻, and to 260 °C in case of the other mixture NiOxal+ 10 % K⁺, see curves (a1&b1) Figure 1. The % mass loss of step-1 for all samples was cited in Table 1. This value was calculated as 18.12 % in the case of NiOxal.

Figure 1. TG and DSC curves of NiC₂O₄·2H₂O (NiOxal) and its mixtures with different (x) wt % of (a1, a2) F-ion and (b1, b2) K₂O, performed in 40 ml/min dry O₂, with 10 °C/min heating rate.

<table>
<thead>
<tr>
<th>Table 1. Summary of TG and DSC results for the dehydration and decomposition of NiC₂O₄·2H₂O and its mixtures with 1–10 wt % of F⁻ and K₂O.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample &amp; Function</td>
</tr>
<tr>
<td>TG- step-1 [ML %]</td>
</tr>
<tr>
<td>TG- step-2 [ML %]</td>
</tr>
<tr>
<td>Total [ML %]</td>
</tr>
<tr>
<td>DSCα[Tmax] [°C]</td>
</tr>
<tr>
<td>(ΔH)°[dehydration], [kJ.mol⁻¹]</td>
</tr>
<tr>
<td>DSCβ[Tmax] [°C]</td>
</tr>
<tr>
<td>(ΔH)°[decomposition], [kJ.mol⁻¹]</td>
</tr>
</tbody>
</table>

[a] values calculated for samples diluted (1:1) (wt/wt) with α-Al₂O₃.
NiOxal, and then gradually increased from 19.19 up to 27.77% due to the addition of 1–10% F− as AHDF to NiOxal. These gradual increments could be associated with the complete decomposition of AHDF in the temperature range of 90–222°C as represented by Equation [2]:

\[ \text{NH}_4\text{F} + \text{HF} \rightarrow \text{NH}_3 \uparrow + 2 \text{HF} \uparrow \]  

(2)

On the contrary, % mass loss of this dehydration step in the other mixtures of NiOxal with K2O decreased gradually with increasing x% added of K2O (see Table 1). The other step in all TG curves, (step-2) that ascribed to the decomposition of the anhydrous NiOxal started at around 325°C and completely ceased at approximately 360°C with the formation of NiO, as shown by Equation [3]:

\[ \text{NiC}_2\text{O}_4 \rightarrow \text{NiO} + \text{CO} \uparrow + \text{CO}_2 \uparrow \]  

(3)

Because of the use of oxygen flow during the thermal analyses experiments, this step seems to be a highly exothermic step due to the oxidation of CO liberated, as shown in Equation [3]. Step-2 was clearly hindered by the addition of 1–10 wt% F−, see curves Figure 1(a1). This may be related to HF molecules that liberated more than NH3 during the decomposition of AHDF, as shown in Equation [2]. On the other hand, the addition of 5 and 10 wt% K2O was associated with a relative enhancement of the decomposition of NiC2O4 at lower temperatures, see Figure 1(b1). This behaviour could be attributed to the fast and easy adsorption of the evolved CO2 by KOH that hosted in these mixtures according to the following reaction in Equation [4]:

\[ 2\text{KOH} + \text{CO}_2 \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O} \]  

(4)

Where H2O simultaneously released during the thermal decomposition course, while K2CO3 remains. This phenomenon will be discussed later when explaining the CO2-TPD results of the samples. The % mass loss of step-2 and the total % mass loss associated with the complete decomposition to get final products of all samples were cited in Table 1. As represented in (Figure 2), the DSC curve related to the decomposition of anhydrous NiC2O4 (step-2) showed a large peak with high exothermic behaviour owing to the oxidation of liberated CO as presented in (Equation [3]). Therefore, dilution of all samples with (1:1) α-Al2O3 (wt/wt), whether pure NiC2O4·2H2O or all its mixtures under study, were done before DSC measurements to keep control on this massive highly exothermic step, as plotted in Figure 1 curves of a2 and b2. The DSC curves exhibit the retarding effect of F− additions, and the enhancements due to the additions of K2O on the decomposition of NiOxal, see curves a2 and b2-Figure 1. Values of peak’s temperatures \( T_{\text{max1}} \) and \( T_{\text{max2}} \) of the dehydration and decomposition steps were recorded and cited in Table 1. Values of \( T_{\text{max1}} \) recorded within the temperature range of 205–211°C, while \( T_{\text{max2}} \) in case of the addition of (1–10 wt%) F− showed a notable shift to higher temperatures in the range of 342.7–356.3°C, compared with \( T_{\text{max2}} \) of the unmodified NiOxal that at 337.2°C. On the other side, \( T_{\text{max2}} \) of NiOxal modified with (1–10 wt%) of K2O were shifted to relatively low temperatures in the range of 336.1–324.5°C, see Table 1. Calculated values of the enthalpy changes during dehydration (\( \Delta H_1 \)) and decomposition (\( \Delta H_2 \)) steps of the non-diluted NiC2O4·2H2O (the huge exothermic peak, Figure 2) were found to agree well with our previously published data[26] as (\( \Delta H_1 = 69.6\text{ kJ mol}^{-1} \)) and (\( \Delta H_2 = 64.9\text{ kJ mol}^{-1} \)) respectively. After dilution of NiC2O4·2H2O with (1:1) α-Al2O3, the calculated values of both (\( \Delta H_1 \) and \( \Delta H_2 \)) differ completely and equal to 39.4 and 57.0 kJ mol−1, respectively. These two functions were calculated for all other mixed samples and cited in Table 1. It is noteworthy that (\( \Delta H_1 \)) recorded for NiOxal and its mixtures with F− have nearly the same values, while the other mixtures with K2O recorded lower values of (\( \Delta H_1 \)) specially NiOxal + 10 wt% K2O, see Table 1. Also, (\( \Delta H_2 \)) values that cited for all samples under study were fairly in a narrow range.

2.1.2. X-ray powder diffraction (XRD) and FTIR analyses

XRD analysis was performed herein to identify the purity and crystallinity of the obtained powders. The XRD patterns of NiO and the final calcination products of NiO modified with (x) wt% of both F− (a-patterns) and K2O (b-patterns), that calcined at 400°C for 3 h in oxygen are demonstrated in Figure 3. All patterns (a and b) showed the characteristic diffractions of NiO that agreed well with ICDD file 44–1159. These patterns displayed a group of sharp reflections of rhombohedral NiO at 2θ = 37.253, 43.296, 62.887, 75.567 and 76.330° that corresponding to (111), (200), (220), (311), and (222) panels for the FCC phase of NiO (ICDD, 44–1159). A single diffraction peak can be observed at 2θ = 44.508° in all patterns of modified NiO samples with both F− and K2O. This diffraction peak could be related to the formation of Ni-metal in these mixtures, that corresponding to (111) panel (ICDD, 87–0712), and appeared to be very weak in case of NiO samples modified with (x) wt% of K2O, while it increased and became strong and sharp diffraction line with increasing of (x) wt% of F−, where x = 5 and 10 wt% F− added to NiO. Another diffraction peak recorded in the rest of patterns (a) of NiO modified with 5 and 10 wt% F− at 2θ = 51.863° that
related to (200) panel of Ni-metal (ICDD, 87–0712). Formation of Ni-metal in these modified samples could be explained by the proposed reaction mechanism as shown in Equation [5]:

$$\text{NiO}_{(s)} + \text{CO}_{(g)} \rightarrow \text{Ni}_{(s)} + \text{CO}_2(\text{g}) \uparrow$$  \hspace{1cm} (5)

According to the XRD results, the crystallite size of all prepared samples was calculated using Debye–Scherer equation,[26] concerning NiO and Ni-metal using the most intense and sharp diffraction peaks at $2\theta = 43.317$ and 44.507°, respectively, see Figure 3 and Table 2. The crystallite size of pure NiO was calculated as 12.5 nm, while NiO modified with 1–10 wt % F− recorded nanocrystalline particles in the range 14.5–17.3 nm. On the other hand, modification of NiO with 1–10 wt % K₂O has resulted in the formation of nanoparticles with relatively bigger size, i.e., 26.8–29.9 nm, as cited in Table 2. The same phenomenon was recognised during calculations of the crystallite size of Ni-metal. In case of NiO modified with 5 and 10 wt % F−, the Ni crystallite size calculated to be 40.6 and 53.7 nm, respectively, whereas NiO modified with 5 and 10 wt % K₂O gave Ni crystallite size equal to 57 and 55.1 nm, respectively.

Figure 4 presents the FTIR spectra (a) of the original sample of NiC₂O₄.2H₂O, its calcination product at 400°C as NiO, its mixed samples with (x) wt % of F− and (b) the other mixed samples with (x) wt % K₂O, all calcined at 400°C for 3 h in oxygen, that recorded within the range 300–3800 cm⁻¹. FTIR

**Table 2.** Crystallite size calculated from XRD patterns as well as the distribution of different basic sites over samples under study, all calcined at 400°C for 3 h in oxygen.

<table>
<thead>
<tr>
<th>Sample Function</th>
<th>pure NiO</th>
<th>NiO-1 wt % F</th>
<th>NiO-5 wt % F</th>
<th>NiO-10 wt % F</th>
<th>NiO-1 wt % K₂O</th>
<th>NiO-5 wt % K₂O</th>
<th>NiO-10 wt % K₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallite size [nm] XRD :</td>
<td>12.5</td>
<td>17.3</td>
<td>14.5</td>
<td>15.7</td>
<td>26.8</td>
<td>28.4</td>
<td>29.9</td>
</tr>
<tr>
<td>NiO (2θ = 43.317°)</td>
<td>28.4</td>
<td>2.31</td>
<td>2.36</td>
<td>2.17</td>
<td>1.47</td>
<td>2.85</td>
<td>7.47</td>
</tr>
<tr>
<td>Ni (2θ = 44.507°)</td>
<td>33.3</td>
<td>43.7</td>
<td>39.2</td>
<td>37.4</td>
<td>25.9</td>
<td>11.1</td>
<td>5.7</td>
</tr>
<tr>
<td>Total No. basic sites</td>
<td>53.1</td>
<td>44.9</td>
<td>48.7</td>
<td>45.9</td>
<td>56.5</td>
<td>73.7</td>
<td>89.2</td>
</tr>
<tr>
<td>[sites × 10²/g]</td>
<td>13.6</td>
<td>11.4</td>
<td>12.1</td>
<td>16.7</td>
<td>17.6</td>
<td>15.2</td>
<td>5.1</td>
</tr>
</tbody>
</table>
spectrum of the original NiC₃O₄·2H₂O, as prepared, exhibited the intense broadband at 3385 cm⁻¹ that may be assigned to the vibration of water of hydration. Another strong, sharp band centred at 1640 cm⁻¹ of the bending mode δ(H₂O), overlaps with the asymmetric vibration (ν as OCO).

Two sharp bands at 1369 and 1319 cm⁻¹ are ascribed to (ν s OCO) and δ(OCO).

Figure 4. FTIR spectra of the original NiC₃O₄·2H₂O (NiOxal) and NiO at 400 °C, besides the samples mixed with F-ion (a), and samples mixed with K₂O(b), all calcined at 400 °C for 3 h in oxygen.
vibrations, respectively,\textsuperscript{(26)} for the bridged oxalate ion. A group of medium and weak bands in the region 840–483 cm\(^{-1}\) arise from the different bending modes of mixed vibrations as follows:\textsuperscript{(27)} \(\nu_3(\text{C}–\text{O}) + \delta(\text{O}–\text{C}–\text{O})\) and \(\delta(\text{O}–\text{C}–\text{O}) + \delta(\text{Ni}–\text{O})\). Finally, the spectrum of original \(\text{Ni}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}\) shows an absorption band at 336 cm\(^{-1}\) assigned to \(\delta(\text{Ni}–\text{O}–\text{C})\) in oxalate compounds.\textsuperscript{(28)} Two sharp bands at 2365 and 2347 cm\(^{-1}\) appeared in all recorded spectra, for all samples herein, due to \(\nu_a\) of a mixture of physisorbed and gaseous \(\text{CO}_2\) over the KBr disc.\textsuperscript{(29)} The spectrum of \(\text{NiO}\), that produced by calcination at 400 °C shows two bands at 443 cm\(^{-1}\) (sharp and strong) and 667 cm\(^{-1}\) (weak band) correspond to \(\text{Ni}–\text{O}\) vibrations modes.\textsuperscript{(30)} The strong band was shifted to a lower value in the range of 433–420 cm\(^{-1}\), as recorded recently,\textsuperscript{(31)} and became a common denominator band in all spectra of the mixed samples, see Figure 4(a,b). In addition to the bands mentioned above, a broadband at 3465 cm\(^{-1}\) recorded for the stretching vibration of the \(\text{OH}\) group of the moisture, because of the hygroscopic nature of \(\text{NiO}\).\textsuperscript{(32)} Also, a group of absorption bands in the range of 1725–1230 cm\(^{-1}\) due to the formation of carbonate species, i.e., bidentate and monodentate carbonate\textsuperscript{(33)} over the surface of the \(\text{NiO}\).

This can be associated with the reaction of \(\text{CO}_2\) molecules from the air with the oxygen anions \(\text{O}^{2-}\) which are Lewis basic sites\textsuperscript{(34)} over the surface of such mixed samples. From the results of IR analysis one can conclude that all samples at 400 °C, whether pure \(\text{NiO}\) or mixed with \(\text{F}\) or \(\text{K}_2\text{O}\), are characterised by its surface basic sites that become stronger with increasing (x) wt\% especially samples contain 5 and 10 wt\% \(\text{K}_2\text{O}\), see Figure 4.

### 2.1.3. \(S_{\text{BET}}\) measurement and morphology

Figure 5 shows the \(N_2\) adsorption/desorption isotherms, as well as the pore diameter profiles of pure \(\text{NiO}\) and its mixtures with 1–10 wt\% \(\text{F}\) (a1–a3) and the other mixtures with 1–10 wt\% \(\text{K}_2\text{O}\) (b1–b3), all samples prepared by calcination at 400 °C for 3 h in oxygen. All samples exhibit typical type-IV isotherms as recommended by IUPAC\textsuperscript{(35a)} with a type H3 hysteresis loops.\textsuperscript{(35b)} The adsorption hysteresis of \(\text{NiO}\) and \(\text{NiO}\) mixed with 1–10 wt\% \(\text{F}\) (a1–a3) located in the P/P\(_0\) region of 0.40–0.49, whereas those of \(\text{NiO}\) mixed with 1–10 wt\% \(\text{K}_2\text{O}\) (b1–b3) recorded in the region of 0.59–0.65 of P/P\(_0\) scale, which indicates that these isotherms are combined with mesoporous nature for these samples.\textsuperscript{(35b)} Table 3 indicates the textural properties of all samples, where the BET-surface area of pure \(\text{NiO}\) measured as 63.3 m\(^2\)/g. The addition of 1–10 wt\% \(\text{F}\) have reflected, firstly, in a slight decrease in the surface area (ca. 60.4 m\(^2\)/g) followed by a gradual increase to 74.1 and 87.1 m\(^2\)/g, with the addition of 5 and 10 wt\% \(\text{F}\), respectively. This could be related to the evolution of both \(\text{HF}\) and \(\text{NH}_3\), as presented by Equation [2] during the calcination process of these samples. On the contrary, a significant contraction of the surface area had resulted with the consequence additions of 1–10 wt\% \(\text{K}_2\text{O}\) to \(\text{NiO}\), see Table 3, where the smallest \(S_{\text{BET}}\) value was measured for \(\text{NiO}-10\text{wt}\%\text{K}_2\text{O}\) (ca. 12.7 m\(^2\)/g). This can be ascribed to the suggested reaction between KOH, that added to \(\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}\) during the preparation of these samples followed by calcination at 400 °C, and molecules of the ambient \(\text{CO}_2\)\textsuperscript{(27)} to form \(\text{K}_2\text{CO}_3\), as shown in Equation [4]. The aggregation of \(\text{K}_2\text{CO}_3\) formed in the bulk of these samples led to the contraction of the surface area of these samples. The majority of mesopores in pure \(\text{NiO}\) located at 6.3 nm pore diameter see Figure 5. This value gradually shifted to lower values of pore diameter (ca. 3.6 and 3.7 nm) by the addition of 1–10 wt\% \(\text{F}\) to \(\text{NiO}\), see Figure 5 (a1–a3). On the other hand, the addition of 1–10 wt\% \(\text{K}_2\text{O}\) to \(\text{NiO}\) produced a wide range of pores with different diameters, i.e., perhaps hierarchical samples with pores ranging from 2.6 up to 18.4 nm in case of \(\text{NiO}-10\text{wt}\%\text{K}_2\text{O}\), see Figure 5(b3).

Pore area vs pore diameter was plotted, as in Figure 6. Values of the pore area recorded for pure \(\text{NiO}\) and samples modified with 1–10 wt\% \(\text{F}\), curves in Figure 5 (a1–a3), and are notably directed to a higher scale. Strong pore area scale reduction was observed (curves b1–b3) for samples of \(\text{NiO}\) modified with 1–10 wt\%\(\text{K}_2\text{O}\). From the above-discussed results of samples under study, one can conclude that \(\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}\) is a suitable precursor for nanocrystalline \(\text{NiO}\) preparation, whether pure or modified samples, that characterised by relatively higher surface area and mesoporous nature with a wide range of pores. The addition of \(\text{F}\) has increased the surface area, total pore volume, and pore area, increasing the wt\% loading of \(\text{F}\) promoter. On the contrary, the addition of \(\text{K}_2\text{O}\) has decreased the surface area, total pore volume and the pore area significantly and created hierarchical samples with different wide pore diameters; see Table 3 and Figures 5 and 6. It is well known that samples characterised by large pore diameter, always gained small values of both surface area and total pore volume and pore area\textsuperscript{(35b,38)}

<table>
<thead>
<tr>
<th>Sample name</th>
<th>BET Surf. Area (m(^2)/g)</th>
<th>Langmuir Surf. Area (m(^2)/g)</th>
<th>External surface area (m(^2)/g)</th>
<th>Total pore volume (cm(^3)/g)</th>
<th>Mesopore volume (cm(^3)/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure (\text{NiO})</td>
<td>63.3</td>
<td>86.8</td>
<td>61.9</td>
<td>0.1573</td>
<td>0.1569</td>
<td>2.5, 3.6, 6.3</td>
</tr>
<tr>
<td>(\text{NiO}-1\text{wt}%\text{F})</td>
<td>60.4</td>
<td>83.8</td>
<td>59.0</td>
<td>0.1397</td>
<td>0.1395</td>
<td>2.8, 3.6, 4.8</td>
</tr>
<tr>
<td>(\text{NiO}-5\text{wt}%\text{F})</td>
<td>74.1</td>
<td>102.8</td>
<td>74.5</td>
<td>0.1456</td>
<td>0.1455</td>
<td>2.5, 3.7</td>
</tr>
<tr>
<td>(\text{NiO}-10\text{wt}%\text{F})</td>
<td>87.1</td>
<td>120.4</td>
<td>85.9</td>
<td>0.1462</td>
<td>0.1461</td>
<td>2.6, 3.6</td>
</tr>
<tr>
<td>(\text{NiO}-1\text{wt}%\text{K}\text{O})</td>
<td>31.1</td>
<td>42.8</td>
<td>26.5</td>
<td>0.1022</td>
<td>0.1002</td>
<td>2.6, 3.6, 4.9, 8.9</td>
</tr>
<tr>
<td>(\text{NiO}-5\text{wt}%\text{K}\text{O})</td>
<td>15.8</td>
<td>21.7</td>
<td>12.9</td>
<td>0.0472</td>
<td>0.0459</td>
<td>2.6, 3.7, 9.8</td>
</tr>
<tr>
<td>(\text{NiO}-10\text{wt}%\text{K}\text{O})</td>
<td>12.7</td>
<td>17.5</td>
<td>10.3</td>
<td>0.0353</td>
<td>0.0342</td>
<td>2.6, 3.6, 4.9, 18.4</td>
</tr>
</tbody>
</table>
The surface morphology of the prepared NiO and two other modified samples as the most active catalysts, at 400 °C, were examined by SEM. Figure 7 shows that SEM image (a) of NiO and (b and c) of NiO modified with 10 wt% F− and 1 wt% K2O, respectively, seems like aggregates of brittle nanoparticles. This may be due to the exothermic process accompanied by a large

Figure 5. N2 adsorption/desorption isotherms and pore diameter profiles of NiO, the calcination products of NiO modified with different (x) wt% of F-ion (a1–a3) and K2O(b1–b3), all calcined at 400 °C for 3 h in oxygen.
amount of heat liberated during the calcination process, as seen from DSC curves in Figure 1(a2,b2). These brittle nano-crystalline particles characterised by less cohesive energy compared with condensed bulk particles. The different additions of F and K$_2$O have no significant effect on the external morphology of the modified samples, Figure 7 images (b and c).

Figure 6. Pore area versus pore diameter curves of NiO, the calcination products of NiO modified with different (x) wt% of F-ion (a1–a3) and K$_2$O(b1–b3), at 400°C for 3 h in oxygen.
2.2. Catalytic activity

The catalytic activity of the nanocrystalline NiO, produced by calcination of oxalate precursor at 400 °C for 3 h in oxygen, during the conversion of SB as a test reaction was performed in a continuous flow fixed-bed reactor under atmospheric pressure. Reactivity tests were carried out at intervals of 25 °C from 200 °C up to 300 °C. It was found that the % conversion of SB, see Figure 8, gradually improved with increasing the reaction temperature. This may be related to activation of the active sites over NiO catalyst with increasing the reaction temperature, as in the recently published work for NiO produced from Ni-galactarate. The main product was in all cases the MEK with a high % selectivity in the range of 85.6–98.2, as confirmed by published articles, see Figure 8, while both trans-2-butene and cis-2-butene have been detected as minor products, with total selectivity in the range 6.3–4.4 %, except for at a low reaction temperature at 200 °C using WHSV = 60000 mL g⁻¹ cat h⁻¹ as illustrated in Scheme 1.

Also, the effect of weight-hourly-space-velocity (WHSV) on the catalyst’s reactivity was investigated using three WHSV values, ca. 15000, 30000 and 60000 mL g⁻¹ cat h⁻¹, respectively, at the same temperature range of 200–300 °C, as shown in Figure 8. As the WHSV was increased steadily from 15000 up to 60000 mL g⁻¹ cat h⁻¹, % conversion of SB drastically decreased especially at higher temperatures, i.e., at 275 and 300 °C. This meant that at a higher value of WHSV ca. 60000 mL g⁻¹ cat h⁻¹, inadequate time for a large amount of SB molecules to react

![Figure 7. SEM images of (a) pure NiO and (b and c) of NiO modified with 10 wt % F⁻ and 1 wt % K₂O, respectively, at 400 °C for 3 h in oxygen.](image)

![Figure 8. Conversion of sec-butanol (SB) as a function of reaction temperature using different GHSV over pure NiO, calcined at 400 °C, focusing on MEK as the main product.](image)

![Scheme 1. Dehydration/dehydrogenation reactions of sec-butanol (SB).](image)
over the catalyst surface has occurred. It is worth noting that % selectivity of MEK, in the temperature range of 200–300 °C, was almost constant using WHSV equal to 15000 and 30000 mL·g⁻¹·h⁻¹ and was in the range of 92.6–98.2%. Therefore, two reaction temperatures were selected ca. 250 and 275 °C with the corresponding value of WHSV = 30000 as experimental conditions to apply, in this study, for the promoted samples of NiO with x wt% of F- and K₂O. The above-discussed results suggested that the main active sites over NiO calcined at 400 °C responsible for MEK production were basic sites with different strength.⁴³⁻⁴⁷

CO₂-TPD results of our samples offer qualitative and quantitative pieces of evidence about the improved basicity on NiO as pure and modified samples with F- and K₂O, as shown in Figure 9. These results frankly indicated that CO₂ was desorbed, on all samples, at four types of basic sites over a wide temperature range from RT up to 400 °C. The CO₂-TPD profiles of samples herein are somewhat complicated due to the overlap between the different basic sites, especially the first three types located at the surface of NiO as pure and those promoted with 1–10 wt% F- as well as NiO-1 wt% K₂O, see Figure 9. The first broad peak located in the temperature range of 60–67 °C, may be attributed to desorption of bicarbonate species from weak basic sites,⁴⁸ followed by another broad peak in the range of 179–185 °C that associated with the desorption of bidentate carbonate, see Figure 9. The monodentate carbonate desorption peak centred at 285 °C, in case of NiO, while it slightly shifted to a lower temperature at 280 °C in NiO-5 wt% F-, [43a] This peak may be merged with the previous basic sites in NiO modified with 1 and 10 wt% F-, see Figure 9. Recalling the CO₂-TPD results of the other modified samples with 1–10 wt% K₂O, curves e–g. It is clearly shown that modification of NiO with 5 and 10 wt% K₂O have changed the shape of desorption peak of pure NiO and obviously created various medium basic sites, especially that sharp and strong desorption peak in the range of 157 and 164 °C, related to bidentate carbonate,[43a] while the other peak appeared in the temperature range of 259–278 °C that associated with the desorption of monodentate carbonate.[43b] It is noteworthy that the distribution of the different types of basic sites over samples, whether pure NiO or modified samples, clearly affected by x wt% addition of both F- and K₂O. Promotion with 10 wt% F- has improved the percentage of strong basic sites. Instead, the addition of x wt% K₂O had appreciably increased percentages of the medium basic sites, at the expense of both weak and strong basic sites, except for NiO-1 wt% K₂O that gained 17.6% of strong basic sites. Finally, another peak associated with strong basic sites observed in all TPD profiles of the samples at T > 320 °C, due to desorption of bridged carbonate,[43b] with large intensity in case of pure NiO, NiO-10 wt% F- and NiO-1 wt% K₂O, see Figure 9 and Table 2. This wide spectrum of basic sites, with variable strength over such samples, can explain the selectivity of these samples towards the production of MEK as the main product. The recorded CO₂-TPD curves, for the samples in this study, are in line with the results published recently by Ewald et al.⁴⁶

2.2.1. Influence of NiO promotion by different x wt% F- or K₂O

The impact of the promotional effect of different wt% (ca. x = 1, 5 and 10, F- or K₂O) added to NiO on its catalytic activity during the conversion of SB to MEK was studied at two reaction temperatures. The results are presented in Figure 10 and Table 4. A significant increase in % conversion of SB can be observed, that are parallel to the increased amounts of F- added to NiO from 1 to 10 wt% of F-, whether the reaction temperature was at 250 or 275 °C. The % selectivity of MEK measured for all samples was approximately >97%. Alternatively, the addition of 1 wt% K₂O to NiO greatly promoted the catalytic activity. The % conversion of SB over pure NiO was 51.99% at 250 °C and 76.8% at 275 °C, respectively, and this has significantly increased to 82.15% and 94.96% over NiO-1 wt% K₂O at the same corresponding temperatures. Increasing the added amounts of K₂O to NiO, i.e., 5 and 10 wt% K₂O, led to a continuous decrease in % conversion of SB to 47.9 and 38.7% at 250 °C, and 69.34 and 54.75% at 275 °C, respectively. Additionally, the selectivity of MEK production over NiO-x wt% K₂O at 250 °C was about 97%, while it was in the range of 95.9–98.3% at 275 °C, respectively. These significant increments of % conversion of SB at 275 °C compared to that at 250 °C, as presented in (Figure 10), could be related to activation of the basic sites that responsible for the formation of MEK, where strong basic sites play a part in the dehydrogenation reaction of SB at temperatures >250 °C, see Figure 9. To better understand the impact of these additions on the catalytic activity of NiO and the behaviour of NiO-x wt% F- catalysts, against the other promoter (NiO-x wt% K₂O), during the conversion of SB to MEK, three main parameters discussed herein.

To understand the different behaviour, of samples under study, of the two systems, i.e., NiO-x wt% F- and NiO-x wt% K₂O during the conversion of SB to MEK, a depth discussion on the responsible key factors is required herein. It seems that the key factor of the catalytic activity may be correlated with three corroborated parameters, sometimes were slightly conflicted, as follows:

Figure 9. CO₂-TPD profiles of pure NiO (a), NiO promoted by 1–10 wt% F-ion (b–d) and by 1–10 wt% K₂O (e–g), all calcined at 400 °C for 3 h in oxygen.
The sample's surface area and its mesoporous nature, where the dehydrogenation reaction of SB was carried out over the active sites spread over a high surface area. This is in agreement with catalysts of NiO-x wt % F<sub>-</sub>, except for NiO-1 wt % F<sub>-</sub>, see Table 3. While the other system NiO-x wt % K<sub>2</sub>O is in line with this parameter. All samples, whether pure NiO or modified NiO, also have a mesoporous nature, as shown in Figure 5.

The % of strong basic sites looks crucial herein, where the strong basic sites start to take part in catalysis at reaction temperatures >250°C, as concluded from CO<sub>2</sub>-TPD (Figure 9) and initiate the production of MEK. This factor is in agreement with % conversion of SB in the case of NIO-x wt % K<sub>2</sub>O, at 250 and 275°C, while the addition of 5 and 10 wt % K<sub>2</sub>O have resulted in the creation of more medium basic sites at the expense of both weak and strong basic sites, see Table 2. Also, this parameter in line too with the surface area, and could be applied for catalysts of NiO-x wt % F<sub>-</sub>, where the most active catalyst NiO-10 wt % F<sub>-</sub> gained a higher percentage of strong basic sites ca. 16.7%.

A Ni/NiO interface. This factor probably is the most crucial parameter, due to the presence of metal/oxide interfaces in the catalysts under study as concluded from XRD analysis of the promoted samples. This phenomenon is clearly observed in NIO-x wt % F<sub>-</sub> see Figure 3a, where Ni-metal diffraction lines steadily grown in the host NiO. As the amount of NH<sub>4</sub>F.HF added was increased, i.e., 5 and 10 wt % to NiO, the diffraction lines of Ni-metal became more intense, and more Ni/NiO interfaces formed through these samples. Therefore, the sample NIO-10 wt % F<sub>-</sub> exhibited higher activity during the conversion of SB to MEK. This behaviour recently cited<sup>[21]</sup> for efficient selective hydrogenation of biomass-derivatives over Ni/NiO composites. Another study about the alkaline hydrogen evolution<sup>[20]</sup> also suggested that the NiO component could accelerate H<sub>2</sub>O dissociation, while Ni-metal could facilitate H<sub>2</sub> formation from H-adsorbed over Ni/NiO nanoscale hetero-surfaces. Li and co-workers<sup>[19]</sup>, in their study, they demonstrated the collaborative effects of NiO/Ni as an excellent catalyst for urea electro-oxidation in 1 M solution.
of KOH. They correlated the catalytic activity and durability of their catalyst to its mesoporous structure. This factor seems to be a secondary factor in the case of NiO-x wt % K₂O samples herein. A single faint diffraction line of Ni metal appeared in XRD analysis, see Figure 3b, without any considerable changes in its intensity. Herein three factors seem to be interlinked and overlapped.

2.2.2. Stability and reusability of the most active catalysts

Stability and usability of the most active catalysts, during the conversion of SB to MEK, are a significant and important goal of our study. To examine the catalytic stability of the most active three catalysts, i.e., pure NiO, NiO-10 wt % F⁻ and NiO-1 wt % K₂O, 6-cycles of the catalytic conversion of SB to MEK consecutively were achieved at 275 °C using WHSV = 30000 mL g⁻¹ cat h⁻¹ and presented in Figure 11. Fresh catalysts in the first cycle during the conversion of SB can be arranged, according to their activities, as follows: NiO-10 wt % F⁻ > NiO-1 wt % K₂O > pure NiO. After 3-cycles, the promoted catalysts lost about 17–20 % of their activity towards the conversion of SB to MEK, whilst pure NiO only lost 5 % of its activity, see Figure 11. As the number of cycles increases, i.e., from 3 to 6-cycles, NiO-10 wt % F⁻ showed a relatively constant catalytic activity ca. ≈83 % conversion. On the other hand, both NiO-1 wt % K₂O and pure NiO continued to experience further losses of their activities. This could be related to the deterioration of the active basic sites over the catalyst surface, as the number of cycles increased up to 6-cycles, perhaps due to the loss of nanostructure of the catalysts at 275 °C. Also, no carbon deposition was observed after the prolonged use of all of these catalysts, as published[33a] in case of NiO prepared from Ni-galactarate salt at 500 °C. Therefore, we strongly recommend using the most active catalyst NiO-10 wt % F⁻ that exhibited a high catalytic performance during the conversion of SB to MEK with higher selectivity, as a good catalyst in this reaction prolonged time. This test for stability and reusability has been applied for different types of catalysts, as cited in the literature, during several reactions.[40]

3. Conclusions

Mesoporous NiO was prepared using NiC₂O₄·2H₂O, as pure and modified with x wt % F⁻ or K₂O by calcination at 400 °C in an oxygen atmosphere. All catalysts were in the nanoscale structure with different types of basic sites spread over their surfaces. The additions of F⁻ ions enlarged the surface area of these modified samples, while addition with K₂O continuously decreased the surface area. Also, a remarkable catalytic performance was recorded for NiO-10 wt % F⁻ and NiO-1 wt % K₂O among all the boosted catalysts, during the conversion of SB to MEK with % selectivity ≥ 96 %. The catalytic activity, of the most active catalysts, was correlated with the presence of Ni/NiO interfaces, different types of basic sites, especially strong basic sites, and the surface area and porosity measurements. Finally, it is worth noting that the novelty herein focused on the simple and facile promotion of NiO by F-ions or K₂O, due to the formation of Ni/ NiO interfaces & the variety of basic sites and applying these catalysts during the production of MEK by catalytic dehydrogenation of SB at low reaction temperatures.

Experimental

Materials and methods

Nickel carbonate, basic hydrate (NiC₂O₄·2·(CHOH)₂·H₂O) and oxalic acid dihydrate (Merck) were utilised in this study. NiC₂O₄·2H₂O was prepared by suspending 50 g of (NiC₂O₄·2H₂O in 100 mL of deionised water at 60 °C with continuous stirring using a magnetic stirrer. Potions of oxalic acid were added regularly to the suspension until the complete transformation of NiC₂O₄·2H₂O, where the effervescence of CO₂ gas was stopped, and the pH of the medium was measured as ≧1.4. The resulting precipitate was instantly filtered off and washed many times with deionised water until the filtrate became neutral. The prepared NiC₂O₄·2H₂O was dried at 100 °C in an oven overnight, and then a sample was directly calcined at 400 °C for 3 h in an oxygen atmosphere to prepare pure NiO. Two promoted NiO-systems were synthesised using F-ions or K₂O that were added to give 1, 5 and 10 % (by wt.) as follows: calculated amounts of ammonium acid fluoride (NH₄F·HF, Hopkin & Williams) or KOH (Prolabo), as cited in Table 5, to produce 1, 5 and 10 % (by wt.) of F⁻ or K₂O was dissolved in deionised water, in Teflon beakers, and well mixed with the corresponding weights of NiC₂O₄·2H₂O, see Table 5. These mixtures were then evaporated until a dry state over a water bath. The resulting mixtures were dried at 100 °C overnight. All these NiO-modified samples were also calcined at 400 °C for 3 h in an oxygen atmosphere. Modification of NiO with F-ions or K₂O was intended to modify the strength and capacity of basic sites, over such catalysts, during their employment in the decomposition of sec-butanol into methyl ethyl ketone.

Characterisation

Thermal analyses of the prepared NiC₂O₄·2H₂O and its mixtures with NH₄F·HF and KOH were conducted using thermogravimetric (TG) and differential scanning calorimetric (DSC) techniques. These were performed at a heating rate of 10 °C.min⁻¹ in a stream of dry oxygen flowing at 40 mL.min⁻¹; using a 50H Shimadzu thermal analyser, Japan. The thermal analyser is equipped with data acquisition and handling system (TA-50WS). Highly sintered α-
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Catalyst activity tests were performed at atmospheric pressure in a pyrex-glass chamber fitted with inlet/outlet allowing for a heated gas sampling cock, type HGS-2 at 140 °C. Sec-butanol (SB) was used as reference material in DSC measurements, while temperature and enthalpy readings were calibrated versus the melting point, i.e. 156.3 °C and the heat of fusion, \( \Delta H_f = 28.24 \text{ J.g}^{-1} \) of Specpure In-metal (a Johnson Matthey product), respectively. X-ray powder diffraction analysis (XRD) of all solid samples calcined at 400 °C was carried out using a D5000 Siemens diffractometer (Germany), equipped with a copper anode generating Ni-filtered CuKα radiation (λ = 1.5406 Å), in the 2θ range between 15–80°. Online data acquisition and handling system were used to facilitate an automatic JCPDS library search and match (Diffrac software, Siemens) for phase identification purposes. Surface textural properties of all samples that were calcined at 400 °C, viz. specific surface area, pore volume and mean pore radius) were calculated from nitrogen adsorption-desorption isotherms recorded at liquid nitrogen temperature (i.e. −196 °C) using an automatic Micromeritics ASAP 2010 (U.S.) equipped with online data acquisition and handling system operating BET and BJH analytical software. All samples were degassed at 200 °C and 10⁻⁵ Torr for 2 h before measurements (1 Torr = 133.3 Pa). The FTIR spectra were recorded using a Magna-FTIR 560 (USA), between 4000–300 cm⁻¹, operating a Nicolet Omnic software and adopting the KBr disk technique. The morphological characterisation of the prepared NiO at 400 °C and two boosted samples by 10 wt % F and 1 wt % K₂O was performed by Scanning Electron Microscopy (SEM) using a FEI Quanta 250 FEG MKII with a high-resolution environmental microscope (ESEM) using XT microscope Control software. The distribution of the surface basic sites strength over all NiO samples, whether pure or modified with F and K₂O, was investigated by temperature-programmed desorption of CO₂ (CO₂-TPD) as explained previously.\(^{[32a]}\) 100 mg of each sample was initially heated at 380 °C for 1 h in air and then, all was immediately transferred into a pyrex-glass chamber fitted with inlet/outlet allowing for a CO₂-stream (50 mL.min⁻¹) to pass at room temperature. After four days, 20 mg of the CO₂-covered sample was subjected to DSC analysis using 40 mL.min⁻¹ as N₂-flow with 20°C.min⁻¹ heating rate.

Catalytic measurements

Catalyst activity tests were performed at atmospheric pressure in a conventional fixed bed U-shaped quartz reactor. 100 mg fresh catalyst was charged for each run and was preheated at 350 °C for 2 h in N₂-flow (100 mL.min⁻¹) before measurements; then the temperature was gradually decreased to 200 °C. Sec-butanol (SB) (Fluka, > 99%) vapours were generated by passing a stream of nitrogen (50°C.min⁻¹) through the liquid SB in a thermostatic water bath stabilised at 0 °C. The gas hourly space velocity of 30,000 mL.g⁻¹.h⁻¹ was used in all the experiments for most of the samples. The reaction temperature was increased gradually from 200 up to 300 °C. The effluent of products and reactants were analysed using an online gas chromatograph (Shimadzu GC-14), equipped with a data processor model Shimadzu Chromatopac C-R4A. An automatic sampling was continuously performed using a heated gas sampling cock, type HGS-2 at 140 °C, using a hydrogen flame ionisation detector (FID) and a stainless-steel column (PEG 20 M 20% on Chromosorb W, 60/80 mesh, 3 m x 3 mm) at 80 °C. The SB conversion % and selectivity % of products were calculated using the following equations 6 and 7:

\[
\% \text{ SB conversion} = \frac{\text{[No. moles SB]_{in} - [No. moles SB]_{out}}}{\text{[No. moles SB]_{in}}} \times 100 \%
\]

(6)

\[
\text{Product selectivity (\%)} = \frac{[\text{No. moles of product}]}{[\text{Total no. moles of products}]} \times 100 \%
\]

(7)

Disclaimer

The views and opinions expressed in this paper do not necessarily reflect those of the European Commission or the Special EU Programmes Body (SEUPB).

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Methyl Ethyl Ketone · Dehydrogenation · NiO · Potassium oxide · Fluoride

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**Table 5.** Theoretical calculations for the preparation of the mixed samples of NiC₄O₄·2H₂O with 1–10 wt% of F and K₂O.

<table>
<thead>
<tr>
<th>Sample</th>
<th>¹⁸Weight [g] of NiC₄O₄·2H₂O to give [%] NiO</th>
<th>Weight [g] of NH₄F·HF to give [%] F</th>
<th>Weight [g] of KOH to give [%] K₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiC₄O₄·2H₂O</td>
<td>7.00 (100%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiO-1 wt %</td>
<td>6.93 (99%)</td>
<td>0.0428 ([x = 1 wt %])</td>
<td>0.0339 ([x = 1 wt %])</td>
</tr>
<tr>
<td>NiO-5 wt %</td>
<td>6.65 (95%)</td>
<td>0.2239 ([x = 5 wt %])</td>
<td>0.1698 ([x = 5 wt %])</td>
</tr>
<tr>
<td>NiO-10 wt %</td>
<td>6.30 (90%)</td>
<td>0.4278 ([x = 10 wt %])</td>
<td>0.3395 ([x = 10 wt %])</td>
</tr>
</tbody>
</table>

[a] According to the TG- total % mass loss of NiC₄O₄·2H₂O as 59.29%, calcination of 7 g NiC₄O₄·2H₂O gives 2.850 g of pure NiO.


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Just got promoted! A highly active and selective promoted Ni-based catalyst is effective for the production of Methyl Ethyl Ketone via the catalytic dehydrogenation of secondary butanol at low reaction temperatures. The catalyst promoters were added to the Ni-based catalyst using simple and facile promotion using F-ions or K$_2$O. The catalytic activity of the most active catalysts, was correlated with the presence of Ni/NiO interfaces, different types of basic sites, especially strong basic sites, and the surface area and porosity.