Highly basic and active ZnO–x% K2O nanocomposite catalysts for the production of methyl ethyl ketone biofuel

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Abstract
Herein we demonstrate the preparation and characterization of nanocrystalline ZnO, either pure or promoted with 1–10 wt.% K2O. All catalysts calcined at 400°C were in the nano-crystallite scale as confirmed by X-ray powder diffraction analysis in the 22.9–28.0 nm range. According to the CO2-temperature-programmed desorption study using thermogravimetric analysis and differential scanning calorimetry techniques, they have a broad spectrum of surface basic sites. Because of the significance of methyl ethyl ketone (MEK) as a next-generation biofuel candidate with high-octane, low boiling point, and relatively high vapor pressure. The prepared catalysts were examined during the direct production of MEK via 2-butanol (2B) dehydrogenation. Among catalysts tested, ZnO promoted with 1% K2O showed a superior catalytic activity towards the conversion of 2B to MEK, that is, 71.7% at a reaction temperature of 275°C. The selectivity for the production of MEK over all catalysts was ≥95% across all catalysts when using N2-gas as a carrier. The use of airflow in this reaction resulted in a clear loss of selectivity toward MEK production as well as the appearance of undesirable products such as acetone and methanol. All catalytic properties of catalysts, particularly those of moderate strength, were highly correlated with the distribution of surface basic sites. Finally, a reaction mechanism was proposed for the dehydrogenation of 2B, followed by the partial oxidation of MEK.

KEYWORDS
2-butanol dehydrogenation, basicity, biofuel, K2O promotion, methyl ethyl ketone, Zinc oxide

1 | INTRODUCTION

Nano-scale particles of metal oxides such as ZnO, whether pure, promoted with additives or supported on other oxides, have recently attracted many researchers to study their physical properties and catalytic activities in many catalytic reactions. Including methanol synthesis via CO2 hydrogenation,1-3 photocatalytic degradation of dyes,4 Suzuki–Miyaura cross-coupling reaction,5 biodiesel production,6,7 steam reforming reaction of methanol,8,9 synthesis of dimethyl ether from syngas,10 ester hydrogenolysis,11 H2-production,12 transesterification synthesis of ethyl methyl carbonate.13 ZnO is considered a nontoxic material owing to its relatively fast electron mobility, high conductivity, photo-corrosion resistance, and low availability. Much attention has been focused on its technological applications in solar cells,14-16
piezoelectric nanogenerators and force sensors, and varistor ceramics. Due to the wide range of technological applications of ZnO, recently, various preparation techniques have been developed. Few years ago, we investigated the catalytic properties of various ZnO samples prepared from different precursors, namely Zn(CH$_3$CO$_2$)$_2$·2H$_2$O, Zn$_3$(C$_6$H$_5$O$_7$)$_2$·2H$_2$O and Zn(NO$_3$)$_2$·6H$_2$O, during the decomposition of ethanol. In addition, we prepared and studied the thermal decomposition of zinc malonate, using different atmospheres, in isothermal and nonisothermal conditions. Thermal decomposition of zinc malonate, using different atmospheres, in isothermal and nonisothermal conditions. Due to the worldwide interest in diversifying clean energy sources other than oil derivatives, such as methyl ethyl ketone (MEK), which has recently been characterized by a high-octane number and as a next-generation biofuel candidate for use in spark-ignition engines. It can be biotechnologically synthesized from biomass or 2,3-butanediol, by hydrogenation of 2,3-butanol, and through dehydrogenation of 2-butanol (2B). For all of these reasons, we have strongly encouraged the development of highly basic modified solid-catalyst, such as ZnO modified with 1%-10% K$_2$O, and to examine these potent catalysts during the production of MEK at a relatively low temperature with high selectivity. The innovation of this study can be summarized in a few points: (i) the simple preparation method of all catalysts at 400°C, (ii) the formation of a broad spectrum of different types of surface basic sites over these catalysts, and (iii) the optimization of the best experimental conditions for the direct production of MEK, at relatively low temperature with high selectivity, using fixed-bed reactor under atmospheric pressure.

2 | EXPERIMENTAL

2.1 | Preparation of the precursor and promoted ZnO samples

Home-made ZnC$_2$O$_4$·2H$_2$O (ZnOxl) was prepared by suspending 20 g of zinc carbonate, ZnCO$_3$ (99%) American elements, in 100 ml of deionized water at room temperature with continuous stirring. A small amount of solid oxalic acid C$_2$H$_2$O$_4$·2H$_2$O was added to the suspension until the effervescence of CO$_2$ was ceased, indicating the complete reaction between the carbonate and the oxalic acid. The pH of the medium was determined to be 1.6. The white precipitate was immediately filtered off and washed several times with distilled water until the filtrate became neutral. The resulting material was dried at 100°C in an oven for 24 h. Based on the % TG-weight loss of pure zinc oxalate dihydrate, calculated amounts of pure KOH (Prolabo) to produce 1%, 5% and 10% K$_2$O (by weight), that is, 0.0256, 0.1279, and 0.2559 g were dissolved, respectively, in deionized water and mixed well the corresponding weights of ZnC$_2$O$_4$·2H$_2$O as: 4.949, 4.751, and 4.5 g, respectively. These mixtures were then evaporated to dryness over a water bath and were dried at 100°C overnight. All these mixtures, as well as pure ZnC$_2$O$_4$·2H$_2$O were calcined at 400°C for 3 h in an oxygen atmosphere (50 ml min$^{-1}$).

2.2 | Characterization methods

Elemental analysis of the prepared ZnC$_2$O$_4$·2H$_2$O was carried out using Perkin Elmer 2400 Series II CHNS/O analyzer. Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) curves of all mixtures and pure zinc oxalate were performed at a heating rate of 10°C min$^{-1}$ in a stream of dry oxygen flowing at 40 ml min$^{-1}$, using an automatically recording model 50H Shimadzu thermal analyzer. The thermal analyzer is equipped with data acquisition and handling system (TA-50WSI). Highly sintered α-Al$_2$O$_3$ was used as the reference material in DSC measurements, while temperature and enthalpy readings were calibrated versus the melting point (i.e., 156.3°C) of Spec-pure Indium metal (a Johnson Matthey product), respectively. X-ray powder diffraction (XRD) of pure ZnO and ZnO mixed with 1, 5, and 10 wt.% K$_2$O at 400°C were carried out using a model D5000 Siemens diffractometer, equipped with a copper anode generating Ni-filtered Cu-K$_\alpha$ radiation (λ = 1.5406 Å), in the 2θ range between 20 and 70°. The online data acquisition and handling system facilitate an automatic JCPDS library search and match (Diffraction software, Siemens) for phase identification purposes. The Fourier transform infrared (FTIR) spectra were recorded using a Magna-FTIR 500, between 4000 and 400 cm$^{-1}$, operating a Nicolet Omnic software and adopting the KBr disk technique. The total surface area of all samples calcined at 400°C were determined from five-points nitrogen adsorption isotherms recorded at liquid nitrogen temperature using an automatic Micromeritics ASAP 2010, equipped with an online data acquisition and handling system operating BET analytical software using 0.75–0.80 g sample weight. All samples were degassed at 200°C and 10$^{-5}$ Torr for 2 h before measurements (1 Torr = 133.3 Pa). The SEM, Scanning Electron Microscopic study of ZnO and ZnO–1% K$_2$O samples at 400°C were carried out using a FEI Quanta 250 FEG MKII with a high-resolution environmental microscope (ESEM) using XT microscope Control software.
2.3 | Basicity measurements

The surface basic sites strength distribution over all ZnO samples, whether pure or modified with K₂O, was investigated by temperature-programmed desorption of CO₂ (CO₂-TPD), as explained previously. ³⁴ 100 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 an inlet/outlet allowing for a CO₂-stream (20 ml min⁻¹) to pass at room temperature. After 4 days, ±20 mg of each CO₂-covered sample was subjected to both TG and DSC analyses using 40 ml min⁻¹ as N₂-flow with 20°C min⁻¹ heating rate. Furthermore, investigation of the basicity of samples under study was performed adopting the dehydrogenation reaction of isopropyl alcohol (IPA). An amount of 100 mg of each sample, 200 ml min⁻¹ N₂-gas as a carrier for 1.6% IPA in the reaction flow at 5°C were used in every experiment. Reaching stability for samples at 350°C for 1 h in N₂ flow before measurements was achieved, then the temperature lowered and fixed at 300°C as a reaction temperature. The reaction products were analyzed and detected using an online gas chromatograph (Shimadzu GC-14), equipped with a data processor model Shimadzu Chromatopac C-R4AD. An automatic sampling was continuously performed using a heated gas sampling cock, type HGS-2 at 140°C, using a hydrogen flame ionization detector (FID) and a stainless-steel column (PEG20 M 20% on Chrmosorb W, 60/80 mesh, 3 m × 3 mm) at 90°C.

2.4 | Production of MEK via decomposition of 2B

Catalyst activity tests were performed at atmospheric pressure in a conventional fixed bed U-shaped quartz reactor. An amount of 200 mg of fresh catalyst was charged for each run and was preheated at 380°C for 2 h in N₂-flow (100 ml min⁻¹) before measurements; then, the temperature was gradually decreased to 250°C. 2B (Fluka, ≥99%) vapors were generated by passing a stream of nitrogen (100 ml min⁻¹) through the liquid 2B in a glass saturator thermostatically stabilized in a water bath at 5°C. The gas hourly space velocity (GHSV) of 30 L g⁻¹ cat⁻¹ h⁻¹ was used in all the experiments. The reaction temperature was increased gradually from 250°C up to 400°C. The effluent of products and reactants were analyzed using the same conditions as above (FID) detector and column temperature at 70°C. The % conversion of 2B and % selectivity of products were calculated as explained previously. ³³ The schematic process of converting 2B into MEK is shown in Figure 1.

3 | RESULTS AND DISCUSSION

3.1 | Elemental analysis

The elemental analysis of the original precursor ZnC₂O₄·2H₂O yielded the following results as: % C = 12.69 while % H = 2.15. These findings are consistent with the dihydrate structure of zinc oxalate, where the calculated theoretical values are 12.68% and 2.13% for carbon and hydrogen content, respectively.

3.2 | Thermal analyses

To investigate the catalytic effect of adding (1–10 wt.% K₂O as KOH) to ZnC₂O₄·2H₂O during its thermal decomposition. TG and DSC profiles of these samples were recorded using a heating rate of 10°C min⁻¹ in dry oxygen flow of 40 ml min⁻¹ as shown in Figure 2A,B.
TG profiles show that pure ZnC₂O₄·2H₂O and the three mixtures decompose first to anhydrous ZnC₂O₄, as the main component, in the temperature range of 115–190°C, due to the dehydration process as shown in Equation (1):

\[ \text{ZnC}_2\text{O}_4\cdot2\text{H}_2\text{O} \rightarrow \text{ZnC}_2\text{O}_4 + 2\text{H}_2\text{O} \uparrow. \]  

Another weight-loss step in the temperature range of 325–415°C was recorded in relation to anhydrous ZnC₂O₄ and associated with the complete decomposition of ZnC₂O₄ to give pure ZnO as follows:

\[ \text{ZnC}_2\text{O}_4 \rightarrow \text{ZnO} + \text{CO}(g) \uparrow + \text{CO}_2(g) \uparrow. \]  

The total mass loss % (% ML) was calculated as 57.7%. This value is in close agreement with the theoretical % ML, ca. 57.042%, due to the complete transformation of ZnC₂O₄·2H₂O into pure ZnO. As the added amounts of (x) wt.% K₂O to ZnC₂O₄·2H₂O gradually increase, the recorded % ML showed a successive decrease from 55.5% to 53.8% and 50.9% in the case of ZnC₂O₄·2H₂O mixed with 1%, 5%, and 10% K₂O, respectively, see Figure 2A.

Based on TG and DSC profiles, an important observation can be made about the effects of improving zinc oxalate dihydrate by adding 1–10 wt.% K₂O (Figure 2A,B). These additions have slightly slowed the dehydration process while accelerating the decomposition of ZnC₂O₄, see Figure 2A. Again, this observation is supported by the DSC profiles recorded in Figure 2B, particularly the exothermic peaks associated with the highly exothermic process during the decomposition of anhydrous ZnC₂O₄ in oxygen. As shown in (Equation 2), the liberated CO during the decomposition step of ZnC₂O₄ undergoes oxidation to CO₂ over the produced ZnO in the oxygen atmosphere used in the experiments; therefore, a strong exothermic peak was recorded in the case of pure zinc oxalate profile, see Figure 2B. Our results are in close agreement with a previously published work.

A recently proposed mechanism for the oxidation of CO by the exchange of inter-lattice oxygen over ZnO was published that is supported by FTIR study by Noei et al. is as follows:

\[ \text{CO} + 2\text{O}^{2-} + 2\text{Zn}^{2+} \leftrightarrow \text{CO}_3^{2-} + 2\text{Zn}^{2+} + 2\text{e}^{-}. \]  

![Figure 2](image_url)
\[ \text{CO}_3^{2-} + 2\text{Zn}^{2+} + \frac{1}{2}\text{O}_2 + 2\text{e}^- \leftrightarrow \text{CO}_3^{2-} + \text{O}_2^{-} + 2\text{Zn}^{2+}, \]  
\[(4)\]
\[ \text{CO}_3^{2-} \rightarrow \text{CO}_2 + \text{O}_2^{-}. \]  
\[(5)\]

In the case of the other profiles recorded for the three mixtures, this exothermic peak appeared with less sharpness. This can be related to the presence of K₂O in these mixtures. K-ions added as KOH to each mixture appear to act as moderators during the oxidation process of CO over these mixtures. K-ions and/or K₂O play an important role in ponding oxygen molecules to produce K₂O₂, as shown below:

\[ 2\text{K} + \text{O}_2 = \text{K}_2\text{O}_2, \]  
\[(6)\]
\[ 2\text{K}_2\text{O} + \text{O}_2 = 2\text{K}_2\text{O}_2. \]  
\[(7)\]

This could explain the controlled exothermic reaction associated with the decomposition step in these mixtures, accompanied by CO oxidation. The addition of 1–10 wt.% K₂O to ZnC₂O₄·2H₂O gradually and noticeably reduced the \(T_{\text{max}}\) of the decomposition step from 393°C, in case of pure zinc oxalate, to 387°C, 371°C, and 361°C due to the addition of 1, 5, and 10 wt.% K₂O, respectively. Actually, the gradual additions of K₂O significantly improve the decomposition step of ZnC₂O₄·2H₂O by about 32°C with 10 wt.% K₂O, as shown in Figure 2B. The thermodynamic parameters for the dehydration and decomposition steps, such as: enthalpy change (\(\Delta H^*\)), the specific heat capacity (\(C_p\)), and the entropy change (\(\Delta S^*\)), were calculated based on the DSC experiment data. As shown in Table 1, the enthalpy change was calculated directly from the heat quantity in each step per unit mass of the sample (J g\(^{-1}\)). As a result, \(\Delta H^*\) was used to calculate the specific heat capacity\(^{41,42}\) as follows:

\[ C_p \text{ (J g}^{-1}\text{K}^{-1}) = \frac{\Delta H}{\Delta T}, \]  
\[(8)\]

where \(\Delta T = T_2 - T_1\), \(T_1\) is the temperature at which the DSC peak starts to leave the baseline, and \(T_2\) is the temperature at which the peak lands.\(^{41}\) Subsequently, \(\Delta S^*\) was calculated using the following equation\(^{41,42}\):

\[ \Delta S^* \text{ (J}^{-1}\text{K}^{-1}) = 2.303 C_p \log(T_2/T_1). \]  
\[(9)\]

A few points that can be drawn from the data in Table 1 are as follows:

1. In Step I (the endothermic dehydration step), the addition of K₂O slightly reduced the enthalpy change (\(\Delta H\)) from 88.66 kJ mol\(^{-1}\) in pure ZnC₂O₄·2H₂O to values in the range of 76.82–69.14 kJ mol\(^{-1}\) in mixtures containing 1–10 wt.% K₂O. These additions also resulted in a slight

| Sample          | Step (I) Dehydration-endo. | Step (II) Decomposition-exo. |
|-----------------|-----------------------------|------------------------------|
| \(T_{\text{max}}\) (°C) | \(\Delta H\) (kJ mol\(^{-1}\)) | \(C_p\) (J g\(^{-1}\) K\(^{-1}\)) | \(\Delta S^*\) (J g\(^{-1}\) K\(^{-1}\)) |
| \(\Delta H\) (J g\(^{-1}\)) | \(C_p\) (J g\(^{-1}\) K\(^{-1}\)) | \(\Delta S^*\) (J g\(^{-1}\) K\(^{-1}\)) |
| Zn-Oxal         | 145                         | 88.66                        | 468.04                       | 7.55                      |
| Zn-Oxal+1% K₂O  | 158                         | 76.82                        | 405.51                       | 5.48                      |
| Zn-Oxal+5% K₂O  | 159                         | 69.14                        | 364.99                       | 4.93                      |
| Zn-Oxal+10% K₂O | 159                         | 69.14                        | 364.99                       | 4.93                      |
decrease in the calculated values of $C_p$ and $\Delta S^*$. This could be attributed to the nature of the dehydration step, which is a physicochemical process.

2. Step II (the exothermic decomposition step of anhydrous ZnC$_2$O$_4$), on the other hand, has seen a gradual improvement in the decomposition step with increasing additions of ($x$) wt.% K$_2$O to zinc oxalate. Therefore, these additions significantly reduced the decomposition enthalpy change values from 85.82 kJ mol$^{-1}$ in case of un promoted anhydrous ZnC$_2$O$_4$ to 35.53 kJ mol$^{-1}$ with the addition of 10 wt.% K$_2$O, as shown in Table 1.

As a result, these additions considerably reduced the heat capacity and entropy change values calculated for un promoted ZnC$_2$O$_4$ to about one-third of $C_p$ and a half of $\Delta S^*$ values with the addition of 10 wt.% K$_2$O. This could be related to the control of oxygen using K$_2$O during the exothermic decomposition of ZnC$_2$O$_4$ in the oxygen atmosphere, as previously explained (see Equations 6 and 7). Furthermore, these gradual additions resulted in a safe and controlled decomposition by lowering the required temperature for this step by about 32°C and decreasing the values of both $C_p$ and $\Delta S^*$ that were calculated for the three mixtures. This obvious effect most likely reflects on the crystallite size and surface area of the produced samples after calcination at 400°C, as shown in Table 2.

### 3.3 Powder XRD and FTIR techniques

XRD analysis was carried out to confirm the purity and the crystallite structure of the produced samples, whether pure ZnO or promoted with $x$ wt.% K$_2$O, after calcination at 400°C in an oxygen atmosphere using Cu-$K_{\alpha}$ radiation ($\lambda = 1.5418 \text{ Å}$) and in the range of 2$\theta = 20$–70°. In all patterns (Figure 2C), nine well-known peaks were recorded along with the crystallographic planes (100), (002), (101), (102), (110), (103), (200), (112), and (201), which correspond to Bragg reflections at 2$\theta$ of 31.80°, 34.43°, 36.29°, 47.586°, 56.652°, 62.902°, 66.011°, 68.062°, and 69.092°, respectively. The presence of three sharp and intense peaks, particularly for the planes of (100), (002), and (101), in all the recorded patterns of these samples, clearly indicates the high crystalline structure and the formation of a single-phase as a hexagonal ZnO$^{43,44}$ (JCPDS card no. 005-0664). There are no other characteristic peaks belonging to K$_2$O or any potassium compounds, such as K$_2$CO$_3$, recorded in all patterns of the mixed samples. This phenomenon could be explained by the successful deep penetration of the added portions of K$_2$O inside ZnO as a hosted oxide, as recently demonstrated in the case of NiO modified with 1–10 wt.% K$_2$O.$^{33}$ The crystallite size of pure ZnO, obtained by direct thermal decomposition of ZnC$_2$O$_4$·2H$_2$O at 400°C, as well as samples of ZnO promoted with 1–10 wt.% K$_2$O at 400°C were calculated using the Debye–Scherer equation,$^{45}$ taking the most intense and sharp diffraction peak at 2$\theta = 36.246°$ as a reference, see Table 2. The crystallite size of pure ZnO was calculated as 28.0 nm, while modified ZnO with 1 wt.% K$_2$O has a slightly crystallite size of 25.2 nm. Increasing the wt.% of K$_2$O up to 5% and 10% resulted in a further reduction in crystallite size to 22.9 and 23.7 nm, respectively. The calculated crystallite size of pure ZnO, that is, 28.0 nm, is quite similar to that published recently by Ezedalisiji et al.$^{46}$

FTIR analysis was used in conjunction with XRD analysis to reveal more structural information about the

| Function         | Sample          | Pure ZnO | ZnO–1% K$_2$O | ZnO–5% K$_2$O | ZnO–10% K$_2$O |
|------------------|----------------|----------|---------------|---------------|----------------|
| $S_{\text{BET}}$ (m$^2$ g$^{-1}$): | 26.6 ± 0.05   | 35.34 ± 0.07 | 44.06 ± 0.09  | 36.22 ± 0.10  |
| Cryst. size (nm): | 28.0           | 25.2     | 22.9          | 23.7          |
| XRD, 2$\theta = 36.246°$ |               |          |               |               |
| Total basicity: No. CO$_2$ mol kg$^{-1}$ | 1.22         | 1.23     | 1.03          | 1.43          |
| Reaction temp. (°C) | 250 275 300 325 | 350 250 275 300 | 325 350 250 275 | 300 325 350 |
| % Conversion     | 11.9 24.4 43.7 | 60.3     | 78.9 71.7 92.7| 99.9 98.8 12.8| 19.4 32.7 55.6| 77.1 10.8 15.7| 22.3 36.0 59.0|
| % S MEK          | 96.9 97.2 96.8 | 96.2     | 95.9 97.1 98.1| 98.1 97.3 95.1| 97.0 98.0 98.3| 98.3 92.5 96.1| 97.2 97.7 98.0|
| % S trans-2-butene | 1.6 2.0 2.8 | 3.5 3.8 0.8 | 1.1 1.4 1.7 | 2.3 1.0 1.0 | 1.1 1.2 | 1.2 1.4 | 1.4 1.5 | 1.5 |
| % S cis-2-butene | 1.5 0.8 0.4 | 0.3 0.2 0.2 | 0.8 1.1 0.5 | 0.4 0.3 0.2 | 0.9 0.5 | 0.5 0.6 | 1.2 1.4 | 1.5 1.5 | 1.5 |
prepared samples. The FTIR spectra of the original ZnC₂O₄·2H₂O, the calcination products at 400°C as ZnO and the promoted samples of ZnO with 1–10 wt.% K₂O are shown in Figure 3. The recorded spectrum of the prepared ZnC₂O₄·2H₂O strongly supports the high purity of the compound, with bands at: 3415 cm⁻¹ (νOH), 1626 cm⁻¹ νas (CO) overlapping δ (HOH),⁴³,⁴⁷ two sharp bands at 1390 and 1320 cm⁻¹ (νs [OCO] and δ [OCO])⁴⁸ related to the vibrations of bridged oxalate ion. A group of bands appeared in the region 823–338 cm⁻¹ as (νO–Zn–O), (δO–C=O + νZn–O) and (νZn–O + νC–C) bending modes of mixed vibrations.⁴⁸ The spectrum of ZnO, prepared by calcination at 400°C, exhibits a strong band at 449 cm⁻¹ that is assigned to the stretching vibration mode of Zn–O.⁴⁸ This band is shifted to a slightly lower value at 437 cm⁻¹ in all spectra of the mixed samples, see Figure 3. Our results are in good agreement with a recently published work.⁴⁹ Also, in spectra of all mixed samples, a broadband appeared around 3415 cm⁻¹ due to (νOH), a group of absorption bands in the range of 1800–1200 cm⁻¹, owing to the formation of bicarbonate, monodentate, and bidentate carbonate species over the surface of these mixed samples.⁴⁷,⁵⁰,⁵¹ The sharpness of these bands increased with increasing the mixing amounts of K₂O, as clearly observed in the spectrum of ZnO–10% K₂O, due to the adsorption of CO₂ molecules from the air and their interaction with oxygen anions O²⁻ as Lewis basic sites.⁵¹ over their surfaces. Finally, two absorption bands located at 848 and 773 cm⁻¹ relate to (νO–Zn–O) and (νZn–O + νC–C),⁴⁷ besides faint bands at 2927 and 2852 cm⁻¹ due to C–H stretching and at 1047 cm⁻¹ assigned to C–H bending vibrations.⁵² Bands of physisorbed and gaseous CO₂ over KBr disc during the recording of all spectra appeared at 2365 and 2347 cm⁻¹, see Figure 3.

3.4 | Surface area measurement and morphology

Table 2 shows the surface area (S_BET) of all samples under investigation. Adding 1% and 5% K₂O to pure ZnO increased its surface area from 26.60 ± 0.05 m² g⁻¹ to 35.34 ± 0.07 and 44.06 ± 0.09 m² g⁻¹, respectively.

![Figure 3](image_url)
Further addition of 10% K₂O to ZnO reduced the surface area to 36.22 ± 0.10 m² g⁻¹. The nanocomposite nature of the prepared samples of pure ZnO and ZnO–1% K₂O, as the most active sample during the conversion of sec-butanol, was characterized by SEM to observe their morphology after calcination at 400°C for 3 h in oxygen. Figure 3B displays two SEM images with varying magnifications as well as a ZnO–1% K₂O sample. These images show aggregates of nanocomposite frail-like particles. This may be associated with the exothermic process that is accompanied by the liberation of large amounts of heat during the calcination of these samples in oxygen, as shown in DSC curves (Figure 2B). The addition of x% K₂O to ZnO has no tangible effect on particle morphology, as seen in Figure 3B.

3.5 | Assessment of the surface basicity

The surface basicity of all samples calcined at 400°C for 3 h in oxygen was determined using two analytical tools. The CO₂ TG and DSC-TPD techniques were used to calculate the population of the total basic sites over each catalyst using TG-TPD of CO₂, while the DSC-TPD technique was applied to monitor types of basic sites with different strengths, as shown in Figure 4A,B and Table 2. To confirm the basicity of these samples, another approach, namely the dehydrogenation of IPA over all catalysts, as a probe reaction using gas chromatography, was used to examine the activity of each catalyst at 300°C for the production of acetone as a selective product over basic sites, as shown in Figure 4C.

3.5.1 | Basicity assessment using TG and DSC-TPD technique

Examining the TPD curves (Figure 4A,B), one can notice that TG-TPD curves of both ZnO and ZnO–1% K₂O begin to lose weight continuously at about 150°C, whereas their DSC-TPD curves exhibit a single huge peak in the temperature range of 125–285°C, see Figure 4B. This peak can be related to the formation of moderate basic sites over the surface of these samples as well as the desorption of bidentate and monodentate carbonates, respectively, formed during CO₂ adsorption over ZnO samples. Increasing the amounts of K₂O added to ZnO, that is, 5% and 10%, resulted in complete changes in their TG and DSC-TPD curves, as shown in Figure 4A,B. The % weight loss due to CO₂ desorption commenced early, around 50°C. This phenomenon is associated with the early appearance of a new burly peak related to the desorption of bicarbonate species from weak basic sites, a decrease in the area of the moderate basic sites, and the appearance of strong basic sites at temperature ≥300°C, which is associated with desorption of bridged carbonate species. The generation of different types of basic sites over ZnO–5% K₂O and ZnO–10% K₂O catalysts, with different strengths, could be related to progressively more frequent formation of Lewis basic sites (O⁻²) as explained by Equations (3)–(5) during the preparation of these mixtures at 400°C in an oxygen atmosphere. The total number of basic sites over all samples was calculated from TG-TPD curves as (no. CO₂ mol kg⁻¹) and is shown in Table 2. The amount of CO₂ desorbed from the surface of pure ZnO was calculated to be 1.22 mol kg⁻¹. Adding 1% K₂O to ZnO slightly increased this value to 1.23 mol kg⁻¹ with a slight change in the shape of the TPD-DSC profile of this sample, as shown in Figure 4B, due to the desorption of bidentate and monodentate carbonates, respectively, from moderate basic sites.

Further addition of K₂O, that is, 5% to ZnO, decreased the desorbed amount of CO₂ to 1.03 mol kg⁻¹. This phenomenon was accompanied by an observable change in the TPD-DSC curve of this sample and the appearance of a new basic sites’ distribution with overlapping between weak, moderate and strong basic sites. The last TPD-DSC curve of 10% K₂O–ZnO showed a similar distribution of these basic sites, with a noticeable increase in both the weak and strong basic sites at the expense of the moderate ones. It is well known that bicarbonate is desorbed from weak basic sites, while bridged carbonate is desorbed from strong basic sites. Finally, the amount of CO₂ desorbed from the surface of 10% K₂O–ZnO was calculated to be 1.43 mol kg⁻¹, see Table 2 and Figure 4B. Table 2 shows that the calculated amounts of CO₂ desorbed from the surface of our samples are approximately three times greater than that calculated for ZnO under the same conditions. According to the abovementioned findings, pure ZnO prepared by calcining ZnC₂O₄·2H₂O in an oxygen atmosphere at 400°C for 3 h is characterized by moderate basic sites that can be divided into two subbasic sites using Gaussian line profiles. This is clearly demonstrated in the case of both DSC-TPD curves of pure ZnO and ZnO–1% K₂O, see Figure 4B. Furthermore, the addition of 5% and 10% K₂O resulted in a sequential decrease in the intensity of these moderate basic sites, as well as a parallel increase in the intensity of both weak and strong basic sites. This change in basic site distribution will have an effect on the catalytic properties of these samples during the proposed test reactions, which will be discussed later.
Basicity assessment applying dehydrogenation of isopropyl alcohol (IPA) as a probe reaction

Many studies have been conducted using IPA chemical reactions, as probe reactions, for various research purposes. The dehydrogenation of IPA was used as a probe reaction to examine the catalytic activity of all samples herein, as shown in Figure 5.

Lokras and his coworkers previously had stated that acetone could be obtained from isopropyl alcohol by either catalytic dehydrogenation or catalytic oxidation reaction, as follows:

\[
\text{CH}_3\text{CHOHCH}_3 + \text{H}_2 \rightarrow \text{CH}_3\text{COCH}_3 + \text{H}_2\text{O}, \quad (10)
\]

\[
\text{CH}_3\text{CHOHCH}_3 + 1/2 \text{O}_2 \rightarrow \text{CH}_3\text{COCH}_3 + \text{H}_2\text{O}. \quad (11)
\]

They declared that reaction (10) is endothermic, while the other one (11) is exothermic and requires more critical temperature control. Therefore, our experiment was carried out in N\(_2\) atmosphere as a catalytic dehydrogenation reaction to compare the catalytic activities of our samples, as shown in Figure 4C.

The dehydrogenation reaction was carried out at 300°C, and the results are presented in Figure 4C to correlate these results with the basicity of such catalysts. The major product among all catalysts was acetone, with measured selectivity in the range of 96.9%–98.5%.

The catalytic activity of these catalysts in the conversion of IPA into acetone, as shown in Figure 4C, is clearly dependent on the catalyst's composition. The most and least active catalysts were ZnO–1% K\(_2\)O and ZnO–10% K\(_2\)O, with 46.2% and 33% conversion of IPA, respectively. This can obviously be associated with the distribution of the different types of basic sites with varying strengths over the surface of each catalyst. The most active catalyst in the decomposition of IPA, that is, ZnO–1% K\(_2\)O (see Figure 4C), has a perfect and balanced distribution of these moderate basic sites (Figure 4B).
The population of these moderate basic sites gradually decreased as the amount of K$_2$O added exceeded 1% K$_2$O. This is clearly seen during the decomposition of IPA with ZnO–10% K$_2$O see Figure 4C. This assumption leads us to believe that the main factor of the catalytic activity of our samples during the catalytic dehydrogenation reaction, as determined by the above-explained results, is strongly associated with the presence of a wide spectrum of different basic sites, particularly moderate ones.

3.6 Production of MEK

MEK is a high-demand chemical with an annual production of over 675 million pounds in the United States alone. Because of its importance as an alternative fuel, the three-step sec-butyl alcohol route currently accounts for 87% of the MEK production as a fine chemical. Its production herein was based on 2B decomposition over ZnO as pure and mixed with 1%–10% K$_2$O that calcined at 400°C for 3 h in oxygen, in the temperature range of 250–400°C, with GHSV of 30 L$_{\text{gcat}}$ h$^{-1}$ in all the experiments.

This part of our work's strategy was carried out in the following steps:

(i) A preliminary test of 2B decomposition over pure ZnO, calcined at 400°C with 100 ml min$^{-1}$ airflow. We investigated the first airflow as a carrier during the 2B decomposition, as shown in Figure 6A. The conversion of 2B over pure ZnO steadily increased with the elevation of the reaction temperature. At 325°C, % conversion of 2B was 85%, and it then increased to 97%–99%. On the contrary, a noticeable negative phenomenon concerning MEK as the main product is observed. In the temperature range of 325–400°C, % selectivity of MEK lost approximately 33% of its value, see Figure 6A. This may be attributed to the partial oxidation of some MEK to the corresponding compounds, at this temperature range and with the presence of H$_2$-located on the basic sites over the ZnO surface, that is, acetone and methanol,

as presented in Figure 7. As previously reported for the selective oxidation of 2B in oxygen over Mn-supported catalysts at 300°C, two compounds were identified by GC during each injection. Besides, two other products of the dehydration reaction of 2B were identified with very low % selectivity cis- and trans-2-butene. To avoid this situation of drastic loss of % selectivity of MEK, as the main product during dehydrogenation reaction of 2B, we re-examined the decomposition reaction of 2B using a fresh sample of ZnO and N$_2$-gas as an inert carrier with 100 ml min$^{-1}$ flow rate and the same conditions as airflow. Figure 6B depicted a detailed comparison of the two carriers in terms of both % conversion of 2B and % selectivity of MEK. When using N$_2$-gas as a carrier, values of % conversion of 2B were always lower than when using air as a carrier. This difference was calculated at 275°C, 300°C, 325°C, 350°C, and 375°C to be 46%, 27.5%, 24.6%, 18.0%, and 5.0%, respectively. As the reaction temperature increased, the active basic sites over the surface of ZnO began to activate, reducing the difference caused using different carriers, air or N$_2$-gas.

Furthermore, the dehydrogenation reaction of 2B in different atmospheres is catalyzed by the presence of Lewis basic sites (O$_2^-$) that spread over the catalyst’s surface, as previously explained by Equations (3)–(5). The clear advantage of N$_2$-gas as a carrier is the consistent % selectivity of MEK, that is, 95.2%–97.2% in the temperature range of 250–400°C, see Figure 6B. Therefore, we carried out the decomposition of 2B over all catalysts using N$_2$-gas as a carrier in the temperature range of 250–350°C.

The kinetic parameters of 2B decomposition over ZnO as pure and mixed with 1%–10% K$_2$O are shown in Table 2. Additionally, Figure 6C shows the most important data on the % conversion of 2B as a function of reaction temperature over all catalysts. Two important observations should be made when reviewing the data in Table 2: (i) all catalysts demonstrated ≥92.5% selectivity of MEK production as the primary product. (ii) The catalytic activity of our samples varied according to their...
basicity. The total basicity calculated over these catalysts is in the range of 1.03–1.43 mol kg$^{-1}$, where the moderate basic sites play the main role in the conversion of 2B to MEK, as we explained earlier. In addition, the most active catalyst was ZnO–1% K$_2$O among all other catalysts tested in this study in all reaction temperatures, see Figure 6C. The ZnO–1% K$_2$O catalyst demonstrated superior activity in the conversion of 2B, with a minimum value of % conversion was calculated as 39.8% at 250°C. This value reached a maximum at 325°C, indicating 99% conversion, and maintained its efficiency as the temperature increased.

### 3.7 Stability and reusability of ZnO

The stability and reusability of ZnO during the conversion of 2B to MEK is considered an important test of the catalyst's suitability for this application. The reaction over fresh ZnO sample lasted about 3 h in the temperature range of 250–375°C and the results are shown in Figure 6B. The same ZnO sample was regenerated by heating at 350°C in N$_2$-flow (100 ml min$^{-1}$) for 2 h inside the reactor before reusing the catalyst in a new experiment under the same previously mentioned conditions. These requirements were imposed to avoid any changes in the reaction conditions, such as catalyst weight, the exact position at which the reactor is inside the vertical furnace, and the catalyst's distribution within the reactor. The dehydrogenation of 2B was then repeated over the used refreshed sample in the temperature range of 250–375°C and the experiment took 4 h. After reaching a steady-state at each temperature, three consecutive injections on the gas chromatograph were recorded. Figure 8 shows a comparison of the obtained results with those obtained in the case of the fresh one. At reaction temperatures of 250°C and 275°C, the used catalyst became approximately 10% and 21.2% more active than the fresh ZnO, as shown in Figure 8, respectively. While at the reaction temperature of 300°C, the used catalyst gained only 4.1% more than the fresh ZnO (as % conversion of 2B). As the reaction temperature increased from 325°C to 375°C, the used ZnO gradually and dramatically lost its reactivity, as shown in Figure 8. On the other hand, % selectivity of MEK did not differ depending on the catalyst used, whether fresh or spent. This behavior of the used catalyst, ZnO after refreshing at 350°C, could be related to the activation of the Lewis basic sites, that is, the moderate basic sites, which are responsible for the dehydrogenation of 2B to MEK. As previously stated, these moderate basic sites were observed at a temperature range of 125–285°C (see Figure 4B). At temperatures of <300°C, these moderate basic sites were most likely subjected to thermal stress, and hence their catalytic activity decreased with increasing reaction temperature. Accordingly, we recommend using these catalysts as pure and modified ZnO with x% K$_2$O, during the conversion of 2B to MEK, at reaction temperatures ≥300°C for better % conversion and MEK selectivity values. Furthermore, based
on the results presented in Figure 8, one can conclude that ZnO at 400°C, as prepared from Zn-oxalate in this study, is considered a stable and active catalyst during the preparation of MEK from 2B.

Based on our literature survey on the dehydrogenation reactions of both IPA and 2B over different types of catalysts, which has recently been published in several articles. We will summarize the most hypotheses that have been proposed to demonstrate the role of some catalysts during the dehydrogenation of IPA and 2B, as follows.

Abdelsadek et al.⁶⁴ and Abdelhamid et al.⁶⁵ have ascribed the production of acetone by dehydrogenation of IPA to the presence of basic sites. Their hypotheses⁶⁴,⁶⁵ strongly supported our findings herein. Others linked nonoxidative dehydrogenation of IPA to the exposed (111) facets of Cu catalyst⁶⁶ based on the calculated values of the energy barrier for the dehydrogenation process, or in the case of the photocatalytic dehydrogenation of IPA, due to the formation of highly defect (001) faceted-ZnO⁶⁷ that facilitate the adsorption of IPA during its dehydrogenation to acetone. Another research team⁶⁸ postulated that there was a strong correlation between the selectivity of dehydrogenation of IPA and the redox couple species evaluated on LaCoO₃ catalyst. To support their proposed mechanism, Lin et al.⁶⁹ employed density functional theory (DFT) to calculate the activation barrier of dehydrogenation and dehydration reactions of IPA over WOₓ/Pt (111) surfaces. In the case of 2B, we had previously attributed the dehydrogenation activity of NiO, whether pure or modified with K₂O or F-ions, during dehydrogenation of 2B to MEK to the presence of basic sites of varying strengths.⁳³,⁳⁴ Biswas et al.,⁷⁰ on the other hand, made no mention of any idea or mechanisms relating to the high conversion of 2B to MEK over zinc-alumina catalysts. This clearly supports our hypothesis that the dehydrogenation activity of all catalysts in this study toward IPA and 2B is strongly associated with the presence of a high population of surface basic sites, especially those with moderate strength.

4 | CONCLUSIVE REMARKS

According to the abovementioned and illustrated results, the use of pure ZnO as pure or modified with 1–10% K₂O calcined at 400°C for 3 h in oxygen, the following remarks can be summarized as follows:
1. Because of its high activity, ZnO is a multitalented, flattering oxide in many processes.1–24 ZnO as pure and modified catalysts were easily prepared herein and characterized by their nanoscale crystallite size in, that is, 22.9–28.0 nm, high basicity (ca. 1.03–1.43 mol kg⁻¹), and consequently high dehydrogenation activity during the decomposition of IPA and 2B to acetone and MEK, respectively. Modified samples of ZnO with 1–10% K₂O, particularly ZnO–1% K₂O, demonstrated a superior catalytic activity during the production of MEK at 275°C, that is, % conversion = 71.7%. All catalysts in this study showed ≥92.5% selectivity toward MEK production, as the main product, at all reaction temperatures in the range of 250–350°C.

The catalytic behavior of our samples during the production of MEK from 2B with selectivity ≥92.5%, using a fixed-bed reactor at atmospheric pressure and the applied experimental conditions, is not comparable with similar published research. Torres-Vinces et al.71 used a reactive distillation column to produce MEK through an intensified process, with a selectivity of 44%. In another study72 for the recovery of 1,3-butadiene and MEK via a 2,3-butanediol-dehydration process, the authors stated that the pilot-test results of selectivity show that MEK with 84.5% and 2-methylpropanal 15.5% based on their proposed scheme. On the other hand, Song73 studied the kinetics of the dehydration of 2,3-butanediol to 1,3-butadiene and MEK over an amorphous Ca-phosphate catalyst and N₂ as feed at a temperature range of 304.0–334.5°C, and GHSV ranging from 1780 to 2222 h⁻¹. With these experimental conditions, authors obtained MEK selectivity ranging from 31 to 34 wt.%. Finally, the present work is regarded as a valuable contribution in catalysis to produce MEK over easily prepared and cost-effective catalysts, at a relatively low temperature, with high conversion of 2B and MEK selectivity (92.5%).

Future work will focus on modifying another catalyst system with a high population of moderate basic sites for the production of MEK at low temperatures with high % selectivity from 2B. Furthermore, our next work will focus on the formation of more intense moderate basic sites and their effects on catalytic activity during the catalytic dehydrogenation reaction of 2B to MEK over such catalysts.

ACKNOWLEDGMENTS
Prof. David W. Rooney and Dr. Ahmed I. Osman wish to acknowledge the support of The Bryden Centre project (Project ID VA5048). The Bryden Centre project is supported by the European Union’s INTERREG VA Programme, managed by the Special EU Programmes Body (SEUPB). The views and opinions expressed in this paper do not necessarily reflect those of the European Commission or the SEUPB. The authors would like to thank Charlie Farrell for proofreading the manuscript.

CONFLICTS OF INTEREST
The authors declare no conflicts of interest.

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**How to cite this article:** Halawy SA, Osman AI, Rooney DW. Highly basic and active ZnO–x% K₂O nanocomposite catalysts for the production of methyl ethyl ketone biofuel. *Energy Sci Eng*. 2022;10:2827-2841. doi:10.1002/ese3.1171