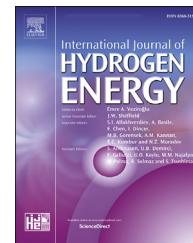


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Hydroisomerization of *n*-hexane over metal oxides-loaded fibrous silica catalyst for cleaner fuel production

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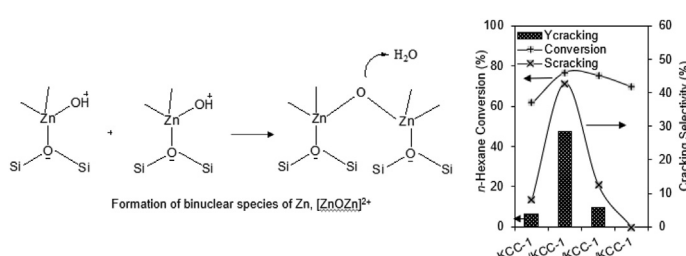
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HIGHLIGHTS

- Metal oxides (CoO, Fe₂O₃, ZnO) were loaded on KCC-1 by impregnation method.
- The binuclear of zinc in the form [ZnOZn]²⁺ were formed at higher temperature.
- The [ZnOZn]²⁺ species widened the strength distribution of Lewis acid sites.
- The [ZnOZn]²⁺ species acts as new acidic center in the *n*-hexane hydroisomerization.
- Zn/KCC-1 had the highest yield of isomers (66.97%) and no cracking products.

GRAPHICAL ABSTRACT



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ABSTRACT

Fibrous silica (KCC-1) was impregnated with cobalt (Co), iron (Fe), and zinc (Zn) oxides which are denoted as Co/KCC-1, Fe/KCC-1 and Zn/KCC-1 for hydroisomerization of *n*-hexane. The characterization analysis revealed that the introduction of Co, Fe, and Zn into KCC-1 significantly altered the physicochemical properties of KCC-1 including reduced surface area, pore volume as well as crystallinity. Pyridine adsorbed IR showed that higher

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amount of the Lewis acid sites (LAS) and Brønsted acid sites (BAS) when introduced the Co, Fe, and Zn into KCC-1. Interestingly, a new band at 1610 cm^{-1} of Zn/KCC-1, corresponds to the presence of LAS by the formation of binuclear species of Zn in the form of $[\text{ZnOZn}]^{2+}$. The formation of $[\text{ZnOZn}]^{2+}$ was further confirmed by the presence of a band at 350 nm and higher intensity of the binding energy at 1022.8 eV from UV-DRS and XPS analysis, respectively. From temperature-programmed reduction analysis, these binuclear species were formed at a higher temperature, which has a stronger interaction with the KCC-1. The proposed formation of $[\text{ZnOZn}]^{2+}$ was also discussed in this work. Based on the *n*-hexane hydroisomerization, the Zn/KCC-1 possessed the most excellent catalytic performance amongst the catalysts owing to the existence of the binuclear species of $[\text{ZnOZn}]^{2+}$, which acts as a new acidic center in the stabilization of generated protonic acid sites by trapping of electrons, resulting in increased isomers yield of *n*-hexane as well as no cracking products. Zn/KCC-1 showed the lowest activation energy compared to other catalysts within 423–673 K.

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Introduction

In recent times environmental issues have become a serious problem. Benzene and its derivatives have been banned or phased out of the gasoline pool because of their toxicity [1]. According to Euro-4 regulations, aromatic hydrocarbon concentrations must be drastically decreased, and benzene content in gasoline must not exceed 1 vol % [2]. Restrictions on certain compounds in gasoline have impacted the quality of the fuel, lowering the research octane number (RON) and engine efficiency. In reality, the RON is one of the most significant markers of fuel efficiency quality [3]. Industrial hydroisomerization procedures for converting linear alkanes to branched alkanes are becoming increasingly relevant in this area since they provide a path to high gasoline octane values. For example, RON increases from 25 to 74 when *n*-hexane is isomerized to 2- and 3-methylpentane [4]. Because of this, there is a resurgence of interest in the isomerization of *n*-alkanes via catalysis.

Alkane isomerization is commonly done with bifunctional metal-acid catalysts that have both metallic and acidic functionalities [5]. In general, the bifunctional catalyst's acid sites are involved in isomerization, while the metal sites are involved in dehydrogenation and hydrogenation [6]. Catalyst efficiency is critical here to achieve high isomer selectivity and minimize unwanted cracking products. Platinum (Pt) supported on halogenated alumina is the current industrial catalyst for hydroisomerization [7]. Meanwhile, many researchers focused on the Pt supported materials including Pd/ZSM-22 [8], Pt/HY [9], Pt/ZWFM [10], Pt/ WO_x - ZrO_2 - TiO_2 [11], Pt/FHY [12], Pt/FMOR [13], etc in isomerization research because Pt may increase the hydrogenation-dehydrogenation reaction. Despite being highly active and operating at a moderate temperature, this type of catalyst is challenging to utilize, causes corrosion, and is extremely sensitive to contaminants such as sulfur compounds and water [14]. Furthermore, researchers should investigate low-cost non-noble metal catalysts with the goal of replacing the current expensive Pt or Pd catalysts for *n*-paraffins isomerization [15]. Research on

catalysts is still going on, intend to discover new and improved catalysts.

The potential of transition metals oxide type catalysts or acid catalytic reactions has been enormously explored in recent years because of their ability to speed up the desorption of olefinic species from the catalyst surface, preventing thermal decomposition of reactants and products as well as a secondary reaction. Chen et al., successfully synthesized gallium oxide and rhenium-promoted tungstated zirconia for *n*-hexane isomerization and the catalyst showed the higher conversion and selectivity of 2,2-dimethylbutane [16]. Nickel (Ni) has better catalytic performance as hydro-/dehydrogenating active sites as reported by Yang et al. which Ni supported on SAPO-5 (Ni/SAPO-5) exhibited a high yield of isomers (54%) [17]. This was due to the strong hydrogenating ability as well as the higher dispersion of Ni. Ni nanoparticles, on the other hand, have limited polarizability and weak interactions with the support [18]. Thus, Yang et al. devised a solid-state ligand aid technique to improve metal dispersion over the Ni/Beta catalyst, resulting in a strong interaction between the Ni-complex and support [19]. It was found that higher dispersed Ni on the Beta gave a superior performance in *n*-hexane hydroisomerization.

Other than that, the preparation of zinc (Zn) oxide supported on HBEA, molybdenum oxide (MoO_3) supported on zirconia, and mesostructured silica nanoparticles for the study of *n*-alkane isomerization were executed successfully in our previous works [6,20,21]. The high activity of the isomerization reaction was attributed to the active sites' abundance and accessibility, as well as the strong Lewis acid sites (LAS). These sites may aid in the hydrogen spillover mechanism via the formation of protonic acid sites. We recently conducted *n*-heptane hydroisomerization over MoO_3 -supported fibrous silica nanosphere (KCC-1) [22]. The conversion rate at $300\text{ }^\circ\text{C}$ improved from $0.02 \times 10^{-8}\text{ s}$ to $0.94 \times 10^{-8}\text{ mol/m}^2$ with a 44.9% yield. The facile desorption of isomer products before cracking has greatly increased the performance of the KCC-1 support. According to Moon et al., mesoporous silica with fibrous shapes have a higher surface area than normal hexagonal or cubic pore structures, making it superior catalytic support [23].

Therefore, considering the advantages of transition metals oxide and KCC-1 as support, we have broadened the scope of our research to include the preparation of transition metals (cobalt (Co), iron (Fe), or Zn oxide) supported on the KCC-1 catalyst as well. For the *n*-hexane isomerization reaction, Co, Fe, and Zn have not yet been used to modify KCC-1. According to the researchers, KCC-1's unique shape would make the active site more accessible, while the addition of Co, Fe, and Zn would enhance the catalytic activity of the isomerization reaction. Previously, the formation of $\text{Zn}(\text{OAl})_2$ or $\text{Zn}^{2+}(\text{O}^-)_2$ on the Zn/HBEA sample surface increased the acidic centers for Lewis acid sites, which may facilitate the formation and maintenance of active protonic acid sites through a hydrogen spillover mechanism [20]. Meanwhile, based on several previous reports, most of the $\text{Zn}(\text{OH})^+$ species contribute significantly to alkane dehydrogenation and alkene aromatization [24,25]. Interestingly, in this study, the formation of the binuclear species $[\text{ZnOZn}]^{2+}$ increased the strength distribution of LAS in the presence of Zn^{2+} ions as confirmed by IR-Pyridine. The UV-DRS, XPS, and H_2 -TPR results confirmed the presence of these binuclear species $[\text{ZnOZn}]^{2+}$. The newly formed acidic center, which serves as a LAS, is critical in stabilizing newly formed protonic acid sites by trapping electrons, allowing for increased isomer production.

Experimental

Sample preparation

To synthesize fibrous silica KCC-1, the hydrothermal technique was employed in accordance with previously published procedures [13]. 1-pentanol (5 mL), cyclohexane (170 mL), and tetraethyl orthosilicate (15 mL) were poured into a Teflon bottle and then stirred vigorously for 30 min. A solution of urea (5 g) and cetylpyridinium bromide (10 g) was then added into the bottle. The resultant solution was heated for 180 min using a microwave, followed by 240 min of drying and calcining at 550 °C. The wetness impregnation technique was used to incorporate the 5 wt% metals into KCC-1. For the preparation of Co-loaded KCC-1 (Co/KCC-1), Fe/KCC-1, and Zn/KCC-1, the aqueous solutions of cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), and zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{CO}_2)_2$) were used as the metal precursor. Briefly, before adding 0.5 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, the KCC-1 support was mixed with distilled water at 40 °C under stirring. After 10 min, the temperature has risen to 80 °C. The catalyst was then dried overnight in an oven before being calcined for 180 min at 550 °C. By simply substituting the precursors for $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, respectively, similar processes were carried out to prepare Fe/KCC-1 and Zn/KCC-1.

Characterization

The XRD was used for the determination of the crystallinity of the catalyst, which was measured using a D8 ADVANCE Bruker X-ray diffractometer. A Cu $k\alpha$ radiation (0.15418 nm) was used to create diffractograms, which were recorded at a 2θ angle varying from 10 to 70° with a scanning rate of 0.02.

The phases were identified with the aid of the Joint Committee on Powder Diffraction Standards (JCPDS) files. Meanwhile, the Beckman Coulter SA 3100 was used to determine textural properties at 77 K. Briefly, at 573 K, 0.10 g of catalyst was degassed for 60 min. Barrett, Joyner, and Halenda techniques were used to determine the pore size distributions and total pore volume from the desorption isotherm. For the determination of specific surface area, BET isotherm plots were employed. The FESEM-EDX JEOL JSM-6701 F was used to examine the morphological structure of the catalyst. The UV diffuse reflectance spectrum (UV-DRS) was measured over a wavelength range of 200–800 nm using an Agilent Cary 60 UV-vis with PIKE Diffuse reflectance auxiliary.

The chemical properties of the catalysts were detected by the potassium bromide method via Agilent Technologies (Cary 640) FTIR spectrometer ($400\text{--}4000\text{ cm}^{-1}$). In addition, for the evaluation of the acidity study, an adsorbed basic probe molecule used is pyridine. In a nutshell, an independent wafer was heated for 3 h in a hydrogen stream and then outgassed for a further 3 h at 400 °C. After reaching an equilibrium pressure of 2 Torr, the pyridine was then adsorbed at 150 °C for 30 min. XPS (X-ray photoelectron spectroscopy) was performed on a Kratos Ultra spectrometer. A temperature-programmed reduction investigation was carried out using Hydrogen Micromeritics Chemisorb 2720 Pulse Chemisorption. A sample weighing 0.04 g was placed into quartz for pretreatment, along with a flow of 20 mL min^{-1} He at 300 °C. With a stream of 10% H_2/Ar , the reduced sample was examined at temperatures ranging from 40 to 1000 °C (20 mL min^{-1}).

Catalytic activity

Hydroisomerization of *n*-hexane under catalytic action was done in the temperature range of 150–350 °C with hydrogen flowing through a micro catalytic pulse reactor. To measure the *n*-hexane hydroisomerization activity, pretreatment was conducted using 0.2 g catalyst at 400 °C for 60 min with hydrogen and oxygen stream of 100 mL min^{-1} for 180 min, respectively, before the experiment. After that, the catalyst was placed in a hydrogen stream and allowed to stabilize at 150 °C. After that, the *n*-hexane (2 mol) was injected into the reactor under the influence of the hydrogen flow over the activated catalyst. For sampling and measurements, an online Gas Chromatograph (6090 N Agilent) was connected to the micro catalytic pulse reactor. In this stage, liquid nitrogen, a cold trapper, condensed the products and unconverted reactant.

The yield (Y), selectivity of products, and conversion (X) were measured by Eqs. (1)–(3):

$$X_i(\%) = \frac{\sum A_i - A_{ri}}{A_i} \times 100\% \quad (1)$$

$$S_i(\%) = \frac{A_i}{\sum A_i - A_{ri}} \times 100\% \quad (2)$$

$$Y_i = \frac{X_i \times S_i}{100} \quad (3)$$

Where A = chromatographic area, $i = \text{C}_6$, and ri = residual of *n*-alkane species.

Results and discussion

Catalytic structures and characteristics

Fig. 1 depicts the crystallographic structure for the two compounds studied, which are metal oxide-loaded KCC-1 and parent KCC-1 in the range of $2\theta = 10\text{--}70^\circ$. A broad peak in KCC-1 below $2\theta = 23^\circ$ is associated with the amorphous silica phase

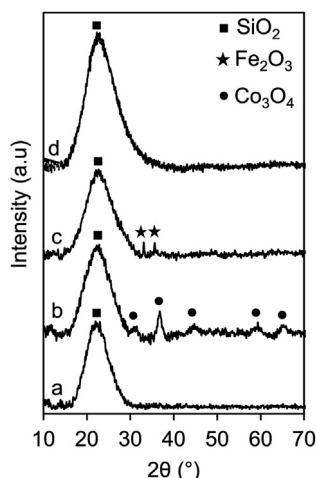


Fig. 1 – XRD patterns of a) KCC-1, b) Co/KCC-1, c) Fe/KCC-1, and d) Zn/KCC-1.

(JCPDS No. 29–0085) (Fig. 1a) [26]. For Fe/KCC-1 and Co/KCC-1, the peak of amorphous silica reduces dramatically, implying the successful impregnation of Fe and Co over the KCC-1. The drop in relative crystallinity may be due to metal species covering the catalyst's surface rather than framework disintegration. The presence of the Co_3O_4 phase, which has five prominent diffraction peaks at $2\theta = 31.3^\circ$ (220), 36.8° (311), 44.8° (400), 56.9° (422), and 71.8° (620), served as evidence that Co exists (JCPDS 78–0431) (Fig. 1b) [26]. Meanwhile, two diffraction peaks were discovered at $2\theta = 33.1^\circ$ and 37.2° in Fe/KCC-1, corresponding to the (200) and (311) planes of Fe_2O_3 , respectively (JCPDS No. 33–0664) (Fig. 1c) [27]. There were no ZnO crystallite diffraction peaks in Zn/KCC-1 ($2\theta = 31.6^\circ$, 34.2° , 36.1° , 56.6°), demonstrating that the Zn^{2+} cations species present in the samples were evenly distributed on the surface of the KCC-1. A similar finding was observed when the absence of ZnO diffraction peaks in Zn/HZSM-5, suggesting that Zn species are widely disseminated over the HZSM-5 and do not alter the zeolite structure [25].

As shown in Fig. 2, microscopic FESEM images of the catalysts were taken. When the KCC-1 was examined under the microscope, it revealed a homogeneous microsphere (300–400 nm) with well-defined fibrous morphology (Fig. 2A). Similar to this, the morphology of catalysts loaded with all-metal oxides was identical. In addition, Fig. 2B–D showed widely distributed elemental mapping of Co, Fe, and Zn throughout the catalyst, respectively. When compared to Fe/KCC-1 and Co/KCC-1, the Zn species is more widely distributed on the KCC-1 which is in line with XRD results. The traces

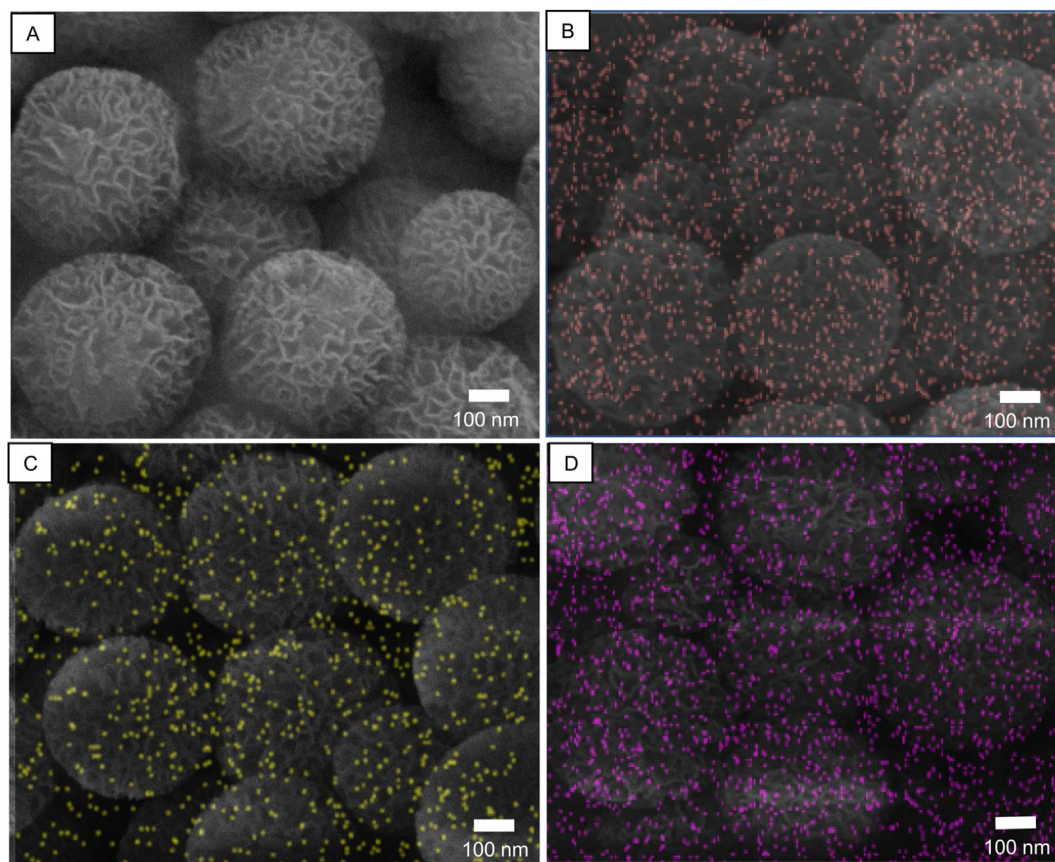


Fig. 2 – FESEM and elemental mapping EDX of (A) KCC-1, (B) Co/KCC-1, (C) Fe/KCC-1, and (D) Zn/KCC-1.

of Co, Fe, and Zn were determined by XRF to be 4.36%, 4.28%, and 4.38%, respectively, indicating that the number of materials employed in this study is closer to the metal oxide loading

quantity of 5 wt% during catalyst preparation. Additionally, 4.65% of Zn species were detected by XPS analysis. TEM images of Zn/KCC-1 in Fig. 3A and B showed Zn species present on the

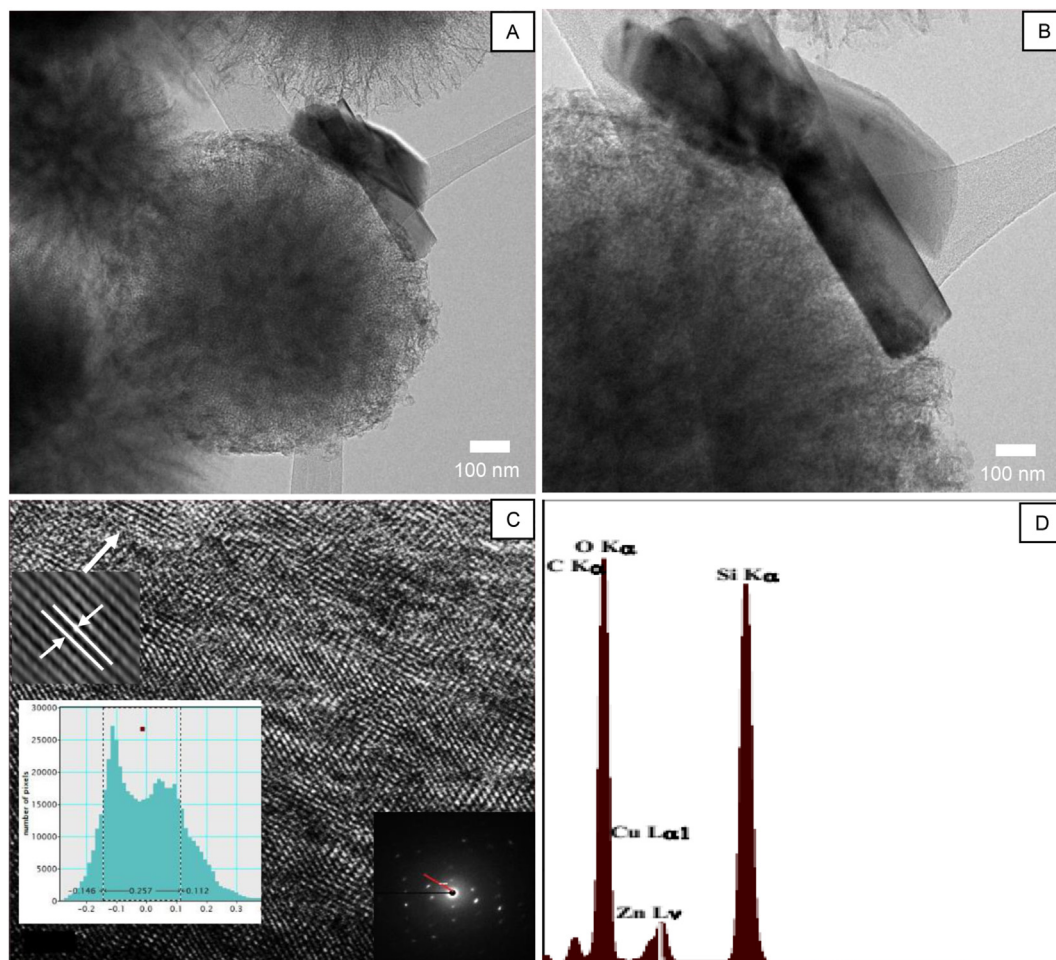


Fig. 3 – (A and B) TEM analysis, (C) HRTEM images and (inset figure) SAED diffraction and (D) Elemental composition of Zn/KCC-1.

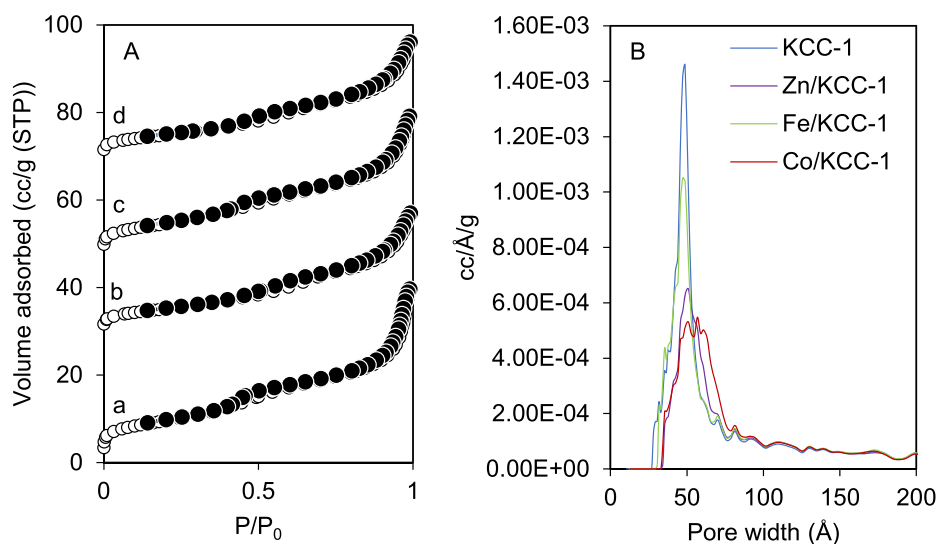


Fig. 4 – (A) Nitrogen adsorption and desorption isotherms at 77 K for (a) KCC-1, (b) Co/KCC-1, (c) Fe/KCC-1, and (d) Zn/KCC-1 and (B) Pore size distribution of the catalysts.

catalyst's surface. The d-spacings of lattice fringes about 0.257 that attributed to the (002) plane of ZnO can be seen in TEM images (Fig. 3C) [28]. These lattice distances were in accordance with the XRD spectra. The inset figure shows the corresponding SAED pattern of the nanocomposite, which demonstrates the crystalline nature [29]. Fig. 3D further confirms the presence of Zn species in the Zn/KCC-1.

In order to determine the specific surface area of the catalysts as-prepared, N₂ adsorption-desorption isotherm analysis was used, as seen in Fig. 4A. The isotherm of catalysts is type IV and has a typical H3 hysteresis loop, proving that all catalysts are mesoporous materials [26]. The KCC-1 photocatalyst had the greatest N₂ uptake when compared to metal-loaded KCC-1 catalysts, suggesting its high surface area and porosity (Table 1). The KCC-1 catalyst's pore volume and surface area decreased (Fig. 4B) with the addition of metal (Co, Fe, and Zn), indicating that the dispersion of metal species onto KCC-1 and subsequently covered partially the pore of KCC-1. This development is not a result of the crystalline framework changing or collapsing [30]. Similar reductions in surface area were observed when molybdenum was added to KCC-1 nanoparticles [22].

FTIR examination validated the chemical composition of the KCC-1 support and catalysts; in particular, the functional group (Fig. 5). KCC-1 was found to have four bands with wavelengths of 1080, 960, 800, and 470 cm⁻¹, showing the existence of asymmetric Si–O–Si, the external Si–OH, the symmetric Si–O–Si, and the bending Si–O–Si, respectively (Fig. 5A/a) [31,32]. With the addition of metal ions, the intensity of bands for KCC-1 in the fingerprint region became decreased, especially at 1080 cm⁻¹ and 470 cm⁻¹ (Fig. 5A/b–d). This implied that

the KCC-1 structure might be altered by the addition of metal oxide species [32]. A similar observation of the lower in the intensity of the fibrous silica tantalum with the inclusion of metal ions [33]. Additionally, in the framework of KCC-1, it was claimed that the interaction between SiO₂ and metal ions becomes stronger with the addition of metal ions [34]. Meanwhile, two new bands at 550 and 650 cm⁻¹ corresponded to the vibrations of Co–O in the Co/KCC-1 catalyst, indicating that the Co was effectively incorporated into the catalyst.

For future analysis, the 960 cm⁻¹ band was fitted with a gaussian curve, since the previous work reported that the external Si–OH peak consists of several significant peaks. Three prominent bands were observed and attributed to the Si–O–M interaction, non-bridging free broken Si–O stretching (948 cm⁻¹), Si–O–H stretching (960 cm⁻¹) (Fig. S1), which the former band referring to the Si–O–Fe (938 cm⁻¹), Si–O–Co (936 cm⁻¹) and Si–O–Zn (930 cm⁻¹). The shift of the Si–O–M can be explained by the equation, $E = hc/\lambda$, in which E is inversely proportional to the λ , indicating that the interaction between metal and support is stronger as the Si–O–Zn exhibited the lowest wavenumber among other catalysts. The band at 960 cm⁻¹ decreased as well as seen in the summarised results in Fig. 5B, which can be attributed to the replacement of metal ions with hydrogen atoms of the terminal –OH groups of KCC-1 for forming the Si–O–M bond. Similarly, when Zn metal was added into mesostructured silica nanoparticles (MSN), those bonds gradually decreased, indicating that Zn ions could easily be exchanged for H atoms in the terminal –OH groups of MSN to form Si–O–Zn bonds [35]. When Zn metal oxide was added to KCC-1, the strength of the Si–O–H bonds gradually decreased in comparison to when Fe and Co were added, indicating that more Si–O–Zn bonds were generated in the Zn/KCC-1 catalyst.

The temperature-programmed reduction (TPR) technique, as shown in Fig. 6, was used to investigate the reducibility of metal oxide-loaded KCC-1. The KCC-1's TPR profile remains constant throughout the experiment, demonstrating the catalyst's exceptional thermal stability (Fig. 6A/a) [36]. There are two reduction peaks at 370 and 660 °C in the presence of Co. The former reduction peaks have corresponded to the reduction of Co³⁺ (Co₃O₄) to Co²⁺ (CoO) and CoO to metallic Co⁰ (Fig. 6A/b). Fe/KCC-1 shows three peaks at 390, 510 and 650 °C, which belong to the stepwise reduction of FeOOH to Fe₂O₃, Fe₂O₃ to Fe₃O₄ and Fe₃O₄ to metallic phase Fe (Fig. 6A/c) [37]. The reduction peak at around 420 °C in Zn/KCC-1 belongs to ZnO particles, whereas the high-temperature reduction peak around 670 °C attributed to the reduction of binuclear [ZnOZn]²⁺ species (Fig. 6A/c) [38]. This results in line with the Zn/SiO₂ catalyst (Fig. S2) which the reduction peak above 400 °C can be assigned to the reduction of bulk ZnO and ~650 °C is associated with the reduction of binuclear [ZnOZn]²⁺ species. Thus, from H₂-TPR, at a high-temperature reduction peak at around 600 °C, the Co and Fe oxides were transformed to the metallic Co and Fe, while ZnO was transformed to the binuclear [ZnOZn]²⁺ species. These results may be explained by the Temperature–Partial Pressure (TPP) simulations, which were studied the stability of the metal phase. The metallic form of Co and Fe could be achieved at low temperatures (300 °C) as compared to Zn, in which the maximum temperature needed for retaining the metallic

Table 1 – Textural properties of catalysts.

	Surface area (m ² /g)	Pore volume (cm ³ /g)
KCC-1	603	0.568
Co/KCC-1	412	0.488
Fe/KCC-1	531	0.483
Zn/KCC-1	393	0.508

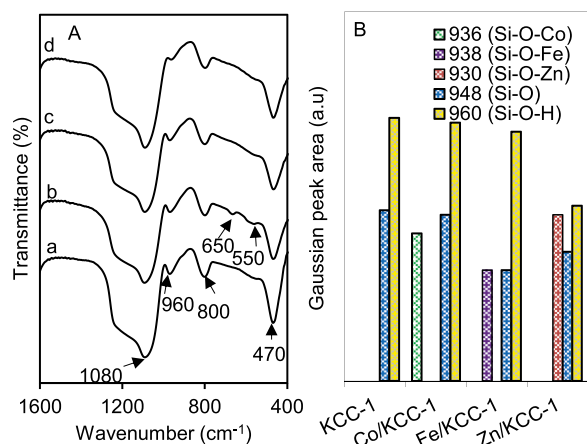


Fig. 5 – (A) FTIR spectra a) KCC-1, b) Co/KCC-1, c) Fe/KCC-1, and d) Zn/KCC-1, and (B) Gaussian peak area at peak 960 cm⁻¹.

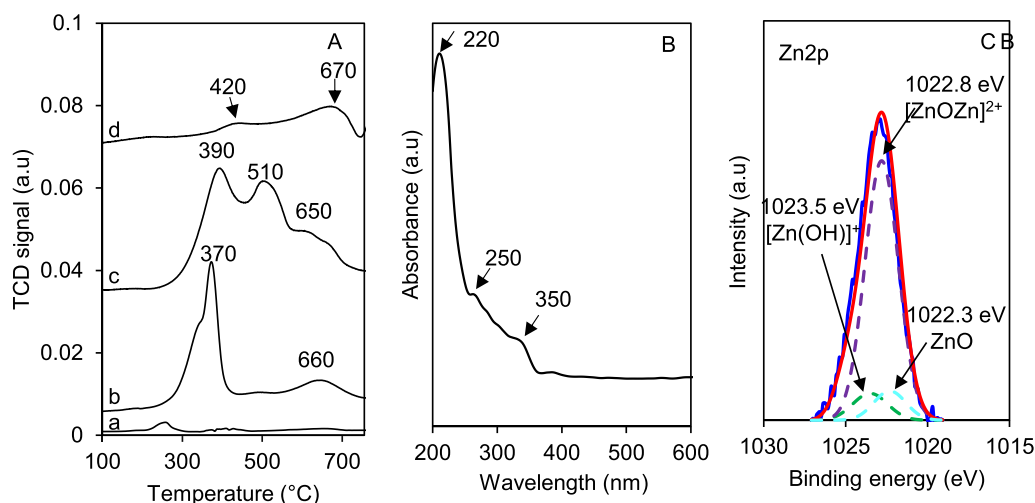


Fig. 6 – (A) H_2 -TPR profile of a) KCC-1, b) Co/KCC-1, c) Fe/KCC-1, and d) Zn/KCC-1, (B) UV-DRS spectra of Zn/KCC-1 and (C) XPS spectra of Zn/KCC-1.

phase was 500 $^{\circ}C$ (Fig. S3). This suggests that ZnO is hardly reducible at low temperatures and forms Zn^{2+} species including $Zn(OH)^{2+}$ and $[ZnOZn]^{2+}$.

The UV-DRS and XPS analysis was used in this study to confirm the presence of binuclear $[ZnOZn]^{2+}$ species. Two bands at 220 nm and 250 nm species are corresponded to the tightly bonded Zn with the framework of KCC-1 and an additional band at 350 nm, attributing to some Zn^{2+} species in the form of $[Zn(OH)]^+$ or $[Zn-O-Zn]^{2+}$ clusters Fig. 6B [25]. Meanwhile, XPS analysis confirmed the predominant Zn^{2+} species in the form of binuclear $[Zn-O-Zn]^{2+}$ as the higher intensity of the binding energy at 1022.8 eV compared to the $[Zn(OH)]^+$ (Fig. 6C). A possible explanation for the dominant $[Zn-O-Zn]^{2+}$ species is probably associated with unstable thermal of $[Zn(OH)]^+$ species and easily undergo dehydration process as reported by Biscardi et al. [39]. Similarly, Su et al. showed $[Zn(OH)]^+$ species cannot be stabilized at isolated Brønsted acid sites and will be condensed to form $[Zn-O-Zn]^{2+}$ when Zn-supported catalyst prepared by incipient wetness impregnation [25]. Thus, it clearly stated that the $[Zn-O-Zn]^{2+}$ species formed in this study via the impregnation process.

Intrinsic acidity of catalysts

Additionally, the FT-IR analysis of adsorbed pyridine is a widely used technique for determining the acidity of solid acid catalysts. This method's primary benefit is the ability to simultaneously detect the Brønsted acidic (BAS) and Lewis acid sites (LAS) in the sample [40]. The infrared spectra of pyridine adsorbed on a silica-based catalyst frequently show multiple characteristic bands, which is consistent with previous observations [41]. The KCC-1 demonstrated two bands at 1442 and 1595 cm^{-1} , which correspond to the vibrations of pyridine ions adsorbed on the LAS, which initiates from the electron pair of Si-OH groups (Fig. 7a) [6,42]. The high intensity indicates a high concentration of acid sites possessed by the catalyst. Because KCC-1 is composed of neutral silica frameworks, it showed almost no peaks at 1586 cm^{-1} which

corresponds to the BAS. Upon adding Co to KCC-1, the intensity of LAS and BAS increased, signifying that Co promotes a higher formation of LAS and BAS. Furthermore, the new band at 1485 cm^{-1} was observed in the Co/KCC-1 catalyst, corresponding to a mixture of BAS and LAS (Fig. 7b) [43]. Similarly, the presence of the band at 1485 cm^{-1} also can be observed in Fe/KCC-1, however, the intensity of those bands is slightly lower compared than Co/KCC-1. The creation of more reactive FeO and CoO species interacting with silanol groups in KCC-1 via dehydration or condensation during calcination, encouraging the generation of Brønsted acid sites' Si-O bonds Si-Fe-OH and Si-Co-OH, respectively, is one possible explanation for the observed trend [44,45]. In addition, the amount of LAS was larger than that of BAS in Fe/KCC-1 (Fig. 7c). Notably, a high amount of BAS promoted cracking products rather than isomers production. Meanwhile, Zn/KCC-1 possessed one additional peak when

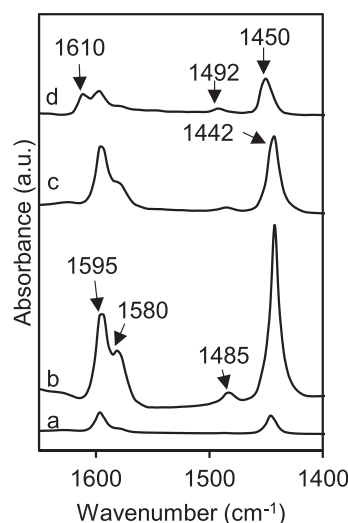
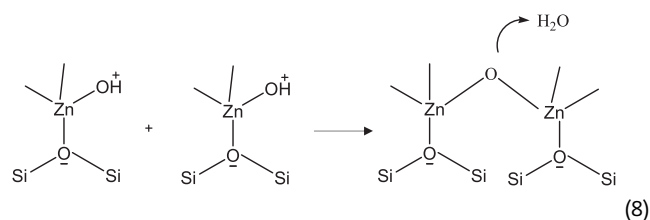
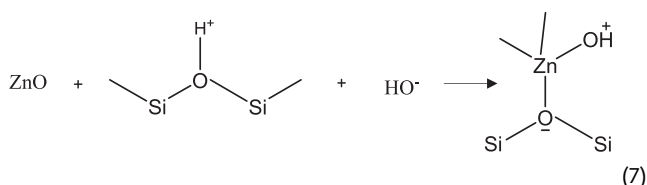
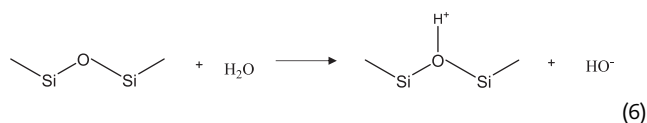
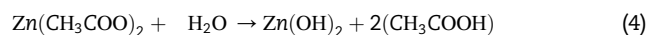


Fig. 7 – (A) IR spectra of pyridine adsorbed on activated catalysts at 423 K, followed by heating in the vacuum at 623 K for a) KCC-1, b) Co/KCC-1, c) Fe/KCC-1, and d) Zn/KCC-1.

compared to Fe/KCC-1, which is 1610 cm^{-1} corresponding to the LAS, signifying that the presence of Zn^{2+} widened the strength distribution of LAS by the formation of binuclear species $[\text{ZnOZn}]^{2+}$ (Fig. 7d) [42]. In addition, the reduced intensity of BAS is consistent with the formation of $[\text{ZnOZn}]^{2+}$ species. This species may behave as a new acidic center in the KCC-1, which is expected to enhance isomers' production by trapping the electron for the formation of protonic acid sites.

The formation of $[\text{ZnOZn}]^{2+}$ species can be proposed as follows: The water addition promotes the hydrolysis step of zinc acetate to form $\text{Zn}(\text{OH})_2$ (Eq. (4)). Upon heating, $\text{Zn}(\text{OH})_2$ was transformed into ZnO (Eq. (5)). In parallel, the KCC-1 was hydrolyzed with water to form protonated KCC-1 (Eq. (6)). The reaction of ZnO and protonated KCC-1 formed the $[\text{Zn}(\text{OH})]^+$ species (Eq. (7)). Since $[\text{Zn}(\text{OH})]^+$ species is unstable thermally and cannot be stabilized at isolated Brønsted acid sites, the dehydration process occurs by coupling of two $[\text{Zn}(\text{OH})]^+$ species to form $[\text{Zn}-\text{O}-\text{Zn}]^{2+}$ (Eq. (8)). and water as supported by UV-DRS and XPS analysis. This phenomenon could be deduced that stronger interaction between metal and support occurred at higher reduction temperature and such interaction was proved by FTIR analysis [46].



Then, the impact of outgassed temperature ($25\text{--}200\text{ }^\circ\text{C}$) towards the distribution of acidic sites is also elucidated in Fig. 8. Pyridine was adsorbed on the activated catalyst and released for 30 min at various temperatures: 25, 50, 100, 150, and $200\text{ }^\circ\text{C}$ to determine the distribution of weak, medium, and strong acid sites, respectively. At room temperature, all catalysts showed a strong interaction between acidic sites and pyridine, which was largely retained in the outgassing. As seen, temperature increases from 50 to $200\text{ }^\circ\text{C}$ resulted in decreasing IR intensity for all catalysts. Obviously, the intensity of LAS in KCC-1 Co/KCC-1 and Fe/KCC-1 dropped significantly at $50\text{ }^\circ\text{C}$ and continuously until $200\text{ }^\circ\text{C}$, indicating the presence of a large number of weak acid sites [6]. However, at a desorption temperature of $200\text{ }^\circ\text{C}$, when compared to another catalyst, all acid sites possessed by Zn/KCC-1 remained apparent, showing that the Zn/KCC-1 was occupied by a moderate-to-strong one due to the interaction between pyridine and Zn species, which known as an electron acceptor that can act as LAS.

Catalytic activity studies

As shown in Table 2 and Fig. 9, metal oxide-loaded KCC-1 catalysts have excellent hydroisomerization catalytic performance at temperatures ranging from $150\text{ to }350\text{ }^\circ\text{C}$. Increasing the reaction temperature generally increases the catalytic activity of all catalysts. KCC-1 was found to have a lower conversion rate than metal-loaded KCC-1. The *n*-hexane conversion in the KCC-1 was 61%, indicating that the lack of a metallic-acid balance function in KCC-1 resulted in a low acidity of the KCC-1. Previous studies had found the carbenium ions were formed during the conversion of alkane to be linked to the BAS-to-olefin adsorption process [6]. Pyridine

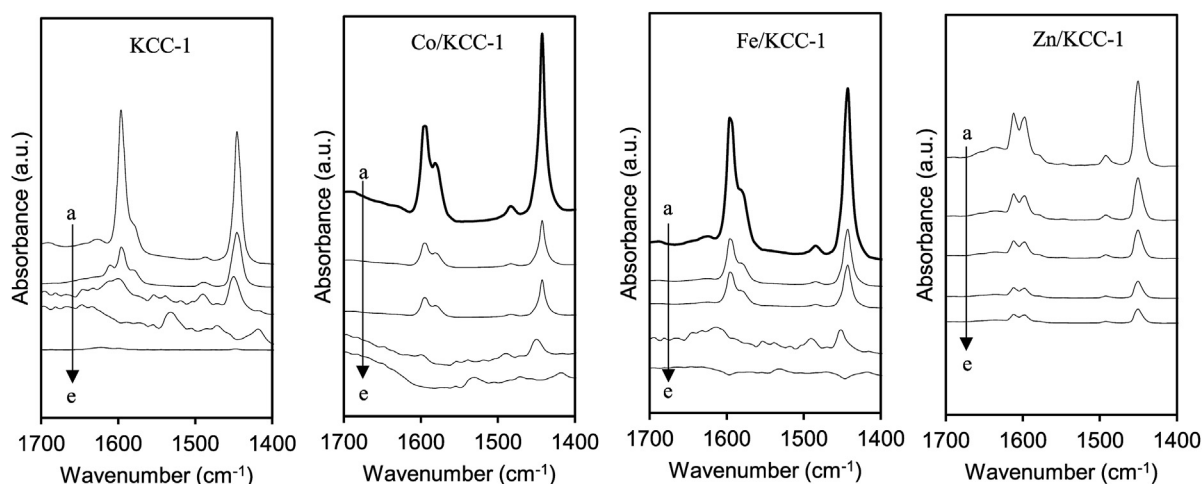


Fig. 8 – (A) IR spectra of all catalyst after pyridine adsorption at $150\text{ }^\circ\text{C}$, then outgassing at (a) $25\text{ }^\circ\text{C}$ (room temperature) (b) $50\text{ }^\circ\text{C}$ (c) $100\text{ }^\circ\text{C}$ (d) $150\text{ }^\circ\text{C}$ (e) $200\text{ }^\circ\text{C}$.

Table 2 – Product Distribution of Isomerization of *n*-Hexane from Temperature 150–350 °C.

Catalyst	Temperature (°C)	Conversion (%)	Selectivity (%)			Yield (%)		
			Isomers	Cracking	Others	Isomers	Cracking	Others
KCC-1	150	20.62	18.52	0.00	81.48	5.46	0.00	94.54
	200	38.70	59.03	0.00	40.97	15.41	0.00	84.59
	250	42.59	30.16	0.00	69.84	31.69	0.00	68.31
	300	57.43	35.17	0.86	63.97	47.60	0.67	51.73
	350	61.34	28.65	7.80	63.55	31.10	6.21	62.69
Co/KCC-1	150	29.956	49.99	0.00	50.01	9.15	0.00	90.85
	200	41.14	53.90	0.00	46.10	22.23	0.00	77.77
	250	46.05	49.76	0.11	50.13	39.74	0.09	60.17
	300	64.57	63.72	6.04	30.24	41.15	5.20	53.65
	350	76.95	60.51	42.79	0	40.81	47.56	0
Fe/KCC-1	150	32.63	0.00	0.00	100	0.00	0.00	100
	200	44.45	30.56	0.00	69.44	9.97	0.00	90.03
	250	53.68	40.16	0.00	59.84	13.72	0.00	86.28
	300	66.45	73.22	0.00	26.78	59.95	0.00	40.05
	350	75.45	63.24	12.59	24.17	50.66	9.50	39.84
Zn/KCC-1	150	28.21	54.92	0.00	45.08	23.47	0.00	76.53
	200	43.20	57.43	0.00	42.57	25.86	0.00	71.14
	250	56.92	75.55	0.00	24.45	63.31	0.00	36.69
	300	62.16	74.64	0.00	25.36	61.66	0.00	38.34
	350	69.79	78.00	0.00	22.00	66.97	0.00	33.02

adsorption IR shows that the continuous concentric lamellar KCC-1 does not contain BAS, which limits its catalytic activity.

The existence of Co species led to a major rise in *n*-hexane isomerization, which about 61%, 77% and 41%, in selectivity, conversion and yield to iso-hexane, respectively. Similarly, in the reaction temperature range 150–350 °C, the Fe/KCC-1 and Zn/KCC-1 both showed a sturdy improvement in *n*-hexane conversion from 33% to 75% and 28–70%, respectively. It was also interesting that the catalytic activity of Fe/KCC-1 and Zn/KCC-1 was superior to that of the pure KCC-1, indicating the necessity of Fe and Zn as active sites for the adsorption-dissociation of molecular hydrogen. However, Co/KCC-1 showed the highest conversion compared to Zn/KCC-1. At 350 °C, Zn/KCC-1 gave the highest isomer yield of 67% compared to Fe/KCC-1 (51%), Co/KCC-1 (43%), and KCC-1 (31%) (Fig. 9A). At lower reaction temperature (150 °C), the isomers of *n*-hexane could reach 23.47%, which is about fourth-fold higher than Fe/KCC-1. It is possible that a new acidic center,

[ZnOZn]²⁺, was formed, and that this acidic center played a role in enhancing the isomerization by forming active protonic acid sites on the Zn/KCC-1 [47]. The yield of cracking products for *n*-hexane hydroisomerization over metal and without metal-loaded KCC-1 is shown in Fig. 9B. There were no cracking products for the Zn/KCC-1, Co/KCC-1, Fe/KCC-1, KCC-1 catalysts when the temperature ranged from 150 °C to 250 °C (Table 2). However, up to 350 °C, KCC-1, Co/KCC-1, and Fe/KCC-1 showed an increased yield of cracking products up to 6, 48, and 10%, respectively. Only isomers were present in the catalysts. This could be due to thermal behaviors that cause cracking and the formation of lighter hydrocarbons. Interestingly, the Zn/KCC-1 has no cracking products observed. It is thus important to note that the Zn/KCC-1 catalyst, which acts as a LAS, contains a new acidic center ([ZnOZn]²⁺) that serves to stabilize the formed protonic acid sites by trapping of electrons. Protonic acid sites are formed and the yield of *n*-hexane isomers is increased, as well, due to the addition of LAS to the surface of the catalyst. In comparison to Fe/KCC-1 (93 kJ/mol), Co/KCC-1 (99 kJ/mol), and KCC-1 (106 kJ/mol), Zn/KCC-1 (90 kJ/mol) had the lowest apparent activation energies, as seen in Fig. 10 and Table 3. This finding demonstrates that Zn/KCC-1 had the best catalytic performance of all the catalysts, owing to the presence of binuclear species [ZnOZn]²⁺, which acts as a new acidic center for hydroisomerization of *n*-hexane.

Table 4 shows the comparison of the catalytic activity of Zn/KCC-1 with other catalysts in the hydroisomerization of *n*-hexane. It is observed that most researchers conducted the isomerization reaction of *n*-hexane at 300–450 °C over zeolite catalysts. Pd supported on ZSM-22 showed higher conversion (83.9%) and yield of isomers in the *n*-hexane hydroisomerization (76.3%) because of the higher dispersion and favorable metal-acid balance [8]. Notably, the latter properties are beneficial for the formation of mono-branched isomers products as well as the inhibition of cracking products.

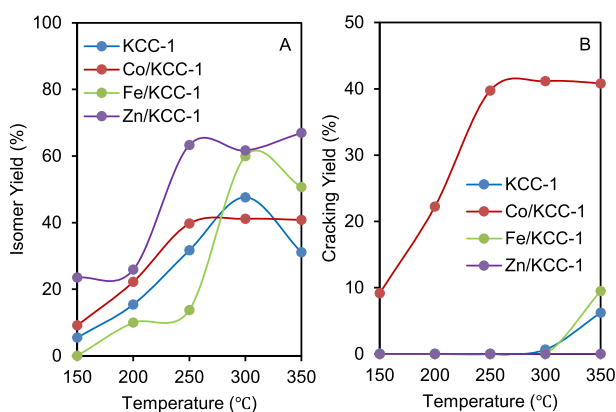


Fig. 9 – (A) Yield of *n*-Hexane isomers and (B) Yield of cracking products in isomerization of *n*-Hexane from 150 to 350 °C.

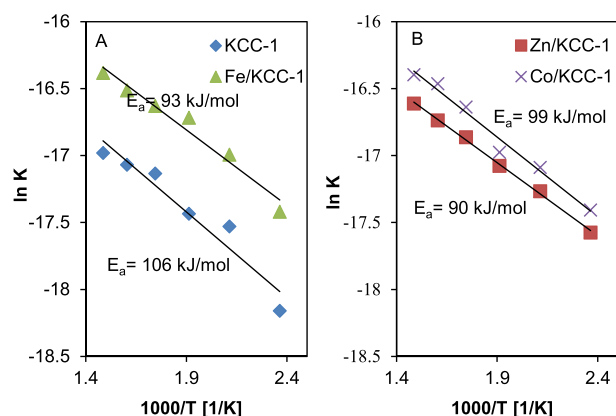


Fig. 10 – Arrhenius plot for activation energy of (A) KCC-1 and Fe/KCC-1 (B) Co/KCC-1 and Zn/KCC-1 catalyst.

Table 3 – Activation energy of catalysts.

Catalyst	Activation energy (kJ mol ⁻¹)
KCC-1	106
Co/KCC-1	99
Fe/KCC-1	93
Zn/KCC-1	90

Meanwhile, Yang et al. successfully synthesized the Ni supported on SAPO-5 (Ni/SAPO-5), which exhibited a high yield of isomers (54%) with high selectivity of cracking (31.5%) [17]. A similar result was found when using the Ni/SAPO-11 for *n*-hexane isomerization [48]. The Ni acts as a strong hydrogenating ability with higher dispersion. Similarly, Chen et al., prepared the NiP supported on H β for *n*-hexane isomerization, in which NiP acts as hydrogenation-dehydrogenation centers [49]. At the same time, Li et al. reported that B-doped NiP/H β showed a higher conversion (80.0%) and selectivity of isomers (78.3%) for *n*-hexane hydroisomerization without producing the cracking products [50]. This catalyst possessed higher isoparaffin products with higher B dopant.

Other than that, Injongkol et al., loaded Pt on the HY for enhanced the catalytic activity in *n*-hexane hydroisomerization [36]. As HY zeolites have proven to be effective hydrocarbon cracking catalysts, they discovered that the addition of Pt could reduce the cracking products. However, the selectivity of cracking products is still higher (24%) over Pt/HY at 450 °C. It may be due to the thermal cracking, as the

cracking products reduced to 15% when the Pt/HY was conducted at 300 °C [51]. To promote C–C bond activation and production, the Pt active site on HY is crucial.

Solid acid catalysts made of metal oxides, in addition to zeolite catalysts, are emerging as the most promising substitutes for *n*-hexane isomerization. Many researchers used tungstated zirconia (ZW) promoted based catalyst for enhanced the catalytic activity of hydroisomerization reaction. For example, Hernández-Pichardo et al., prepared Pt loaded on ZW with the Fe and Mn (Pt/ZWFM) and exhibited 68% of the yield of isomers and low cracking products at 260 °C [10]. Similarly, Vera-Iturriaga et al. also used ZW with the addition of TiO₂ (Pt/WO_x-ZrO₂-TiO₂) for hydroisomerization of *n*-hexane at 260 °C and showed 55% of the yield of isomers [11]. In contrast, this catalyst exhibited higher selectivity of cracking products at a lower temperature. Interestingly, in this study, Zn/KCC-1 has no cracking products with a higher yield of isomers compared to another study even though the isomerization of *n*-hexane was conducted at a higher temperature. This was due to the existence of the binuclear species of [ZnOZn]²⁺, which acts as a new acidic center in the stabilization of generated protonic acid sites by trapping of electrons.

Conclusion

Zn/KCC-1, Co/KCC-1, and Fe/KCC-1 catalysts were produced using the wetness impregnation approach and used to conduct isomerization of *n*-hexane in this investigation. The incorporation of Co, Zn, and Fe into KCC-1 led to the preservation of the bicontinuous concentric lamellar morphology, as demonstrated by the FESEM images. However, XRD showed that the introduction of Co, Fe, and Zn on KCC-1 decreased the peak intensity of amorphous silica. A decrease in Si–O and Si–OH band intensity was confirmed by FTIR analysis, attributed to the replacement of metal ions with hydrogen atoms of the terminal –OH groups of KCC-1 for forming the Si–O–M bond. In addition, Zn/KCC-1 had the greatest reduction in Si–OH band intensity, owing to a higher number of stronger interactions between Zn and KCC-1. The pyridine IR also revealed that the introduction of Co, Fe, and Zn promotes LAS and BAS's higher formation. Importantly, the presence of Zn²⁺ widened the strength distribution of LAS by the formation of [ZnOZn]²⁺ species. The formation of this species was supported by the UV-DRS and XPS analysis. The H₂-TPR analysis also confirmed the high-temperature reduction peak around 670 °C attributed to

Table 4 – Catalytic activity of catalysts for *n*-hexane isomerization.

Catalyst	Conversion (%)	Yield of isomers (%)	Selectivity of cracking (%)	Reaction temperature (°C)	Reference
Zn/KCC-1	69.8	67.0	0	350	This study
Pd/ZSM-22	83.9	76.3	9.1	320	[8]
Ni/SAPO-5	77.1	54	31.5	360	[17]
Pt/HY	80.0	25	15.0	300	[51]
NiPB/HB	80.0	78.3	98(Isoparaffins)	300	[50]
Ni/SAPO-11	74.3	49.6	43.7	360	[48]
NiP/H β	72.0	73.0	0.9	200	[49]
Pt/HY	–	25	24	450	[9]
Pt/ZWFM	66.5	68	1.0	260	[10]
Pt/WO _x -ZrO ₂ -TiO ₂	63.0	55	7.0	260	[11]

the reduction of binuclear $[\text{ZnOZn}]^{2+}$ species. Based on the n-hexane hydroisomerization, Zn/KCC-1 possessed the highest isomers selectivity and yield, and no cracking products compared to Co/KCC-1 and Fe/KCC-1. This was due to the existence of the binuclear species of $[\text{ZnOZn}]^{2+}$, which acts as a new acidic center in the stabilization of generated protonic acid sites by trapping of electrons.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2023.02.106>.

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