Highly Selective Conversion of Isopropanol to Propene Over CeFeO₃/Spherical Silica Nanocomposite

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Abstract: Cerium iron mixed oxide (CFO) nanocomposite materials supported on spherical silica particles were explored for gas phase dehydration of isopropyl alcohol (IPA). The samples were formed by a sol-gel process. Utilization of silica as a matrix for reducible CeO₂-Fe₂O₃ mixed oxides formation of thermally stabilized textural CeO₂-Fe₂O₃/silica nanocomposite materials. Thus, a series of 10-30% (w/w) CFO/silica was directly formed, dried, and calcined at 550°C. XRD, TG-DTA, ATR-FTIR, nitrogen adsorption–desorption, and TEM images were used to analyze the samples. The catalytic performance of materials has been estimated. The catalytic activity of the catalytic materials was evaluated to measure the dehydration reaction of IPA at 250 °C in the air atmosphere. According to the results, 20% CeFeO₃/silica calcined at 550°C exhibits a high conversion of IPA amounts to ~89% with selectivity (100%) for propene, as well as a high rate of propene production (7.9 mol h⁻¹). The higher catalytic activity of the supported catalyst was related to its improved textural and thermal stability, based on these results, propene is efficiently produced.

Keywords: mixed oxide, spherical silica, nanocomposite, IPA, propene.

1. Introduction

The high demand for lower olefins, which are fundamental elements of the chemical industry and have a wide range of industrial uses (including synthetic fibers, anti-freezing agents, packaging materials, and solvents) [1]. Thus, the process of converting short-chain alcohols (such as methanol, ethanol, butanol, isopropanol, etc.) to olefin is one of the ideal approaches for developing novel, environmentally friendly technologies for generating lower olefins to supplement the limited petroleum feedstock supply[2, 3].

The need for polypropylene up to 64% and their derivatives from propylene oxide, acrylonitrile, oxo alcohol, and others reach 36% increases annually [4], raising the global production rate of propylene by 4–5%. In the chemical industry, propene is regarded as one of the fundamental ingredients because it is used to make many significant products, including polypropylene and propene oxide [5]. Steam thermal cracking of naphtha, catalytic cracking of C4 alkenes [6], catalytic propene dehydrogenation [7], and catalytic dehydration of IPA [8, 9] are the processes used in the industrial manufacture of propene. For catalytic dehydration of IPA to propene, solid acid catalysts for instanceWO₃/ZrO₂ [10], Al₂O₃-TiO₂ [11], WO₃/ACP [12], phosphate zeolite [13] and Fe₂O₃/γAl₂O₃ [14] have been employed as catalyst. Significant thermal mechanical chemical properties, the surface characteristics, and morphology of SiO₂ materials [15] succeed in the utilization of silica as catalyst support Therefore, Numerous heterogeneous catalysis methods have recently been investigated as prospective support catalysts for petrochemical, as well as petrochemical processes [16–18] and gas-liquid-phase oxidation processes [19]. However, it has some drawbacks due to hydrothermal activity reactivity [20]. Additionally, the supporting phenomena can be advantageous when loading an active phase on support [21–23]. Thus, active phases have become the research focus.

It has been found that doping silica with cerium has a positive impact on enhancing ment redox properties of ceria [24]. The catalytic activity of ceria-based materials due to their redox behavior (Ce³⁺/Ce⁴⁺) and the ability of formation of oxygen vacancies for improving structural and chemical properties doping ceria with iron due to its redox behavior [25]. Numerous reports that cerium iron mixed oxide composites have various uses in catalysis such as catalytic oxidation and photocatalytic degradation of nitroaromatic compounds [26], which are highly affected by the preparation methods, iron content, sintering temperature, and phase composition [27].

Some advanced applications have been explored for Cerium iron mixed oxide nanostructured, including photodegradation of Congo dye [28], Selective catalytic reduction of NOx [29], ozonation of nitrobenzene in water [30], oxygen carrier and hydrogen generation [31,32] and photocatalyst [33, 34]. Several investigations have demonstrated that improving catalytic performance is significantly connected with the dispersion and particle size of the metal [23, 35–37]. Mixed oxides or perovskite have been utilized for modification of silica towards gas phase alcohol dehydration reaction. Perovskite oxide types are considered very promising catalytic materials owing to low cost, excellent
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thermophysical stability, adjustable redox ability, and oxygen mobility. Lanthanum-iron mixed oxide perovskite has gained great interest in numerous catalytic applications including electrocatalysis catalytic oxidation [38, 39] and combustion of volatile organic compounds (VOCs) via catalysis [40].

The present study used direct dispersion of 10, 20, and 30% (w/w) Cerium-iron mixed oxides precursors into freshly formed Stöber silica particles. Utilization of silica as a matrix for reducible CeO₂-Fe₂O₃ mixed oxides formation of thermally stabilized textual CeO₂-Fe₂O₃/silica nanocomposite materials that were calcined for three hours at 550°C using static air. Many standard bulk and surface characterization methods were used to describe the supported catalysts. Examinations of the novel catalysts for isopropyl alcohol to propene gas phase dehydration. The surface structure and texture of supported catalysts correlate to their catalytic activity.

2. Materials and methods

Iron(III) nitrate nonahydrate, Fe(NO₃)₃·9H₂O, (assayed), 98%, solid product of (Prolabo, France); Cerium(III) nitrate hexahydrate, Ce(NO₃)₃·6H₂O; Citric acid, C₆H₈O₇·H₂O, purified (Merck, India); tetraethyl orthosilicate, Si(OC₂H₅)₄, (TEOS), 98%, liquid, (Sigma-Aldrich Company, Ltd. (Germany); isopropyl alcohol (IPA), pyridine (PY), 2,6-dimethyl pyridine (DMPY); Ethyl alcohol C₂H₅OH, 99.5%, (Adwic, Egypt) and 33% NH₃ aqueous ammonia solution (BDH, Ltd., England) were acquired and used exactly as directed.

2.1. Silica support synthesis

The Stöber method [41] was used to synthesize the blank silica material. The preparation process is described in further detail elsewhere [41–43]. Briefly, TEOS (19.0 mL) was dispersed into a solution containing absolute alcohol (207 mL) and ammonia (155 mL) after that, keep stirring continuously for 1 h with magnetic stirring (400 rpm), to produce freshly Stöber silica sol. The solution was filtered after being aged at ambient temperature for a week before being dried for a full day at 120 °C. The dry material was calcined for three hours in static air at a ramp rate of 1°C min⁻¹ up to 550°C and labeled as silica support 550.

2.2. Synthesis of CFO/SiO₂ composite material

CFO/SiO₂ composite materials with weight percentages of 10, 20, and 30% were prepared as follows, computed amount of Fe(NO₃)₃·9H₂O, Ce(NO₃)₃·6H₂O, and C₂H₄O₂H₂O. H₂O was dissolved in 50 mL of water. The final product was mixed with recently produced silica sol. For one hour, the solution was swirled magnetically at 400 rpm. The finished mixture was allowed to sit at room temperature for a week. The resulting material was then filtered and dried at 120°C during the following day. Portions of dried material were maintained at this temperature of 550°C for three hours in the muffle furnace using static air at a ramp rate of 1°C min⁻¹. The calcined materials produced were referred to as calcined 10, 20, and 30% w% CFO/SiO₂ 550 composites.

2.3. Characterization Methodologies.

X-ray diffraction patterns were acquired using a diffractometer (a Phillips type Spectrometer version PW 2103/00 outfitted with a Ni-filtered, CuK radiation (=1.5418)) to confirm the structure and crystallinity of the materials, FTIR spectra have been detected utilizing. A 400-4000 cm⁻¹ Bruker-Alpha FT-IR spectrometer (Germany).

Thermogravimetric analysis was performed on a TA 60 thermal analyzer apparatus (Shimadzu, Japan) at a heating rate of 10 °C/min and a flow rate of 30 mL/min of air and nitrogen. At 196°C, nitrogen adsorption–desorption analyses were performed using a Micromeritics instrument (model ASAP 2010, Micromeritics Corporation, USA) Before measuring, test samples were degassed for 2 hours at 200 °C to 0.1Pa. The Brunauer-Emmett-Teller (BET) equation was used to get the specific surface area, SBET, was calculated by applying the Brunauer-Emmett-Teller (BET) equation[44]. The Barrett-Joyner-Halenda (BJH) method [45] was used to create the mesopore width distribution, and all measurements and analyses were carried out following IUPAC standards[46]. Transmission electron microscopy (TEM) image was tested using a 100kV Joel 2000 device. For EDX analysis, Oxford instrument X-MAX,80mm².

2.4 Catalytic Performance Examination

The current composite catalysts’ catalytic performance was examined for the Vapor phase dehydration of isopropanol employing chromatographic analysis by FID with a Unicam Pro GC2000 [12, 22, 47]. In a typical experiment 300 mg using of catalyst, in the temperature range 120-250°C, air atmosphere as a carrier gas, and the total flow rate was 50 ml min⁻¹, 2.7 % isopropanol (IPA) in the gas feed and space-time (GHSV 10,000mlg⁻¹h⁻¹).

For calculation, the following formulas were used:

IPA conversion (%) = \frac{[IPA]_{in} - [IPA]_{out}}{[IPA]_{in}} \times 100

Propene Selectivity (%) = \frac{[Propene]}{[IPA]} \times Selectivity \times 100

Propene Yield (%) = \frac{[propene]}{conversion \times Selectivity \times 100}

3. Results and Discussion:

3.1. XRD Diffractometer:

XRD diffraction patterns for blank silica support and the 10-30 CFO/silica composite’s composites calcined at 550 °C for 3 h are displayed in Fig.1. The XRD patterns displayed blank silica support without additional peaks at the position characteristics for CeFe₂O₃ or CeO₂ or Fe₂O₃ were observed. Furthermore, the broad peak at 25 attributes for silica was dramatically reduced as the CFO loading percentage was raised. The above observation for the supported catalysts suggests that CFO or mixed oxides were substantially scattered or present as extremely small nanoparticles of CFO, which were either amorphous or extremely small in comparison to the XRD detection limits [18].

3.1.2. FTIR spectra

FTIR spectra for 10, 20, and 30 CFO/Silica composite catalysts, along with silica support are shown in Fig 2. The spectrum displays several bands that exactly correlate to the silica gel band positions [43, 42]. The band at 3212 cm⁻¹ corresponds to the ν(O–H) mode of (H-bonded) water
molecules, the band located at 1598 cm\(^{-1}\) refers to the \(\delta(\text{OH})\) mode; the band at 940 cm\(^{-1}\) corresponds to \(\nu_{\text{as}}\) (\(\text{Si} - \text{O} - \text{Si}\)) and \(\nu_{\text{v}}\) (\(\text{Si} - \text{O} - \text{Si}\)) modes, respectively; and the band at 446 cm\(^{-1}\) corresponds to the \(\delta(\text{Si} - \text{O} - \text{Si})\) mode. The band observed at 1430 cm\(^{-1}\) may be related to the presence of adsorbed nitrate species. However, as the CFO ratio increased, the intensity of the \(\text{Si-OH}\) vibration \(\nu(962\ \text{cm}^{-1})\) band decreased slightly. This reduction in \(\text{Si-OH}\) vibration intensity suggests ongoing surface alteration of the silica substrate.

3.1.3 Thermal Analysis (TGA and DTA)

Thermogravimetric and derivative thermogravimetric analyses (TGA and DTG) for 10, 20, and 30CFO/SiO\(_2\) composite materials with the corresponding silica support in N\(_2\) and O\(_2\) atmosphere, respectively are shown in Fig. 3 (A and B), numerical data were listed in Table S.1. TGA curves reveal stable mass in the (200-750°C) range for SiO\(_2\) support, whereas mass loss continues in this range for composite materials.

TGA–DTG results for 10, 20, and 30CFO/SiO\(_2\) demonstrate three decomposition stages in each curve. Loss of adsorbed water is a result of the first stage below 150 °C. The range of the second stage of (170–400°C) was characterized by peaks at 227, 230, and 231 °C for 10, 20, and 30 CFO/SiO\(_2\) in the N\(_2\) atmosphere. However, in the O\(_2\) atmosphere peaks were observed almost at the same position observed in N\(_2\) typically at 225, 228, and 232 °C for 10, 20, and 30 CFO/SiO\(_2\), respectively. The above results demonstrate that weight losses recorded in the N\(_2\) atmosphere were more than those recorded in the O\(_2\) atmosphere and DTG curves showed a peak around 230 for the composite materials in N\(_2\) or air atmosphere, whereas such a peak was not observed at all for silica support. Data demonstrates that the thermal event at ~230 corresponded to the decomposition of the CFO precursor material and there was little effect of oxygen on that event.

Fig. 4 (A and B) show simultaneous DTA results for the above materials 10, 20, and 30CFO/SiO\(_2\) in N\(_2\) and O\(_2\) atmosphere. In the flow of N\(_2\), an exothermic peak was observed for the composite materials (but not for the blank silica) around 240 °C. Moreover, a shoulder peak was also observed around 300 °C. Similar exothermic peaks were observed in the flow of air at the same position 240°C; however, no shoulders were accompanied by this peak. This suggests that the shoulders observed in the flow of N\(_2\) were properly related to the decomposition of a minor number of organics (no weight loss was observed for this event).

3.1.4 Nitrogen adsorption/desorption

The materials' textural properties were evaluated using N\(_2\) adsorption–desorption isotherms in Fig. 5 and Table 1. Silica support showed an Isotherm of type II with no discernible hysteresis loop based on the original IUPAC classification [46]. However, the composite catalytic materials showed isotherms of type IV isotherms with \(H_3\) hysteresis loops. The surface area amounts to 25.6, 52.0, and 81.4 m\(^2\)g\(^{-1}\) were obtained for the 10, 20, and 30 CFO/silica catalyst, whereas a
small surface area amounts to 11.6 m²g⁻¹ was obtained for the blank silica supports. Total pore volume \( V_p \) values (0.027, 0.052 and 0.094) and external surface area \( S_t \) values (21.8, 41.8 and 71.5) were obtained for the blank silica, 10CFO/silica, 20CFO/silica and 30CFO/silica, respectively. Total pore volume and external surface values follow the same order observed for \( S_{BET} \) surface area. Further textural characteristics including pore width distribution are shown in Table 1.

Pore width, and \( W_p \), (via the average \( 4V_p/S_{BET} \) method and BJH method) were estimated, for the 10, 20, and 30 CFO/silica composite along with the silica support are depicted in Fig. 6. Values amounts to 108, 64, 62, and 54 were obtained by BJH method for the blank silica support, 10, 20 and 30 CFO/silica composite catalysts, respectively. Pore width distributions in the mesoporous range are presented in Fig. 6. This observed trend demonstrates that the PWD was maximized in the higher and higher range of mesoporosity with increasing the loading ratio.

Table. 1: Textural characteristics for silica support and composites 550.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( S_{BET} ) m²g⁻¹</th>
<th>( C_{BET} )</th>
<th>( V_p ) cm³g⁻¹</th>
<th>( t)-method m²g⁻¹</th>
<th>( 4V/S_{BET} )</th>
<th>( S_{mic} )</th>
<th>( W_p ) Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica support</td>
<td>11.6</td>
<td>67.44</td>
<td>0.0118</td>
<td>0.166</td>
<td>10.99</td>
<td>42.2</td>
<td>108</td>
</tr>
<tr>
<td>10CFO/S550</td>
<td>25.6</td>
<td>107.3</td>
<td>0.027</td>
<td>3.7</td>
<td>21.8</td>
<td>42.4</td>
<td>64.1</td>
</tr>
<tr>
<td>20CFO/S550</td>
<td>52.00</td>
<td>126.70</td>
<td>0.052</td>
<td>10.2</td>
<td>41.8</td>
<td>40.1</td>
<td>62.2</td>
</tr>
<tr>
<td>30CFO/S550</td>
<td>81.4</td>
<td>86.6</td>
<td>0.094</td>
<td>9.97</td>
<td>71.5</td>
<td>47.3</td>
<td>53.8</td>
</tr>
</tbody>
</table>

3.1.5 TEM micrograph

Images of TEM and EDX analysis for 20CFO/Silica 550, are shown in Fig. 7. Confirm that microscopic particles have a regular spherical shape with a size range of 200-600 nm. Many particles of CFO are present as single ones; some other particles are aggregating into small aggregates. EDX spectra for 20CFO/Silica550 show the presence of C, Si, Ce, Fe, and O in the silica matrix.

3.1.6. Catalytic measurements

The catalysts' catalytic activity was investigated under optimal reaction conditions, towards the dehydration reaction of isopropyl alcohol (IPA) in the flow of an air atmosphere in a flow bed catalytic reactor. The catalytic activity results at 250 °C were investigated and are shown in Fig. 8. Results reveal very high catalytic activity for the composite materials, whereas very low catalytic activity was obtained for the blank silica support.
Fig. 7: TEM micrograph and EDX Spectra for 20/CFO silica550.

The catalytic activity was in the order of 20CFO/silica > 30CFO/silica > 10CFO/silica > CFO > silica. The 20CFO/Silica catalyst showed the highest catalytic activity with conversion percent 89.0% at 250 °C and 100% selectivity for propene formation. The superior catalytic material (20CFO/Silica550) was examined in the temperature range of 120–250°C shown in Fig. 9. Increasing the temperature of the catalytic reaction enhances the conversion to propene over the 20CFO/Silica550. It demonstrates that CFO mixed oxide phase loading enhanced surface activity in terms of increasing the acidic sites and enhancement of the surface oxygenated groups. As well known, IPA reaction over the surface of the catalyst only screens the total acidity. To distinguish between the two types of acidic sites and estimate the nature and strength of these sites. Therefore, the chemisorption of basic probe molecules such as pyridine (PY), and dimethyl pyridine (DMPY), was utilized for testing and distinguishing between Lewis (L), and Brønsted (B) acid sites. The effect of admission time of pyridine (PY), and dimethyl pyridine (DMPY) during the dehydration of IPA, at reaction temperature 200 °C, for 20 CFO/Silica 550, is shown in Fig. S1. reveals that the IPA conversion decreases with increasing admission time of PY and DMPY vapors. IPA conversion continuously reduces to reach a steady state of conversion 26% after 35 minutes, respectively. In addition, the conversions in the case of PY and DMPY are overlapped indicating that the nature of these acid sites is mainly due to Brønsted acid sites[48].

Fig. 8: Catalytic dehydration of isopropanol of IPA for calcined10,20 and 30CFO/Silica along with Silica support and pure CFO 550.

Fig. 9: Catalytic temperature on catalytic performance over 20 CFO/ Silica 550 towards dehydration of isopropyl alcohol into propene.
4. Conclusion

The present work showed the investigation of dispersion of different ratios (10 to 30) % of CFO mixed oxides into the silica matrix. The appearance of CFO mixed oxide dispersion nanoparticles or even clusters on the silica support's surface resulted in the formation of a mesoporosity texture of non-porous silica with enhanced surface area and porosity. Amorphous mixed oxide formation or perovskite of CFO into silica matrix enhanced the surface acidity of silica matrix and improved the catalytic dehydration of isopropyl alcohol to propene. The 20 CFO/Silica 550 displayed a high conversion percent and remarkable selectivity in the production of propene. This approach demonstrated that the effective dehydrent catalyst towards propene production can be formed by the dispersion of amorphous CFO mixed oxide into silica support. The validated performances of the presented novel 20 CFO/Silica 550 composite catalysts, on the other hand, motivate additional research into surface fine structure which is related to catalytic reaction conditions.

CRediT authorship contribution statement:
Walaa A. Elhamdy: Conceptualization, Methodology, Supervision, Writing – original draft, Investigation, Formal analysis, Data creation, Writing – review & editing. Abd-El-Aziz.A.Said:Supervision,Methodology,Visualization. Kamal M.S. Khalil: Supervision,Visualization, Validation, Investigation.

Data availability statement
The data used to support the findings of this study are available from the corresponding author upon request.

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.

5. References

Table. 2: Comparison between the catalytic performance of the present work and the other literature.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reaction temperature (C)</th>
<th>IPA Conversion (%)</th>
<th>Propylene selectivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-SBA-15</td>
<td>250</td>
<td>96</td>
<td>100</td>
<td>[49]</td>
</tr>
<tr>
<td>Pb/AlGa-x</td>
<td>300</td>
<td>&gt;95</td>
<td>97</td>
<td>[50]</td>
</tr>
<tr>
<td>SiO2-ZrO2</td>
<td>300</td>
<td>90</td>
<td>100</td>
<td>[8]</td>
</tr>
<tr>
<td>Fe2O3/γ-Al2O3 acid</td>
<td>250</td>
<td>63</td>
<td>45</td>
<td>[14]</td>
</tr>
<tr>
<td>Fe2O3-CuO/γ-Al2O3 basic</td>
<td>290</td>
<td>70</td>
<td>100</td>
<td>[14]</td>
</tr>
<tr>
<td>BNP13</td>
<td>260</td>
<td>57</td>
<td>&gt;99</td>
<td>[51]</td>
</tr>
<tr>
<td>CFO/Silica 550</td>
<td>250</td>
<td>89</td>
<td>100</td>
<td>Our work</td>
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