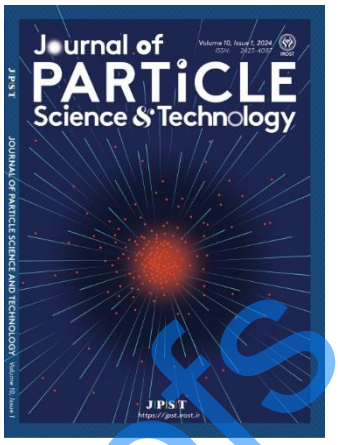
Journal Pre-proofs



Fe–Zr–Cu mixed-metal oxide nanocatalyst for selective oxidation of benzyl alcohols: Synthesis, characterization, and catalytic performance

Hoda Haghi, Alireza Sedrpoushana

DOI: https://doi.org/10.22104/jpst.2026.8484.1300
Manuscript number: JPST-2608-1300

To appear in: *Journal of Particle Science and Technology (JPST)*

Received Date: 9 August 2026
Received Date in revised form: 29 August 2026
Accepted Date: 6 September 2026

Please cite this article as: Haghi, H., Sedrpoushana, A., Fe–Zr–Cu mixed-metal oxide nanocatalyst for selective oxidation of benzyl alcohols: Synthesis, characterization, and catalytic performance, *Journal of Particle Science and Technology* (2026), doi: https://doi.org/10.22104/jpst.2026.8484.1300

Fe–Zr–Cu mixed-metal oxide nanocatalyst for selective oxidation of benzyl alcohols: Synthesis, characterization, and catalytic performance

Hoda Haghi, Alireza Sedrpoushan*

Department of Chemical Technologies, Iranian Research Organization for Science and Technology (IROST), P.O. Box 33535111, Tehran, Iran

Abstract

A mixed nano-metal oxide of Fe-Zr-Cu was synthesized using a hydrothermal technique. The chemical structure and nature of the catalyst were characterized using the XRD, SEM, EDS and Elemental map. SEM images revealed a sample with Cauliflower-like shape. The resultant heterogeneous catalyst was used to selectively oxidize different alcohols to corresponding aldehydes, under mild conditions with acetonitrile as a solvent and hydrogen peroxide as an oxidizing agent. The influence of reaction temperature and the ratio of molar alcohols to oxidant were examined according to the material/product ratio. Conversion efficiencies ranging from 65 to 80% were achieved under optimal conditions at the presence of benzyl alcohol. The results are so promising and demonstrate the potential application of the heterogeneous catalyst for selective oxidation of benzyl alcohols.

Keywords: Mixed nano-metal oxides, Heterogeneous catalyst, Oxidation, Benzyl alcohol

1. Introduction

Catalytic processes (such as removing toxic and costly chemicals, minimizing by-products, and shortening workup methods) have received significant attention in recent years due to the increased request for environmentally friendly technology in chemical reactions in the industry [1,2,3].

The selective oxidation of benzylic alcohols to benzaldehydes is one of the long-standing problems in organic chemistry. Many researchers worked to develop a new approach for chemo selective mono-oxidation particularly in the development of environmentally benign and sustainable catalytic processes [4–6]. Among various oxidation products, aromatic aldehydes are indispensable intermediates for the synthesis of pharmaceuticals, fragrances, agrochemicals, and fine chemicals, creating a continuous demand for highly selective and recyclable heterogeneous catalytic systems [7–10]. Various reports on synthesizing aldehydes have been presented in this subject, using different types of oxidants, (e.g., HNO_3, N_2O_5, $NaIO_4$, *meta*-chloroperoxybenzoic acid, halogens, and high-valence metal salts) [11–14]. These techniques suffer drawbacks such as the need for complicated reaction processes or the utilization of hazardous chemicals [15] ,as well as the conversion of alcohol to carboxylic acid, or similar undesired by-products [16].

To avoid these restrictions, aqueous 30% hydrogen peroxide (H_2O_2) has been used in various research to design new and effective catalytic systems, as the last green oxidant. Oxidant hydrogen peroxide is mild, inexpensive, bio-friendly characteristics, has a good oxygen concentration, and produces only water as a by-product [17,18].

While, at the presence of a homogeneous catalyst, the issue of separating the pricey catalyst from the yield arises, requiring a separation technique for the recyclability [19]. Hydrogen peroxide is considered one of the most attractive oxidants for the selective oxidation of alcohols because of its high active oxygen content, environmental compatibility, and the formation of water as the only by-product [20]. Despite the significant advances made in this subject, the construction of a

heterogeneous catalyst with high yield chemo selective mono oxidation of alcohols to aldehydes, remains a problem.

Particularly, transition-metal oxides have received considerable attention because their tunable electronic structures endow them with excellent redox activity, adjustable acid–base properties, high structural stability, and remarkable heterogeneous catalytic performance. These characteristics make mixed-metal oxide catalysts especially attractive for selective oxidation reactions. [21,22].

Transition metal oxide nanoparticles have attracted considerable attention as heterogeneous catalysts owing to their remarkable ability to promote the selective oxidation of alcohols [23]. Many transition metal oxide catalysts are fundamental given their profits like, low-cost procedures, easy regeneration, toxic ligands elimination, and selective reactivity. The catalytic activity can be attributed to the presence of partially filled d-shells in the metal ions and their interaction with the surrounding oxide field. The morphology and the diameter of the resultant nanostructure depends on type of metal ion used. In addition, nanostructures can even change in morphology due to specific reaction types. Iron-Zirconium-copper nanowires with a diameter of about 20 nm, can be transformed into iron- Zirconium -copper oxide nanotubes by oxidation [24,25].

The development of mixed-metal oxide catalysts has emerged as an effective strategy for enhancing the activity, selectivity, and stability of heterogeneous catalysts in selective oxidation reactions by exploiting the synergistic interactions among multiple metal species. Each metal's presence in the mixed-metal oxide has advantages. For instance, iron improves the rate of reaction in chemical processes. Iron species are widely recognized as redox-active centers capable of activating hydrogen peroxide through reversible Fe^{3+}/Fe^{2+} redox cycling. This property facilitates the generation of reactive oxygen species, making iron-based catalysts highly attractive for selective oxidation reactions [26,27]. Additionally, copper oxide exhibits excellent redox properties and can promote electron-transfer processes during catalytic oxidation. The incorporation of copper into mixed-metal oxide systems has been reported to improve catalytic activity, enhance reaction kinetics, and increase

product selectivity through synergistic interactions with other transition metals. Since copper nanoparticles belong to the same group as noble metals like gold and silver, they make a perfect substitution, copper increases catalytic activity with consistent morphology. Zirconium oxide is widely employed as a catalyst support owing to its remarkable thermal stability, chemical resistance, and tunable acid–base properties. In mixed-metal oxide catalysts, zirconia can improve the dispersion of active metal species, enhance structural stability, and contribute to the formation of highly accessible catalytic sites [28]. The integration of Fe, Cu, and Zr into a mixed-metal oxide framework is expected to generate a synergistic catalytic system in which iron provides redox-active centers, copper facilitates electron transfer, and zirconia stabilizes and disperses the active species [29].

Single-metal oxides such as Fe_2O_3, CuO, and ZrO_2 provide distinct catalytic functionalities; however, their individual physicochemical characteristics may limit the simultaneous availability of complementary redox and surface properties. The combination of two metal oxides can overcome some of these limitations by introducing interactions between different metal centers. For instance, incorporation of Zr into Fe-containing oxides has been reported to substantially modify the particle size, surface area, dispersion, and physicochemical properties of Fe species compared with Fe_2O_3 alone. In one study, the formation of Fe–Zr mixed oxides reduced the particle size markedly relative to pure Fe_2O_3, while increasing the Zr content resulted in a significant increase in specific surface area, demonstrating the important role of metal–oxide interactions in tailoring the properties of the parent oxide[30]. Nevertheless, binary systems may still provide a relatively limited range of active environments. The incorporation of a third metal can introduce additional complementary functions and generate multiple interfacial sites. For example, Ce–Fe–Zr ternary oxides have been reported to generate synergistic dual active sites, where Fe species were associated with reactant activation while neighboring oxygen vacancies facilitated oxygen transfer, leading to enhanced catalytic performance [31]. Similarly, systematic studies of ternary CeO_2–ZrO_2–MnO_x catalysts have demonstrated that the coexistence of highly dispersed transition-metal oxide species and oxide–oxide interfaces can produce synergistic effects that are not simply attributable to the individual components [32]. Therefore, the

transition from single to binary and ultimately ternary-metal oxides provides an opportunity to engineer a greater diversity of redox centers, surface defects, and interfacial environments. In this context, combining Fe, Cu, and Zr is expected to provide complementary redox and structural functions, potentially creating cooperative Fe–Cu and Fe–Zr environments that can enhance oxidant activation and catalytic oxidation performance compared with the corresponding single or binary metal oxide systems.

In the selective oxidation of benzyl alcohol, the development of multicomponent oxide catalysts is particularly attractive because efficient benzaldehyde formation requires not only activation of the alcohol and oxidant, but also control over subsequent over-oxidation pathways. Single-metal Fe-based oxides can provide redox-active sites for H_2O_2-mediated oxidation; however, incorporation of a second redox-active metal can introduce complementary adsorption and electron-transfer functionalities. In this regard, $CuFe_2O_4$ has been reported as an efficient mixed-metal oxide for the selective oxidation of benzyl alcohol with H_2O_2, affording 66.95% conversion with 96.07% selectivity toward benzaldehyde, while binary Cu–Fe oxides have also demonstrated highly selective benzyl alcohol oxidation through complementary Cu and Fe active sites [33]. The incorporation of a third component such as Zr can further modify the structural, electronic and surface properties of the oxide matrix and generate additional oxide–oxide interfacial environments, as demonstrated for Zr-containing mixed oxides employed in benzyl alcohol oxidation [34]. Therefore, a Fe–Cu–Zr oxide architecture may provide a combination of Fe- and Cu-based redox centers together with Zr-modified interfacial environments, potentially facilitating H_2O_2 activation while maintaining high selectivity toward benzaldehyde.

The excellent catalytic performance of the Fe–Zr–Cu mixed-metal oxide catalyst can be attributed to the combined effects of its architecture and the synergistic interactions among the metal components. The optimized nanostructure promoted efficient dispersion of active species, improved accessibility of active sites, facilitated mass transport, and enhanced structural stability, ultimately leading to high catalytic activity, selectivity, and durability [28,35].

The selection of Fe, Cu, and Zr for the preparation of the ternary oxide catalyst was based on the complementary catalytic properties of these metal species. Fe was selected owing to its reversible Fe^{2+}/Fe^{3+} redox behavior and its ability to activate H_2O_2 through Fenton-like pathways, which can generate reactive oxygen species for alcohol oxidation. Previous studies have demonstrated the effectiveness of Fe-based oxides for the selective oxidation of benzyl alcohol to benzaldehyde using H_2O_2 [36,37]. Cu was incorporated because Cu-containing oxides possess redox-active Cu^{+}/Cu^{2+} centers and can participate in benzyl alcohol and H_2O_2 activation [38,39]. In contrast, Zr was introduced primarily as a structural and surface-property promoter, since Zr-containing oxide environments can modify Lewis acidity and the local environment of neighboring active sites, potentially enhancing substrate activation and benzaldehyde selectivity [40,41]. Therefore, the combination of Fe, Cu, and Zr was expected to provide complementary redox and surface functions, creating a synergistic catalytic environment for the H_2O_2-assisted selective oxidation of benzyl alcohol to benzaldehyde.

Furthermore, the fluoride-free synthesis not only simplifies the preparation procedure but also offers a greener and more scalable approach for the fabrication of Fe–Zr–Cu mixed oxide catalysts. Therefore, the rational combination of Fe, Cu, and Zr within a mixed-metal oxide framework is expected to generate a synergistic catalytic system by integrating the unique physicochemical properties of each metal component. Moreover, the rational design of a dispersed Fe–Zr–Cu mixed-metal oxide nanocatalyst is expected to combine the synergistic effects of the three metals with the structural advantages of a nanostructure, providing an efficient catalytic system for the selective oxidation of benzylic alcohols to aldehydes. The synthesized catalyst was characterized by XRD, SEM, EDS, and elemental mapping techniques, and its catalytic performance was evaluated in the oxidation of aromatic alcohols. The developed catalyst exhibited high catalytic activity and selectivity using hydrogen peroxide as a green oxidant, demonstrating the potential of this inexpensive mixed-metal oxide system for sustainable heterogeneous oxidation processes.

2. Materials and Methods

2.1. Materials Section

Energy-dispersive X-ray spectroscopy (EDS) and elemental mapping were employed to characterize the chemical composition and distribution of the constituent elements throughout the Fe–Zr–Cu oxide catalyst.

The catalyst was examined using a Zeiss 'Ultra plus's scanning electron microscope (SEM). An EQUINOX 3000 Advance X-ray diffraction (XRD) examined the powder. Also, the synthesis grade of solvents and chemicals was bought from Sigma-Aldrich and Merck.

2.2. Catalysis Preparation

A modified hydrothermal method, inspired by previously reported hydrothermal synthesis of ternary metal oxides, was employed for the preparation of the Fe–Zr–Cu oxide catalyst [42]. The precursors of the metals in the proper quantities, $FeCl_3.6H_2O$ (1 mmol, 0.270g), $ZrCl_4$ (1mmol, 0.233g), $Cu(NO_3)_2.3H_2O$ (1 mmol, 0.25g), and urea (15 mmol) were dissolved at room temperature in distilled water (70 mL). The solution was then transferred into an autoclave and maintained at 100 °C for 24 h. After cooling the autoclave to room temperature, the resulting precipitate was washed with water and ethanol and dried for 12 hours. The resulting material was then calcinated at 350 ° C to give the mixed metallic nanocatalyst .

2.3. Catalyst Testing for Benzylic Alcohols

Catalytic oxidation of alcohols to corresponding aldehydes, was investigated at 80 ° C using a catalyst (10 mg), 30 wt. % aqueous H_2O_2 (0.023 ml, 0.75 mmol) as oxidant, and benzylic alcohol (0.5 mmol) in acetonitrile (5 mL). The reactions were achieved to get the optimal point in different solvents, temperatures, and the molar ratios of substrate/oxidant. We were performed the oxidation reactions of benzylic alcohols in reflux conditions using thin-layer chromatography (TLC (EtOAc/*n*-

hexane)) monitoring. Finally, the catalysis was filtered, washed with hot acetone, and dried in a vacuum desiccator to reuse and test the recycling capability. Conversion efficiencies were measured by gas chromatography (GC) analysis.

3. Results and Discussion

The catalytic performance of Fe–Zr–Cu oxide in the oxidation of benzylic alcohols was investigated in the following section.

3.1. Catalyst Characterization

Powder X-ray diffraction (XRD) analysis was conducted to identify the crystalline phases present in the prepared mixed-metal oxide. The powder XRD patterns (Fig. 1) displays the various metal oxide phases in the prepared Fe-Zr-Cu oxide (High Score plus version 3.0.5 software).

The XRD pattern of the Fe–Zr–Cu mixed metal oxide catalyst revealed the coexistence of crystalline α-Fe_2O_3, together with weakly crystalline $CuFe_2O_4$ and $CuZrO_3$-related phases. The diffraction peaks observed at 2θ = 24.19°, 33.2°, 35.64°, 40.89°, 49.39°, 54.09°, 57.59°, 62.49°, and 64.0° are in good agreement with the characteristic reflections of α-Fe_2O_3 (hematite), which can be indexed to the (012), (104), (110), (113), (024), (116), (018), (214), and (300) crystal planes, respectively, according to JCPDS Card No. 33-0664. In addition, the reflections at 2θ = 35.64°, 57.59°, and 62.49° can be associated with the (311), (511), and (440) crystal planes of spinel $CuFe_2O_4$, respectively, in accordance with JCPDS Card No. 25-0283. The relatively weak intensity of these reflections suggests that $CuFe_2O_4$ is present as a weakly crystalline and/or highly dispersed phase. Furthermore, the reflections at 2θ = 24.19°, 40.89°, 49.39°, and 54.09° show correspondence with the (012), (023), (040), and (322) crystal planes of $CuZrO_3$, respectively, based on ICSD/JCPDS reference No. 00-043-0953. Considering the weak intensity of these reflections and their overlap with the intense reflections of α-Fe_2O_3, the $CuZrO_3$ phase is considered to be weakly crystalline and/or

highly dispersed within the mixed metal oxide matrix. Overall, the XRD results indicate that α-Fe_2O_3 is the dominant well-crystallized phase, while $CuFe_2O_4$ and $CuZrO_3$ are present as weakly crystalline secondary phases.

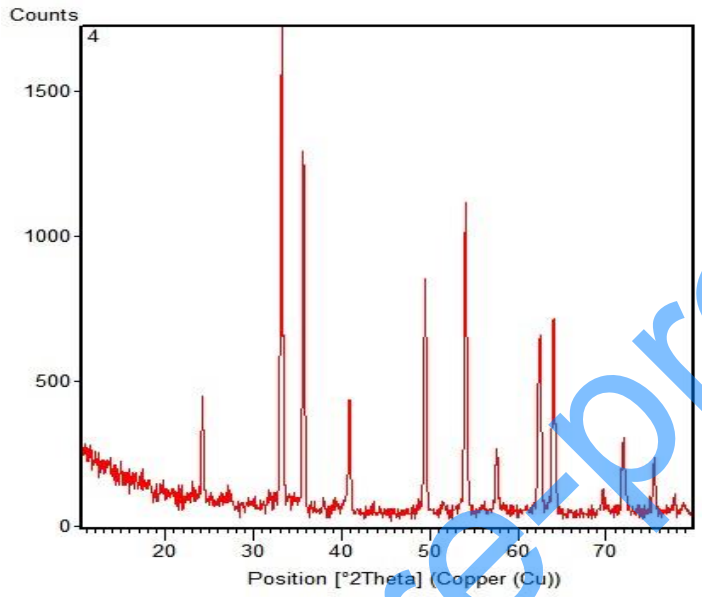


Fig. 1. X-ray diffraction (XRD) pattern of the Fe-Zr-Cu nanocatalyst.

FESEM imaging at higher magnification was performed to examine the morphology and particle size of the Fe–Zr–Cu oxide catalyst (Fig. 2). Image (a) 2 µm and Image (b) in 1 µm in size show two different kinds of Cauliflower-like structures. It has been indicated that irregular shapes with lighter colors have higher masses. The synthesized Fe–Zr–Cu mixed oxide exhibits a cauliflower-like hierarchical morphology composed of densely packed nanosized particles, as shown in Fig. (c) and (d). The cauliflower-like aggregates have characteristic dimensions of approximately 200 nm while the primary nanosized particles constituting these aggregates are estimated to be around 20 nm in diameter. Thus, the catalyst can be described as a hierarchical nanostructure in which nanosized primary particles are assembled into larger cauliflower-like aggregates.

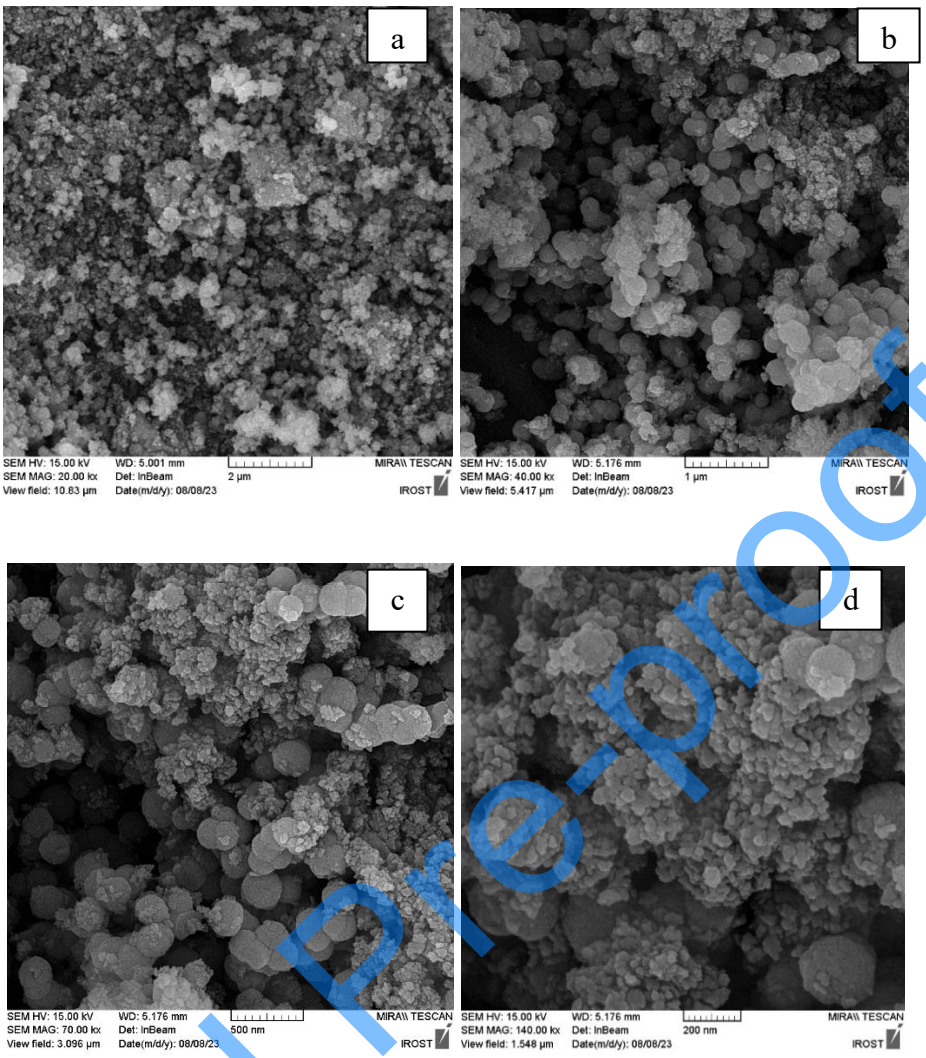


Fig. 2. (a,b) Low-magnification and (c,d) high-magnification SEM images of the Fe-Zr-Cu nanocatalyst.

Additionally, EDS analysis provided additional evidence for the image's dispersion. The consequences of the EDS microanalysis were within the predicted ranges (Fig. 3, Table 1). Uniformities of Iron, Zirconium, and Copper in the crystals were confirmed by elemental map. Quantitative findings and elemental mapping were agreed (Fig. 4).

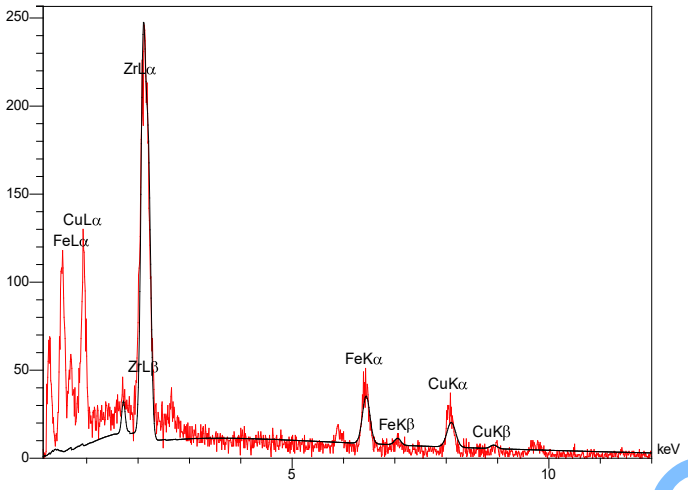


Fig. 3. EDS of Fe-Zr-Cu nanocatalyst.

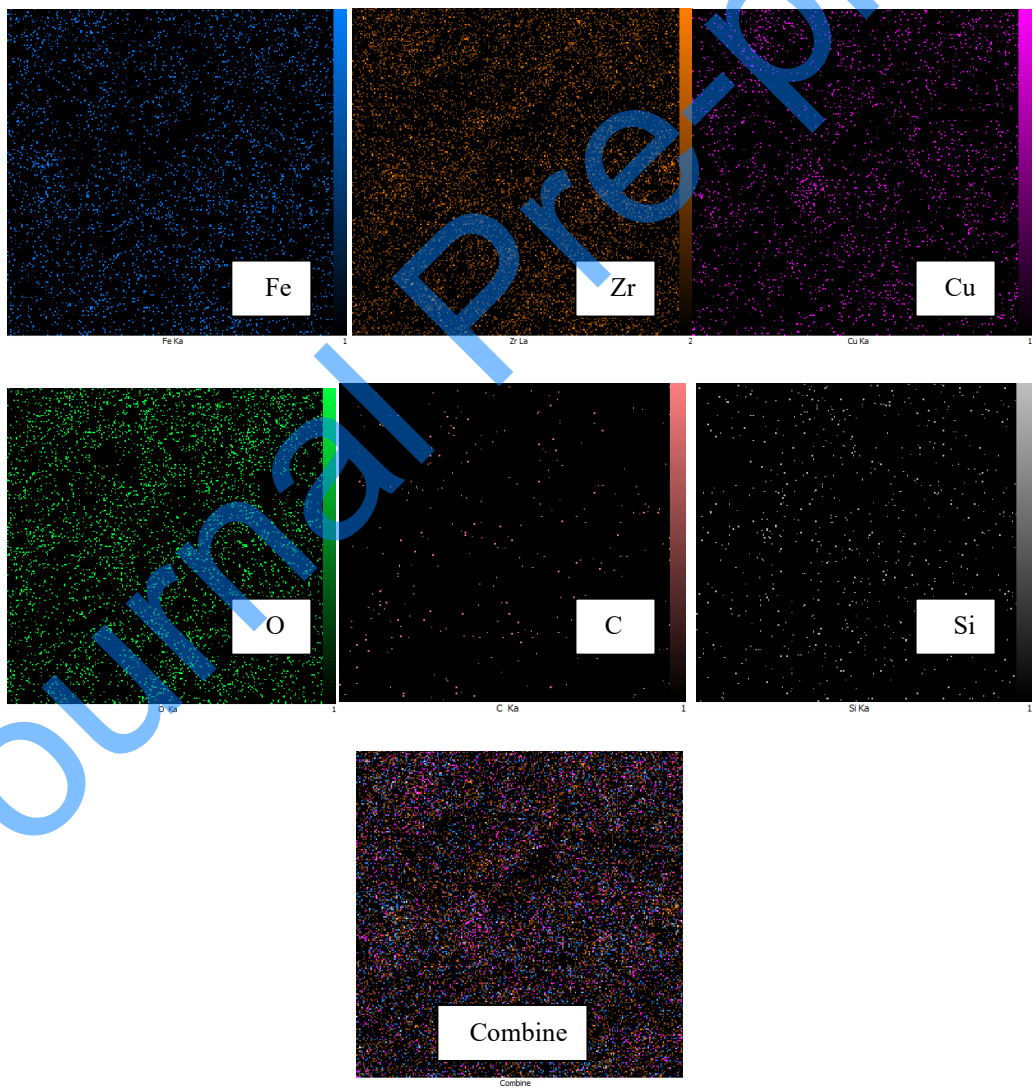


Fig. 4. Elemental mapping images of Fe-Zr-Cu nanocatalyst

Table 1. EDS quantitative results.

Elt	Line	Int	Error	K	Kr	W%	A%	ZAF	Formula	Ox%	Pk/Bg	Class	LConf	HConf	Cat#
Fe	Ka	15.0	0.4770	0.2363	0.2191	20.35	26.74	1.0765		0.00	5.22	A	18.51	22.19	0.00
Cu	Ka	9.0	0.6407	0.2885	0.2674	26.22	30.28	1.0199		0.00	4.21	A	23.17	29.28	0.00
Zr	La	75.1	5.6155	0.4751	0.4404	53.43	42.98	0.8243		0.00	16.20	A	51.27	55.58	0.00
				1.0000	0.9269	100.00	100.00			0.00					0.00

3.2. Catalyst Evaluation

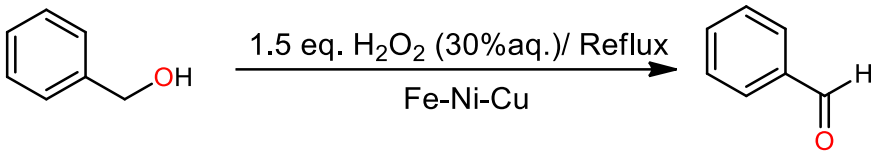
3.2.1. Optimization

We optimized oxidation reactions using Fe-Zr-Cu as the catalyst amount, considering the effects of solvent, temperature, time, and the alcohol/oxidant molar ratio.

We used 2.5, 5, 7.5, 10, and 15 mg of Fe-Zr-Cu while maintaining the other parameters unchanged to examine the function of the catalyst amount in oxidation. The volume increase in the catalyst did not affect the yield or selectivity. As a result, 10 mg of catalyst was used in all subsequent research. When the reaction was achieved without a solvent, a product of 40% was obtained (Table 2, entry 1). Acetonitrile, which ultimately dissolved the alcohol substrate and thus facilitated oxidation, produced the desired benzaldehyde with a yield of 80%, yielding the catalyst's best performance (Table 2, entry 10).

Additionally, we studied the importance of the benzylic alcohol/oxidant molar ratio for oxidation of alcohols to benzaldehyde. The 1.0:1.0, 1.0:2.0, and 1.0:3.0 molar ratios produced 40%, 60%, and 79% alcohol conversion after 6 hours at reflux conditions, respectively. The chemoselectivity towards the desired aldehydes was unaffected, though. We chose for more in-depth analysis, a molar ratio of 1:3.0 benzylic alcohol /H_2O_2.

Table 2. Solvent optimization in oxidation of benzyl alcohol.



Entry	Solvent	Time (h)	Yield (%)
1	No Solvent	4	40
2	n-hexane	5	42
3	CH_2Cl_2	6	35
4	$CHCl_3$	4	61
5	Ethyl acetate	5	63
6	CH_3OH	6	31
7	EtOH	6	40
8	Isopropanol	5	41
9	CH_2Cl_2:CH_3OH (1:1)	6	62
10	CH_3CN	8	80
11	CH_3CN:H_2O (1:1)	4	70
12	CH_3CN: H_2O (2:1)	5	75
13	H_2O	6	38
14	EtOH/H_2O	6	57
15	Acetone	4	62

Yields indicate the isolated yield of benzaldehyde

Reaction conditions: 10 mg Catalyst, 0.5 mmol benzyl alcohol, 0.75 mmol 30% H_2O_2, 5 mL Solvent at reflux conditions.

We examined the impact of the reaction temperature on benzylic alcohol. Thus, after carrying out the reaction at either 25, 50, or 80°C for 6 hours, the yields were 30, 50, and 79.5%, respectively. As a result, the reaction's temperature was set at 80 °C for the standard protocol (Table 3).

Table 3. Effect of reaction temperature during oxidation of benzyl alcohol over the Fe-Zr-Cu catalyst

Entry	Temperature (ºC)	Yield (%)
1	r.t	30
2	50	50
3	80	80

Reaction conditions: Benzyl alcohol = 0.5 mmol, H_2O_2 =0.75 mmol, catalyst = 10 mg, solvent = CH_3CN (5 mL), time = 8 h.

3.2.2. The Effect of Fe-Zr-Cu Oxide Catalyst for Benzylic Alcohols Oxidation

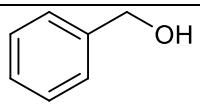
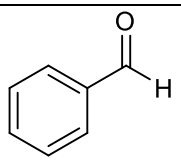
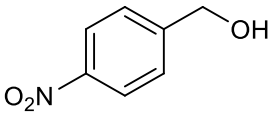
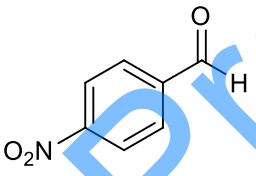
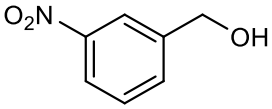
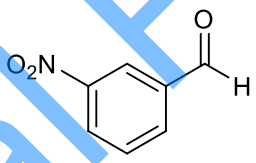
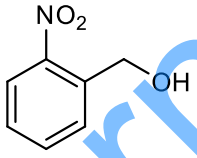
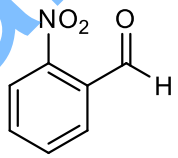
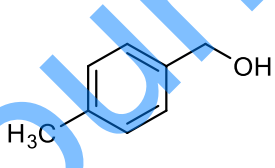
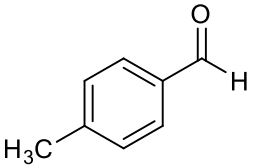
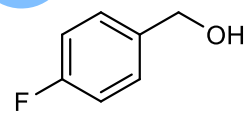
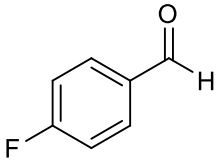
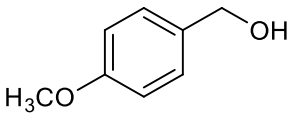
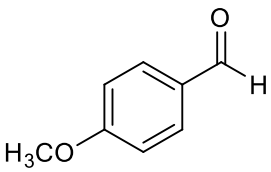
By creating the optimal conditions for the reaction, the use of the new category of metal oxide catalysts for oxidation of benzyl alcohols was investigated. The nature of the mixed-metal oxide played a role in the conversion that occurred in the presence of the catalysts.

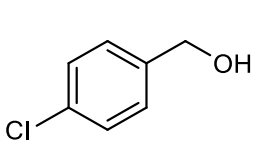
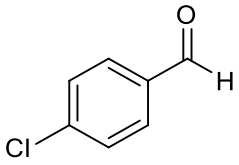
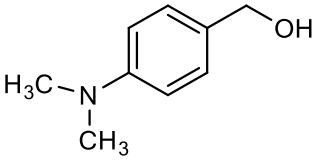
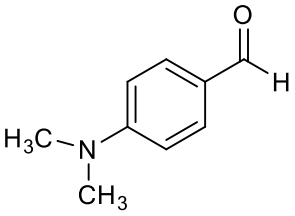
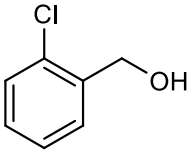
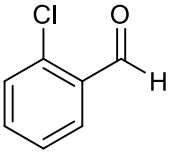
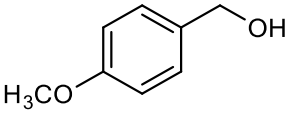
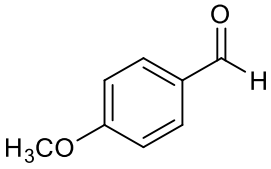
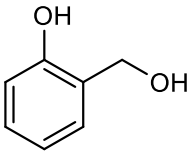
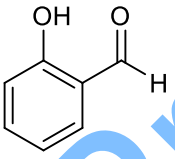
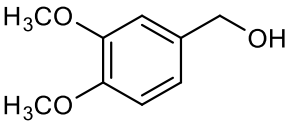
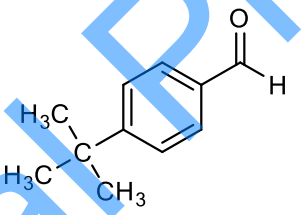
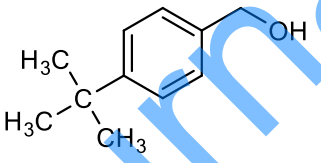
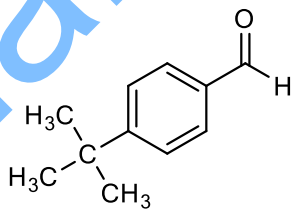
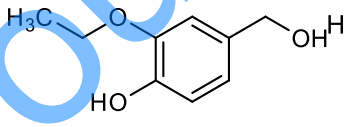
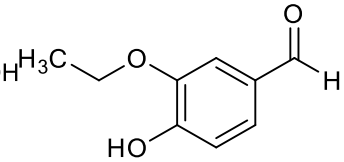
Excellent metal dispersion can enhance the effect of the catalysts along with smaller particle sizes. Zr and Cu oxides typically exhibit higher Bronsted acidity compared to Fe oxide [43,44]. The mixed-metal oxide catalyst comprises an equal distribution of Lewis basic and Bronsted acidic sites because iron has a high Lewis basic nature. Due to the catalyst's Bronsted acidic nature, the oxidant(H_2O_2), is adsorbed on its surface.

Different kinds of benzylic alcohols to the corresponding benzaldehydes with electron-donor and electron-withdrawing substitutes were used as substrates to examine the generality of the catalyst. The approach revealed extensive applicability, yielding the appropriate aldehydes in excellent quantities. Halogen atoms, ester, methoxy, and nitro groups were among the functional groups that were well tolerated. Benzyl alcohols that are electron-rich and those that are electron-poor both respond well to the reaction. These studies are presented in Table 4. Benzylic alcohols were oxidized to the corresponding aldehydes with reasonable to excellent conversion percentages (65%–80%) within a suitable time. Observations revealed that electronic and steric effects significantly influence the rate of oxidation reaction. According to entries 11-14, benzylic alcohols with electron-donating groups like -OH, -OR, and -N $(CH3)_2$ on the phenyl ring were more reactive than benzylic alcohols and oxidized more quickly. The increasing steric hindrance appears to cause this long reaction time. There was no noticeable difference in the conversion amount and reaction time in the presence of the weak electron donor group, -CH3 (Entry 5). According to the findings, the presence of electron-withdrawing groups, such as -F, -NO2, and -Cl on the aromatic ring, caused the substrate to become inactive and the reaction to go on longer (Entries 2,3,4,6,8,10). Also, Fig.IR2 in the supplementary file demonstrates the FTIR spectra of 3-Ethoxy-4-hydroxybenzaldehyde (Entry 15). As can be seen:

3362 (O-H stretching of benzene ring), 2988 (C-H stretching of alkene), 2935 (C-H stretching of aldehyde), 2891 (C-H stretching of alkane), 1682 (C=O of aldehyde), 1580 (C=C stretching), 1510 (C-H of aldehyde), 1438 (O-H of benzene ring), 1279 (C-O). Fig. NMR1 in the supplementary file shows the ^{1}HNMR ($CDCl_3$) spectra data of 3-Ethoxy-4-hydroxybenzaldehyde (Entry 15):1.5 (t, 3H), 4.2 (q, 2H), 6.5 (brs, 1H), 7.1 (d, 1H), 7.3 (m, 2H), 9.8 (s, 1H).

Table 4. Oxidation of different benzylic alcohols to benzaldehydes using Fe-Zr-Cu.

Entry	Alcohols	Product	Yield (%)	Time (h)	Mp/Bp (C)	Ref. Found-Lit.
1			80	8	175-177	177 [45]
2			70	8	104	104-106 [45]
3			73	8	59	58-59 [45]
4			72	8	43-44	42-44 [45]
5			74	8	58	58 [45]
6			70	8	180	179-180 [45]
7			74	8	245-246	246 [45]

8			78	8	46-47	47 [45]
9			65	8	73-75	73-75 [46]
10			77	8	210-212	210-215 [46]
11			72	8	245-246	246-248 [46]
12			73	8	196	196-198 [46]
13			76	8	43-44	42-44 [46]
14			70	8	129	128-130 [46]
15			70	8	75-76	74-76 [46]

Reaction conditions: benzyl alcohol (0.5 mmol), 0.75 mmol 30% H_2O_2, 5 mL acetonitrile, Fe-Zr-Cu (10 mg).

3.2.3. Recyclability of Fe-Zr-Cu

The ability to easily filter and separate the heterogeneous catalyst from the reaction medium to reuse it for other reactions is one of the main expectations for this type of catalyst. It should also be

recyclable and stable after the reaction. As a result, it was determined whether the Fe-Zr-Cu catalyst could be reused in these oxidation reactions. Without losing much of its activity, the catalyst Fe-Zr-Cu nano-metal oxide was used five more times to oxidize benzyl alcohol. After each reaction, the catalyst was removed by hot filtration, cleaned with new ethanol and water, and dried at 120 °C for three hours before being used for the following reaction (Fig. 5).

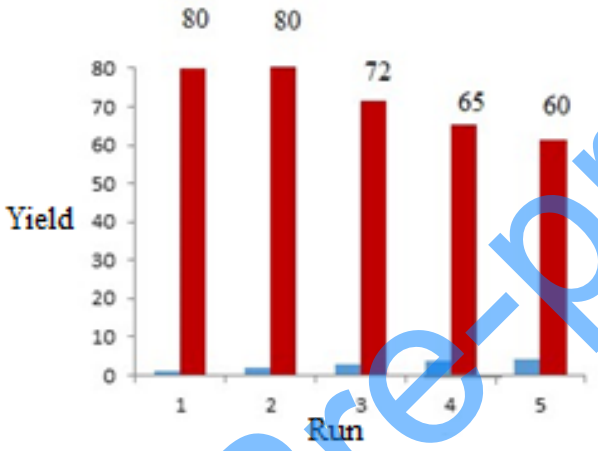


Fig. 5. The recycling of the heterogeneous catalyst (Fe-Zr-Cu) for the selective oxidation of benzyl alcohol to benzaldehyde with 30% H_2O_2.

To further investigate the morphological stability of the catalyst, SEM analysis was performed after five consecutive catalytic cycles. As shown in Fig. 6, at scale bars of 200 nm, the overall polyhedral/faceted morphology of the catalyst was largely preserved after repeated use, with no pronounced morphological alteration compared with the fresh catalyst. This observation, together with the negligible leaching of Fe, Cu, and Zr detected by AAS (0.005, 0.002, and 0.004 $mg.L^{-1}$, respectively), supports the good morphological and operational stability of the catalyst under the reaction conditions. The very low concentrations of the metal species in the reaction solution further indicate that significant dissolution of the catalyst did not occur during the catalytic process.

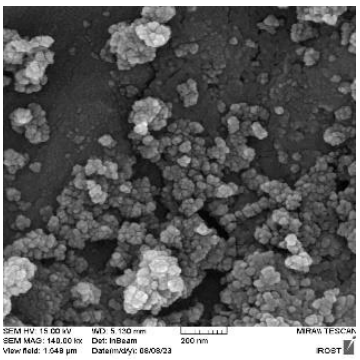


Fig. 6. SEM images of the Fe–Zr–Cu oxide catalyst after five consecutive catalytic cycles at scale bars of 200 nm.

3.2.4. Comparison of the Catalytic Efficiency of Fe-Zr-Cu with Other Catalysts in the Oxidation Reactions

The catalytic performance of the Fe–Zr–Cu mixed oxide was compared with those of recently reported metal-oxide-based catalysts for the selective oxidation of benzyl alcohol to benzaldehyde using H_2O_2. The enhanced performance may be associated with the synergistic interaction among Fe, Cu, and Zr oxide species, which can provide complementary redox properties and facilitate H_2O_2 activation while favoring the selective oxidation pathway toward benzaldehyde (Tables 5).

Table 5. Comparing of the present procedure with literature for the preparation of benzaldehyde in the presence of 30% H_2O_2

Entry	Catalyst	Reaction conditions	Catalyst loading	Time (h)	BZ-OH Conversion (%)	BZ-CHO Selectivity (%)	Yield (%)	TON & TOF	Ref.
1	Mn (Me_2EBC) Cl_2	H_2O_2, CH_3CN/ H_2O, 30 °C	0.5 %mol	18	98	99	77	NR	[47]
2	Fe_3O_4 microspheres	H_2O_2, H_2O, 60°C	2 g/l	4	35	97	34	NR	[48]
3	Fe/MCM-41	H_2O_2, CH_3CN, 70°C	0.1g/l	7	55	90	48	NR	[49]
4	$CuFe_2O_4$	H_2O_2, 90°C	4 g/l	4	66.95	96.07	64.32	NR	[50]
5	CuO_x/SBA-15	H_2O_2, 80°C	8 g/l	0.5	73	54	39.4	NR	[51]
6	$CuCo_2O_4$/SBA-15	H_2O_2, 80°C	8 g/l	3	78.13	71.7	56	NR	[52]
7	$CuMnO_x$	H_2O_2, 80°C	8 g/l	7	50<	100	50<	NR	[39]
8	Fe-Zr-Cu	H_2O_2, CH3CN, 80°C	0.01 g/l	8	80	99.6	80	2.94 & 0.367 h^{-1}	This work

NR: Not reported.

3.2.5. Reproducibility and Statistical Analysis of Catalytic Performance

The optimization experiments were performed in triplicate, and the results are presented as mean values with standard deviations (mean ± SD). Error bars represent the standard deviation of the repeated experiments.

The effects of the main reaction parameters, including catalyst loading, H_2O_2 amount, reaction temperature, and reaction time, were investigated to determine the optimum conditions for the selective oxidation of benzyl alcohol to benzaldehyde over the Fe–Zr–Cu oxide catalyst. Under the optimized reaction conditions, the experiment was independently repeated three times to evaluate the reproducibility of the catalytic performance. Benzaldehyde yields of 78%, 80%, and 81% were obtained, giving an average yield of 79.7 ± 1.5% (n = 3). The relatively low standard deviation demonstrates good reproducibility of the catalytic results. Accordingly, the optimization data are reported as mean values with standard deviations where replicate measurements were performed. The reported yield of 80% in the manuscript was rounded from the experimentally obtained average value of 79.7 ± 1.5% based on three independent experiments (n = 3).

3.2.6. Evaluation of Catalytic Activity using TON and TOF

To further assess the intrinsic catalytic efficiency of the prepared Fe–Zr–Cu oxide catalyst, the apparent turnover number (TON) and turnover frequency (TOF) were calculated under the optimized reaction conditions. In the catalytic reaction, 0.5 mmol of benzyl alcohol was treated with 10 mg of catalyst for 8 h, affording 80% conversion and 99.6% selectivity toward benzaldehyde, corresponding to a yield of 79.7%.

According to the EDS analysis, the catalyst contained 20.35 wt.% Fe, 26.22 wt% Cu, and 53.43 wt% Zr. Thus, 10 mg of catalyst contained 2.035 mg Fe (0.03644 mmol), 2.622 mg Cu (0.04126 mmol), and 5.343 mg Zr (0.05856 mmol), corresponding to a total metal content of 0.1363 mmol. Since 0.400 mmol of benzyl alcohol was converted at 80% conversion, the apparent TON was

calculated as 2.94. The corresponding apparent TOF, calculated from the 8 h reaction time, was 0.367 h^{-1}. The obtained TON and TOF values further support the effective catalytic activity of the Fe–Zr–Cu oxide catalyst toward the selective oxidation of benzyl alcohol to benzaldehyde.

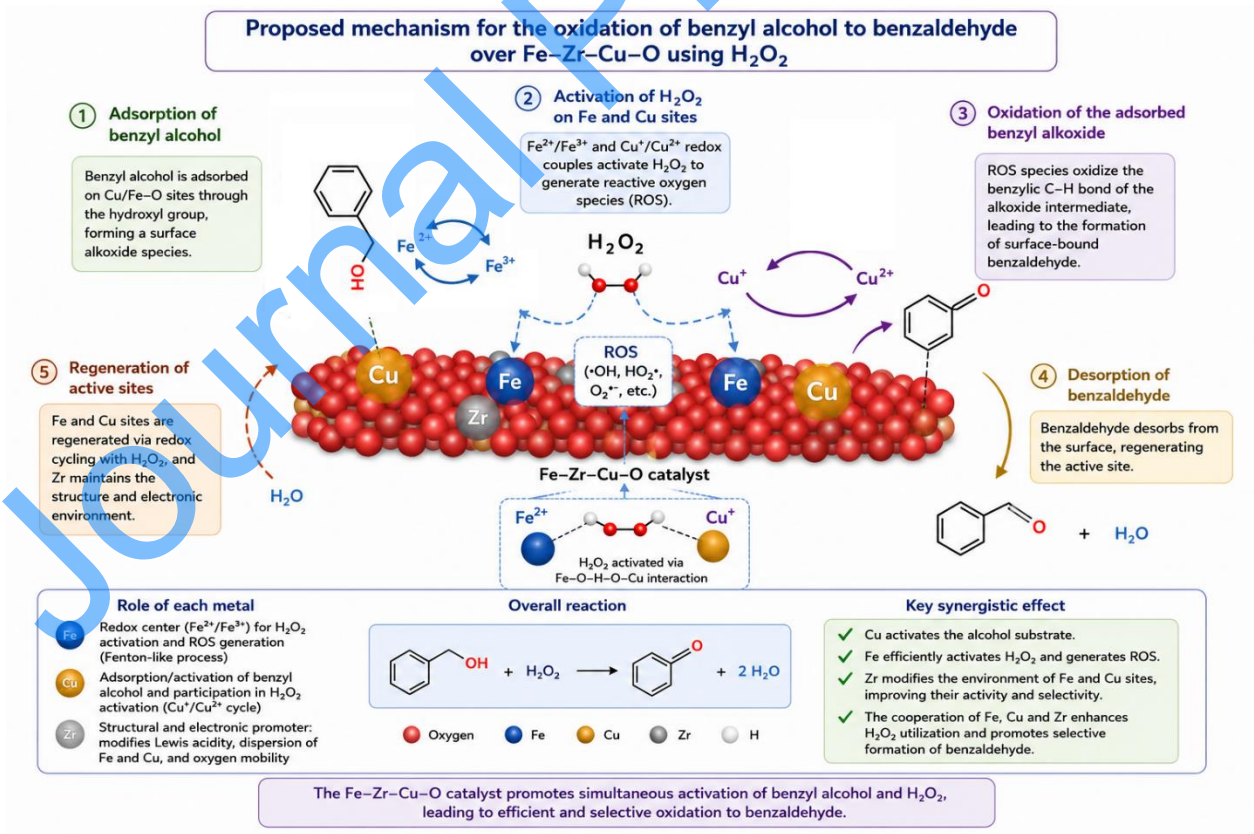
3.2.7. Catalyst Stability, Leaching and Hot Filtration Tests

To investigate the stability and heterogeneous nature of the Fe–Zr–Cu oxide catalyst under the oxidative reaction conditions, a leaching test was performed using the standard catalytic reaction conditions. After completion of the reaction, the solid catalyst was separated from the reaction mixture by centrifugation followed by filtration. The resulting liquid phase was collected and analyzed by atomic absorption spectroscopy (AAS) to determine the concentrations of Fe, Cu, and Zr species released into the solution. The extent of metal leaching was calculated from the amount of each metal detected in the liquid phase relative to its initial amount in the catalyst. The combination of the AAS leaching analysis and hot filtration test provides complementary evidence for evaluating catalyst heterogeneity. Nevertheless, hot filtration alone cannot completely exclude transient leaching followed by redeposition; therefore, the AAS results provide an important independent assessment of the extent of metal dissolution [53]. AAS analysis revealed negligible leaching of the metallic species into the reaction medium. The leaching percentages were calculated to be only 0.00123%, 0.00038%, and 0.00037% for Fe, Cu, and Zr, respectively. These results demonstrate the high resistance of the Fe–Zr–Cu oxide catalyst toward metal dissolution under the employed oxidative reaction conditions and strongly support the predominantly heterogeneous nature of the catalytic process.

3.3. Proposed Reaction Mechanism for the Oxidation of benzyl Alcohol over Fe–Zr–Cu Oxide using H_2O_2

The oxidation of benzyl alcohol over the Fe–Zr–Cu oxide in the presence of H_2O_2 is proposed to proceed through a cooperative redox mechanism. Initially, benzyl alcohol is adsorbed on Cu/Fe–O active sites and converted into a surface benzyl alkoxide intermediate. Meanwhile, the Fe^{2+}/Fe^{3+} and

Cu^{+}/Cu^{2+} redox couples can facilitate H_2O_2 activation and the generation of reactive oxygen species (ROS), which promote benzylic C–H oxidation and subsequent formation of benzaldehyde. Fenton-like activation of H_2O_2 by iron oxide has been reported to generate reactive oxygen species and promote the selective oxidation of benzyl alcohol to benzaldehyde [36,54,55]. In the ternary oxide, Zr^{4+} is proposed to act mainly as a structural and electronic promoter rather than a redox center, modifying the local coordination, Lewis's acidity, and surface environment of Fe and Cu sites. Thus, the synergistic interaction of Cu for benzyl alcohol activation, Fe for H_2O_2-mediated redox processes, and Zr for surface and structural modulation may facilitate the cooperative activation of benzyl alcohol and H_2O_2, enhancing the selective formation of benzaldehyde [56]. Based on the experimental results obtained in this study and previously reported literature, a plausible reaction pathway for the oxidation of benzyl alcohol over the Fe–Zr–Cu oxide catalyst is proposed. We propose a graphical mechanism with Fe-Zr-Cu oxide catalyst in Scheme 1.



Scheme 1. A proposed mechanism for benzyl alcohol oxidation over Fe-Zr-Cu oxide catalyst

4. Conclusion

A novel heterogeneous Fe–Zr–Cu mixed oxide nanocatalyst was successfully synthesized via a hydrothermal method using commercially available precursors. The synthesized catalyst was characterized by XRD, SEM, EDS, and elemental mapping analyses. For the first time, the catalytic performance of this Fe–Zr–Cu oxide was investigated for the selective oxidation of benzylic alcohols. In the presence of the Fe–Zr–Cu nanocatalyst and hydrogen peroxide as a green oxidant, a variety of benzylic alcohols were efficiently converted into the corresponding aldehydes with high yields and excellent selectivity. The superior catalytic performance is likely associated with the synergistic interactions among the Fe, Cu, and Zr components, together with the homogeneous dispersion of the active species within the mixed oxide framework. The optimal reaction conditions were established using benzyl alcohol as the model substrate, including 20 mol% catalyst (10 mg), a substrate-to-H_2O_2 molar ratio of 1:1.5, reflux at 80 °C, and acetonitrile as the reaction solvent. Furthermore, comparison with previously reported catalysts demonstrated that the catalytic performance of the Fe–Zr–Cu mixed oxide nanocatalyst is competitive, highlighting its potential as an efficient, low-cost, and environmentally friendly heterogeneous catalyst for selective alcohol oxidation.

Compared with single and binary metal oxides, ternary mixed-metal oxides can offer a greater diversity of chemically distinct active sites and interfacial environments, arising from the synergistic interactions among their constituent metal species. Furthermore, the incorporation of a third metal can generate additional cooperative sites and modify the electronic and oxygen-transfer properties of the oxide matrix. Therefore, the incorporation of Fe, Cu, and Zr into a multiple oxide architecture is expected to provide complementary redox and structural functions, while the formation of Fe–Cu- and Cu–Zr-containing phases may create interfacial sites with physicochemical properties that are not readily accessible in the corresponding single- or binary-metal oxides. In the present Fe–Zr–Cu oxide catalyst, the coexistence of α-Fe_2O_3 as the major phase with minor $CuFe_2O_4$ and Fe_2 $CuZrO_5$

phases may provide multiple redox and interfacial environments, potentially offering synergistic catalytic functions beyond those of the individual oxide components.

Conflict of 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.

Acknowledgments

This project was supported by the Iranian Research Organization for Science and Technology (IROST).

References

[1] H. Nur, S. Ikeda, B. Ohtani, Phase-Boundary Catalysis of Alkene Epoxidation with Aqueous Hydrogen Peroxide Using Amphiphilic Zeolite Particles Loaded with Titanium Oxide, J. Catal. 204 (2001) 402–408. https://doi.org/10.1006/JCAT.2001.3386

[2] A. Kate, L.K. Sahu, J. Pandey, M. Mishra, P.K. Sharma, Green catalysis for chemical transformation: The need for the sustainable development, Curr. Res. Green Sustain. Chem. 5 (2022) 100248. https://doi.org/10.1016/J.CRGSC.2021.100248

[3] M.E. Ali, M.M. Rahman, S.M. Sarkar, S.B.A. Hamid, Heterogeneous metal catalysts for oxidation reactions, J. Nanomater. 2014 (2014). https://doi.org/10.1155/2014/192038

[4] R.H. Wu, J. Wu, M.X. Yu, L.G. Zhu, Ti(Phen)$(OC_2H_5)_2Cl_2$: a highly efficient pre-catalyst for selective oxidation of organic sulfides to sulfoxides by hydrogen peroxide, RSC Adv. 7 (2017) 44259–44264. https://doi.org/10.1039/C7RA06883B

[5] X.T. Zhou, H.B. Ji, Z. Cheng, J.C. Xu, L.X. Pei, L.F. Wang, Selective oxidation of sulfides to sulfoxides catalyzed by ruthenium (III) meso-tetraphenylporphyrin chloride in the presence of

molecular oxygen, Bioorganic Med. Chem. Lett. 17 (2007) 4650–4653. https://doi.org/10.1016/j.bmcl.2007.05.073

[6] J. Rahimi, M. Azizi, M. Niksefat, M. Heidari, M. Naderi, A. Maleki, An efficient superparamagnetic PEO-based nanocatalyst for selective oxidation of sulfides to sulfoxides, Inorg. Chem. Commun. 148 (2023). https://doi.org/10.1016/j.inoche.2022.110320

[7] C. Cui, X. Zhao, X. Su, W. Gao, J. Zhan, X. Zhang, G. Li, X.L. Zhang, Y. Sang, H. Liu, Selective oxidation of benzyl alcohol using a $Ni(OH)_2$-modified CdS-MoS_2 composite photocatalyst under ambient conditions, J. Environ. Chem. Eng. 9 (2021) 106416. https://doi.org/10.1016/j.jece.2021.106416

[8] A. Hinzmann, M. Stricker, J. Busch, S. Glinski, K. Oike, H. Gröger, Selective TEMPO-Oxidation of Alcohols to Aldehydes in Alternative Organic Solvents, European J. Org. Chem. 2020 (2020) 2399–2408. https://doi.org/10.1002/EJOC.201901365

[9] R. Zhang, M. Shao, Z. Li, F. Ning, M. Wei, D.G. Evans, X. Duan, Photoelectrochemical Catalysis toward Selective Anaerobic Oxidation of Alcohols, Chem. – A Eur. J. 23 (2017) 8142–8147. https://doi.org/10.1002/CHEM.201701107

[10] N.M. JamJam, Y.H. Taufiq Yap, E.N. Muhamad, M. Izham Saiman, T.A. Saleh, Free solvent oxidation of molecular benzyl alcohol by newly synthesized AuPd/titania catalysts, Inorg. Chem. Commun. 107 (2019). https://doi.org/10.1016/j.inoche.2019.107471

[11] V. Pappula, S. Adimurthy, Nitric Acid Assisted In Situ Generation of BrOH: A Selective Catalyst for Oxidation of Benzylic Alcohols, J. Org. Inorg. Chem. 03 (2017) 1–5. https://doi.org/10.21767/2472-1123.100024

[12] I. Kani, M. Kurtça, Synthesis, structural characterization, and benzyl alcohol oxidation activity of mononuclear manganese(II) complex with 2,2'-bipyridine: $[Mn(bipy)_2(ClO_4)_2]$, Turkish J. Chem. 36 (2012) 827–840. https://doi.org/10.3906/kim-1110-4

[13] P. Gallezot, Selective oxidation with air on metal catalysts, Catal. Today 37 (1997) 405–418.

https://doi.org/10.1016/S0920-5861(97)00024-2

[14] K. George, S. Sugunan, Nickel substituted copper chromite spinels: Preparation, characterization and catalytic activity in the oxidation reaction of ethylbenzene, Catal. Commun. 9 (2008) 2149–2153. https://doi.org/10.1016/j.catcom.2008.03.040

[15] A.K. Saikia, S. Tsuboi, Chemistry of trichlorofluromethane: Synthesis of chlorofluromethyl phenyl sulfone and fluoromethyl phenyl sulfone and some of their reactions, J. Org. Chem. 66 (2001) 643–647. https://doi.org/10.1021/jo000825r

[16] J.P. Zhao, W.Y. Hernández, W.J. Zhou, Y. Yang, E.I. Vovk, M. Capron, V. Ordomsky, Selective Oxidation of Alcohols to Carbonyl Compounds over Small Size Colloidal Ru Nanoparticles, ChemCatChem 12 (2020) 238–247. https://doi.org/10.1002/CCTC.201901249

[17] R. Ciriminna, L. Albanese, F. Meneguzzo, M. Pagliaro, Hydrogen Peroxide: A Key Chemical for Today's Sustainable Development, ChemSusChem 9 (2016) 3374–3381. https://doi.org/10.1002/CSSC.201600895

[18] S. Hemmati, M. Hekmati, D. Salamat, M. Yousefi, B. Karmakar, H. Veisi, Anchoring Mn(IV) in multi pyridine modified mesoporous silica SBA-15: An efficient nanocatalyst for selective oxidation of sulfides to sulfoxides, Polyhedron 179 (2020) 114359. https://doi.org/10.1016/j.poly.2020.114359

[19] D.J. Cole-Hamilton, Homogeneous catalysis - New approaches to catalyst separation, recovery, and recycling, Science (80-.). 299 (2003) 1702–1706. https://doi.org/10.1126/science.1081881

[20] H.H. Kim, H. Lee, D. Lee, Y.J. Ko, H. Woo, J. Lee, C. Lee, A.L.T. Pham, Activation of Hydrogen Peroxide by a Titanium Oxide-Supported Iron Catalyst: Evidence for Surface Fe(IV) and Its Selectivity, Environ. Sci. Technol. 54 (2020) 15424–15432. https://doi.org/10.1021/ACS.EST.0C04262/SUPPL_FILE/ES0C04262_SI_001.PDF

[21] Y. Sun, G. Chen, S. Xi, Z.J. Xu, Catalytically Influential Features in Transition Metal Oxides,

ACS Catal. 11 (2021) 13947–13954. https://doi.org/10.1021/ACSCATAL.1C04393/ASSET/IMAGES/MEDIUM/CS1C04393_M001.GIF

[22] M.S. Chavali, M.P. Nikolova, Metal oxide nanoparticles and their applications in nanotechnology, SN Appl. Sci. 2019 16 1 (2019) 1–30. https://doi.org/10.1007/S42452-019-0592-3

[23] A. Akbari, M. Amini, A. Tarassoli, B. Eftekhari-Sis, N. Ghasemian, E. Jabbari, Transition metal oxide nanoparticles as efficient catalysts in oxidation reactions, Nano-Structures and Nano-Objects 14 (2018) 19–48. https://doi.org/10.1016/j.nanoso.2018.01.006

[24] R. Nakamura, G. Matsubayashi, H. Tsuchiya, S. Fujimoto, H. Nakajima, Formation of oxide nanotubes via oxidation of Fe, Cu and Ni nanowires and their structural stability: Difference in formation and shrinkage behavior of interior pores, Acta Mater. 57 (2009) 5046–5052. https://doi.org/10.1016/j.actamat.2009.07.006

[25] S. Hemmati, L. Mehrazin, M. Hekmati, M. Izadi, H. Veisi, Biosynthesis of CuO nanoparticles using Rosa canina fruit extract as a recyclable and heterogeneous nanocatalyst for C-N Ullmann coupling reactions, Mater. Chem. Phys. 214 (2018) 527–532. https://doi.org/10.1016/j.matchemphys.2018.04.114

[26] index@pubmed.ncbi.nlm.nih.gov, (n.d.). https://pubmed.ncbi.nlm.nih.gov/?term=Liu+J&cauthor_id=34822943

[27] H.R. Arandiyan, M. Parvari, Studies on mixed metal oxides solid solutions as heterogeneous catalysts, Brazilian J. Chem. Eng. 26 (2009) 63–74. https://doi.org/10.1590/S0104-66322009000100007

[28] M.B. Gawande, R.K. Pandey, R. V. Jayaram, Role of mixed metal oxides in catalysis science - Versatile applications in organic synthesis, Catal. Sci. Technol. 2 (2012) 1113–1125. https://doi.org/10.1039/c2cy00490a

[29] Y. Huang, Z. Duan, Research progress in Cu–ZrO_2 catalysts: a systematic review of their preparation, doping, and applications, J. Mater. Chem. A 13 (2025) 4043–4089. https://doi.org/10.1039/D4TA05742B

[30] D. Yan, J. Xin, Q. Zhao, K. Gao, X. Lu, G. Wang, S. Zhang, Fe–Zr–O catalyzed base-free aerobic oxidation of 5-HMF to 2,5-FDCA as a bio-based polyester monomer, Catal. Sci. Technol. 8 (2018) 164–175. https://doi.org/10.1039/C7CY01704A

[31] X. Tong, J. Yu, X. Sun, M. Yang, J. Zhang, L. Zhang, J. Sun, Noble-metal free Ce-Fe-Zr ternary oxides with synergistic dual active sites for accelerating NO reduction, Chem. Eng. J. 453 (2023) 139847. https://doi.org/10.1016/J.CEJ.2022.139847

[32] M. V. Grabchenko, G. V. Mamontov, M. V. Chernykh, O. V. Vodyankina, M.A. Salaev, Synergistic effect in ternary CeO_2-ZrO_2-MnO_x catalysts for CO oxidation and soot combustion, Chem. Eng. Sci. 285 (2024) 119593. https://doi.org/10.1016/J.CES.2023.119593

[33] Y. Chen, P. Tang, X. Lu, J. Ma, H. Li, H. Chen, Preparation of $CuFe_2O_4$ composite metal oxides and selective oxidation of benzyl alcohol, Ferroelectrics 609 (2023) 57–65. https://doi.org/10.1080/00150193.2023.2198952

[34] G. Bathula, S. Rana, S. Bandalla, V. Dosarapu, S. Mavurapu, A. Rajeevan V. V, B. Sharma, S.B. Jonnalagadda, M. Baithy, C.S. Vasam, The role of WOx and dopants (ZrO_2 and SiO_2) on CeO_2-based nanostructure catalysts in the selective oxidation of benzyl alcohol to benzaldehyde under ambient conditions, RSC Adv. 13 (2023) 36242–36253. https://doi.org/10.1039/D3RA06828E

[35] S. Najafishirtari, K. Friedel Ortega, M. Douthwaite, S. Pattisson, G.J. Hutchings, C.J. Bondue, K. Tschulik, D. Waffel, B. Peng, M. Deitermann, G.W. Busser, M. Muhler, M. Behrens, A Perspective on Heterogeneous Catalysts for the Selective Oxidation of Alcohols, Chem. – A Eur. J. 27 (2021) 16809–16833. https://doi.org/https://doi.org/10.1002/chem.202102868

[36] S. Xiao, C. Zhang, R. Chen, F. Chen, Selective oxidation of benzyl alcohol to benzaldehyde

with H_2O_2 in water on epichlorohydrin-modified Fe_3O_4 microspheres, New J. Chem. 39 (2015) 4924–4932. https://doi.org/10.1039/c5nj00434a

[37] W. Chen, L. Xiong, F. Chen, Solvothermal synthesis of sub-200 nm Fe_3O_4 submicrospheres with enhanced catalytic performances by using acicular goethite as solid precursor, Micro Nano Lett. 12 (2017) 711–713. https://doi.org/10.1049/MNL.2017.0206;PAGE:STRING:ARTICLE/CHAPTER

[38] P. Cruz, Y. Pérez, I. Del Hierro, M. Fajardo, Copper, copper oxide nanoparticles and copper complexes supported on mesoporous SBA-15 as catalysts in the selective oxidation of benzyl alcohol in aqueous phase, Microporous Mesoporous Mater. 220 (2016) 136–147. https://doi.org/10.1016/J.MICROMESO.2015.08.029

[39] Q. Yang, Y. Tang, H. Zhang, J. Chen, Z. Jiang, K. Xiong, J. Wang, X. Liu, N. Yang, Q. Du, Y. Song, Classic deep oxidation $CuMnO_x$ catalysts catalyzed selective oxidation of benzyl alcohol, Appl. Surf. Sci. 610 (2023) 155364. https://doi.org/10.1016/J.APSUSC.2022.155364

[40] P. Wu, L. Song, Y. Wang, X. Liu, Z. He, P. Bai, Z. Yan, High-performance benzyl alcohol oxidation catalyst: Au-Pd alloy with ZrO_2 as promoter, Appl. Surf. Sci. 537 (2021). https://doi.org/10.1016/j.apsusc.2020.148059

[41] P. Tamizhdurai, S. Sakthinathan, P. Santhana Krishnan, A. Ramesh, V.L. Mangesh, A. Abilarasu, S. Narayanan, K. Shanthi, T.W. Chiu, Catalytic activity of ratio-dependent SBA-15 supported zirconia catalysts for highly selective oxidation of benzyl alcohol to benzaldehyde and environmental pollutant heavy metal ions detection, J. Mol. Struct. 1176 (2019) 650–661. https://doi.org/10.1016/J.MOLSTRUC.2018.09.007

[42] C. Wu, L. Chen, X. Lou, M. Ding, C. Jia, Fabrication of Cobalt-Nickel-Zinc ternary oxide nanosheet and applications for supercapacitor electrode, Front. Chem. 6 (2018) 425096. https://doi.org/10.3389/FCHEM.2018.00597/TEXT

[43] C.G. Ramankutty, S. Sugunan, Surface properties and catalytic activity of ferrospinels of

nickel, cobalt and copper, prepared by soft chemical methods, Appl. Catal. A Gen. 218 (2001) 39–51. https://doi.org/10.1016/S0926-860X(01)00610-X

[44] T. Varila, H. Romar, U. Lassi, Catalytic Effect of Transition Metals (Copper, Iron, and Nickel) on the Foaming and Properties of Sugar-Based Carbon Foams, Top. Catal. 62 (2019) 764–772. https://doi.org/10.1007/s11244-019-01171-4

[45] F. Hosseini-Eshbala, A. Sedrpoushan, B. Breit, F. Mohanazadeh, H. Veisi, Ionic-liquid-modified CMK-3 as a support for the immobilization of molybdate ions (MoO42-): Heterogeneous nanocatalyst for selective oxidation of sulfides and benzylic alcohols, Mater. Sci. Eng. C. Mater. Biol. Appl. 110 (2020). https://doi.org/10.1016/J.MSEC.2019.110577

[46] F. Hosseini Eshbala, F. Mohanazadeh, A. Sedrpoushan, Tungstate ions (WO4=) supported on imidazolium framework as novel and recyclable catalyst for rapid and selective oxidation of benzyl alcohols in the presence of hydrogen peroxide, Appl. Organomet. Chem. 31 (2017) 3–8. https://doi.org/10.1002/aoc.3597

[47] Z. Zhang, L. Khrouz, G. Yin, B. Andrioletti, Efficient Oxidation of Benzylic and Aliphatic Alcohols Using a Bioinspired Cross-Bridged Cyclam Manganese Complex with H2O2, European J. Org. Chem. 2019 (2019) 323–327. https://doi.org/10.1002/EJOC.201801140

[48] S. Xiao, C. Zhang, R. Chen, F. Chen, Selective oxidation of benzyl alcohol to benzaldehyde with H2O2 in water on epichlorohydrin-modified Fe3O4 microspheres, New J. Chem. 39 (2015) 4924–4932. https://doi.org/10.1039/C5NJ00434A

[49] A.L. Cánepa, V.R. Elías, V.M. Vaschetti, E. V. Sabre, G.A. Eimer, S.G. Casuscelli, Selective oxidation of benzyl alcohol through eco-friendly processes using mesoporous V-MCM-41, Fe-MCM-41 and Co-MCM-41 materials, Appl. Catal. A Gen. 545 (2017) 72–78. https://doi.org/10.1016/j.apcata.2017.07.039

[50] Y. Chen, P. Tang, X. Lu, J. Ma, H. Li, H. Chen, Preparation of CuFe2O4 composite metal oxides and selective oxidation of benzyl alcohol, Ferroelectrics 609 (2023) 57–65.

https://doi.org/10.1080/00150193.2023.2198952

[51] D. Polidoro, D. Ballesteros-Plata, A. Perosa, E. Rodríguez-Castellón, D. Rodríguez-Padrón, M. Selva, Controlled alcohol oxidation reactions by supported non-noble metal nanoparticles on chitin-derived N-doped carbons, Catal. Sci. Technol. 13 (2023) 2223–2238. https://doi.org/10.1039/d3cy00082f

[52] J. Ma, P. Tang, X. Lu, Y. Chen, F. Mei, Y. Ding, H. Chen, Preparation of Mesoporous Supported CuCo2O4 Catalyst and Selective Oxidation of Benzyl Alcohol, Integr. Ferroelectr. 234 (2023) 79–87. https://doi.org/10.1080/10584587.2023.2191552

[53] C. Sievers, S.L. Scott, Y. Noda, L. Qi, E.M. Albuquerque, R.M. Rioux, Phenomena Affecting Catalytic Reactions at Solid?LiquidInterfaces, ACS Catal. 6 (2016) 8286–8307. https://doi.org/10.1021/ACSCATAL.6B02532

[54] J. Zhang, S. Xiao, R. Chen, F. Chen, Promotional effect of short-chain saturated alcohols on Fe 3 O 4 -catalyzed decomposition of H 2 O 2 and its application in selective oxidation of benzyl alcohol, J. Chem. Technol. Biotechnol. 94 (2019) 1613–1621. https://doi.org/10.1002/JCTB.5929;CTYPE:STRING:JOURNAL

[55] L. Xiong, R. Chen, F. Chen, One-step solvothermal synthesis of Al-promoted Fe3O4 magnetic catalysts for the selective oxidation of benzyl alcohol to benzaldehyde with H2O2 in water, RSC Adv. 6 (2016) 101048–101060. https://doi.org/10.1039/C6RA23019A

[56] P. Wu, L. Song, Y. Wang, X. Liu, Z. He, P. Bai, Z. Yan, High-performance benzyl alcohol oxidation catalyst: Au-Pd alloy with ZrO2 as promoter, Appl. Surf. Sci. 537 (2021) 148059. https://doi.org/10.1016/J.APSUSC.2020.148059