

RESEARCH ARTICLE

Efficient Conversion of Fructose Into 5-HMF Over Zr-O-W Catalysts: Role of WO_x Sub- and Nanoclusters

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ABSTRACT

This work is dedicated to the development of new performing Zr-O-W-mixed oxide catalysts for the direct conversion of fructose to 5-hydroxymethylfurfural (5-HMF) under soft operational conditions. By using sol-gel method, nanoclusters of WO_x as active phase could be formed on the surface of the catalyst at low W loading (i.e., atomic ratio of W/Zr = 1/9), as revealed by different physico-chemical characterizations (scanning transmission electron microscope with a high-angle annular dark field [STEM-HAADF], X-ray diffraction [XRD], X-ray photoelectron spectroscopy [XPS], etc.). The prepared catalysts show very good catalytic performance in the direct conversion of fructose into 5-HMF under soft reaction conditions with the highest HMF yield of 95.8% (reaction conditions: 10 g/L catalyst loading, 120°C, 2 h of reaction, 5 wt.% of fructose in dimethyl sulfoxide [DMSO] solvent).

1 | Introduction

Fossil resources are limited, leading to problems with the supply of fuels and petroleum-derived chemicals. Besides, the use of fossil fuels also causes global warming problems with CO₂ emissions [1, 2]. Thus, renewable and environment-friendly sources of raw materials have been sought during the last decades. Today, biomass conversion is a potential way that has attracted a lot of attention. Converting biomass into valuable compounds passes through a series of reactions before reaching the desired product. In such a value chain, 5-hydroxymethylfurfural (5-HMF) is a key intermediate compound. This platform molecule can be used for the synthesis of various final valuable prod-

ucts, such as levulinic acid (LA), 2,5-dimethylfuran (DMF), and 2,5-furandicarboxylic acid (FDCA) [3–7]. The key step to produce 5-HMF is the reduction of three water molecules from fructose or glucose molecules, which is generally catalyzed by an acid catalyst. Many studies have been conducted on homogeneous catalysts, such as inorganic acids (e.g., HCl, H₃PO₄) or Lewis acids (e.g., AlCl₃, SnCl₄, and CrCl₃) [8–10]. For homogeneous catalysis, various challenges exist, including the ability to separate the catalysts from products, reusability of the catalysts, corrosion risk, and environmental threats. Therefore, to overcome these disadvantages, heterogeneous catalysts, such as super-acid catalytic groups (ZrO₂/SO₄²⁻, Al₂O₃-ZrO₂/SO₄²⁻), heteropolyacid (H₃PW₁₂O₄₀), ion exchange resins

Abbreviations: BET, Brunauer–Emmett–Teller; EDS, energy-dispersive X-ray spectroscopy; NH₃-TPD, ammonia temperature-programmed desorption; SEM, scanning electron microscopy; STEM-HAADF, scanning transmission electron microscope with a high-angle annular dark field; TEM, transmission electron microscopy; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction.

(Amberlyst15), and oxide ($\text{TiO}_2\text{-ZrO}_2$), have also been developed [11–17].

Among heterogeneous acid catalysts, WO_x -based materials have been found as efficient catalysts in many organic reactions, such as metathesis, dehydration, isomerization, esterification, and selective catalytic reduction of NO_x [18–25]. The WO_x active phase is usually supported on different oxides, such as SiO_2 , Al_2O_3 , ZrO_2 , and Nb_2O_5 [18–25]. Among them, the WO_x supported on ZrO_2 oxide was the most studied [19, 22, 26, 27]. Several parameters affecting its catalytic activity, such as W content, synthesis method, and precursors, have been investigated. The textural structure and the dispersion of the WO_x and its interaction with catalyst support generally play important role [28–30]. As examples, Wachs et al. studied methanol dehydration over ZrO_2 -loaded WO_3 catalysts, the latter being synthesized from ammonium metatungstate salt $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}$ with zirconium hydroxide $\text{Zr}(\text{OH})_4$ instead of directly impregnating the salt on ZrO_2 oxide. They proved that the Zr-stabilized distorted WO_3 nanoclusters were the active sites in this reaction [28, 29]. Thus, in order to improve the WO_3 -based catalyst activity, it is important to maximize the formation of WO_3 nanoclusters instead of WO_3 polytungstate or nanoparticles. By the conventional impregnation method, the WO_x phase is mainly formed through the decomposition of precursors deposited inside the pores of support, which could favor the formation of nanoparticles or polytungstate layer rather than WO_x nanoclusters.

In this work, for the first time, a series of mixed oxides of zirconium (Zr) and tungsten (W) have been synthesized by the sol–gel method using WCl_6 and ZrOCl_2 as W and Zr precursors and investigated in the conversion of fructose to produce 5-HMF in the dimethyl sulfoxide solvent (DMSO). This synthesis approach is expected to well disperse W^{6+} and Zr^{4+} ions together, which can favor the formation of WO_3 nanoclusters. In addition, the atomic dispersion level of both W and Zr precursors is expected to favor a strong metal-support interaction for a good catalyst stability. These catalysts were compared to the counterpart prepared by the conventional impregnation method using tungsten salt as the WO_x precursor and ZrO_2 oxide as the support.

2 | Experimental Section

All the chemicals used were of analytical purity: $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ 99%, WCl_6 99%, $\text{C}_2\text{H}_5\text{OH}$ 99%, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (P123), DMSO, and nitrogen gas 99%.

A series of mixed oxides of Zr and W, with different Zr:W atomic ratios and denoted as Zr_xW_y (x, y : 1 to 9) were synthesized by the sol–gel method. The typical procedure is as follows: An amount of 1 g of copolymer P123 was dissolved in 10 mL of ethanol under vigorous stirring up to the complete dissolution (Solution A). Then, calculated amounts of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and WCl_6 were dissolved in ethanol (Solution B). Solution A was added to Solution B, and the mixture was kept under stirring at room temperature for 2 h, followed by the aging step at 40°C for 5 days. Finally, the mixture was dried at 70°C for 24 h to eliminate the solvent, and the solid was calcined in air at 400°C for 5 h with a heating rate of 1°C/min. The single

oxides, ZrO_2 , and WO_3 , were synthesized by the same procedure. For comparison, a supported catalyst, WO_x/ZrO_2 , having the atomic ratio W:Zr = 1:9, denoted as W_1/Zr_9 , was prepared by the conventional impregnation method using the WCl_6 precursor and the single ZrO_2 oxide synthesized above. To evaluate the stability of the catalyst, it was thoroughly washed with ethanol several times after each use and then dried at 70°C.

The X-ray diffraction (XRD) patterns were collected with a Bruker D8 using Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$). The transmission electron microscopy (TEM) images were obtained with a JEM 1400-Jeon. The images of scanning transmission electron microscope with a high-angle annular dark field (STEM-HAADF) were carried out on a JEOL JEM ARM200F microscope. The scanning electron microscopy (SEM)–energy-dispersive x-ray spectroscopy (EDS) spectra were carried out on Hitachi Tabletop Microscopes TM4000Plu with a detector of Oxford EDS Micsf+/X-stream2. The measurements of temperature-programmed desorption of ammonia (NH_3 -TPD) were done with a Micromeritics Tristar 3000. X-ray photoelectron spectroscopy (XPS) was performed with a K-alpha (Thermo Fisher Scientific). XPS data were analyzed using Casa XPS software [31]. Peak fitting is performed with a nonlinear Shirley-type background, using a weighted least-squares calculation method with 15% Lorentzian and 85% Gaussian line shapes, along with full width at half maximum (FWHM) constraints [32]. The specific surface area was obtained by nitrogen adsorption–desorption isotherm, using a Micromeritics ASAP 2020 instrument. The results were treated by applying Brunauer–Emmett–Teller (BET) model.

The conversion of fructose to 5-HMF was carried out in a 100 mL three-necked flask connected to a condenser. For a given reaction, 100 mg of catalyst was put into the three-necked flask and flushed at a given reaction temperature (100–160°C) under an N_2 flux (200 mL/min) for 1 h to desorb all adsorbed gaseous impurities on catalyst surface. Then, 10 mL of DMSO containing dissolved fructose (2.5–15 wt.%) was added to the flask. The reaction mixture was continuously stirred at the reaction temperature (100–160°C) for 1–4 h under N_2 atmosphere. Finally, after a rapid cooling with water, the product was separated from the catalyst by filtration using a 0.45 μm filter. The products of the reaction were analyzed by using a high-performance liquid chromatography (HPLC), L-800, Shimadzu, equipped with an analytical column C18.

3 | Results and Discussion

3.1 | Catalyst Characterization

XRD results are presented in Figure 1. The small angle XRD pattern of ZrO_2 (Figure 1a) reveals a broad peak at about $2\theta \approx 1^\circ$, which confirms the mesoporous structure of this oxide [30]. The large angle XRD pattern of ZrO_2 (Figure 1b) showed net peaks at 2θ positions of 30.2°, 49.8°, and 60.0°, which correspond to the (1 0 1), (1 1 2), and (2 1 1) planes, respectively, indicating the presence of ZrO_2 tetragonal phase. The wide-angle XRD pattern of the pure WO_3 oxide showed peaks at 2θ values of 23.1°, 26.4°, 28.6°, 33.4°, 33.5°, 41.3°, 49.7°, and 55.6°, corresponding to the (0 2 0), (1 2 0), (1 1 2), (0 2 2), (2 0 2), (2 2 2), (4 0 0), and (4 2 0) planes, respectively, which confirms the formation of the monoclinic WO_3 phase in this material. In addition, no

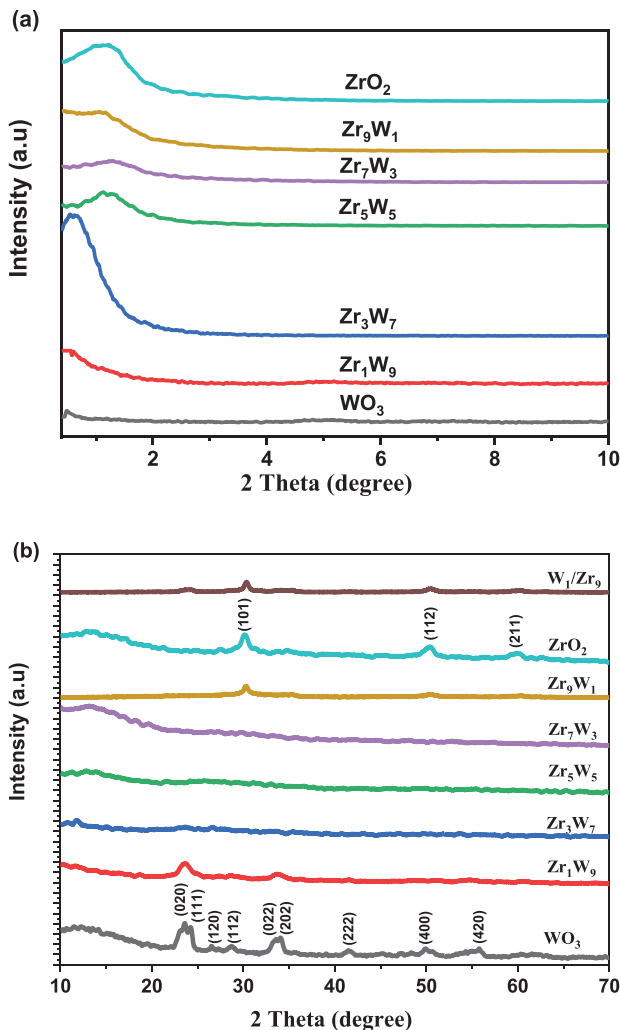


FIGURE 1 | XRD patterns of synthesized materials at small angle (a) and large angle (b).

discernible diffraction peaks could be found in the small angle XRD pattern of WO_3 . About the mixed oxides prepared by the sol-gel method, small angle XRD patterns of Zr_5W_5 , Zr_7W_3 , and Zr_9W_1 (Figure 1a) show the broad peak of ZrO_2 at about $2\theta \approx 1^\circ$, whereas at lower Zr contents (Zr_1W_9 , Zr_3W_7), this peak did not appear. Within 2θ of 10° – 70° (Figure 1b), the increase of W content from Zr_9W_1 to Zr_1W_9 led to a progress apparition of WO_3 peaks, and a progress disappearance of ZrO_2 peaks. Finally, W_1/Zr_9 sample, which was synthesized by the conventional impregnation method, showed the simultaneous existence of ZrO_2 and WO_3 monoclinic phases (Figure 1b).

Figure 2 illustrates the N_2 adsorption-desorption isotherms. In most of cases, a hysteresis of Type IV can be observed, indicating the presence of mesoporous structures.

As summarized in Table 1, single oxides (ZrO_2 and WO_3) show relatively small specific surface areas of 40 and 25 m^2/g . Small mesopores were present in ZrO_2 (mean pore diameter of 4.9 nm), whereas large mesopores were observed for WO_3 (mean pore diameter of 30.5 nm). Thus, even the total pore volume in WO_3 is higher, its specific surface area is smaller in comparison to ZrO_2 . Surprisingly, the deposition of WO_3 on ZrO_2 by the conventional

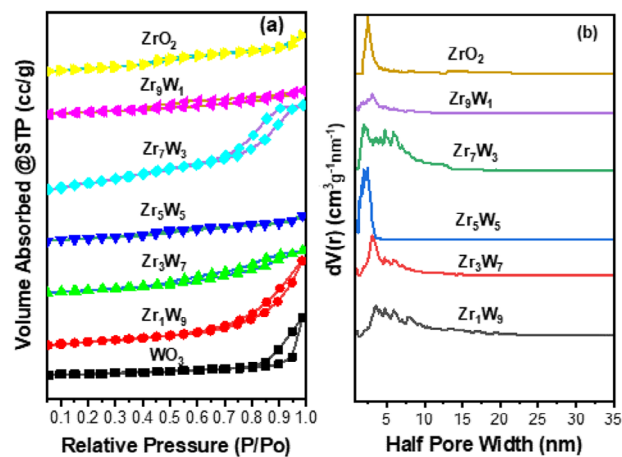


FIGURE 2 | N_2 adsorption-desorption isotherms (a) and pore size distribution (b) of the synthesized materials.

TABLE 1 | Specific surface area (S_{BET}), mean pore diameter (D_{pore}), and total pore volume (V_{pore}) of synthesized catalysts.

Catalyst number	Catalyst name	S_{BET} (m^2/g)	D_{pore} (nm)	V_{pore} (cm^3/g)
1	WO_3	25	30.5	0.17
2	Zr_1W_9	62	7.0	0.18
3	Zr_3W_7	51	6.1	0.10
4	Zr_5W_5	98	4.9	0.08
5	Zr_7W_3	94	3.8	0.19
6	Zr_9W_1	106	5.2	0.14
7	ZrO_2	40	4.9	0.08
8	W_1/Zr_9	57	7.1	0.13

impregnation method led to an increase in total pore volume, mean pore size, and specific surface area compared to ZrO_2 alone. This may suggest that surface physico-chemical phenomena took place between W precursor and ZrO_2 surface during the impregnation and thermal treatment steps of its preparation. About mixed oxides prepared by the sol-gel method, they mostly present small mesopores (mean pore size of 3.8–7.0 nm), leading to high specific surface areas (51–106 m^2/g).

The textural properties of W_1/ZrO_2 and Zr_9W_1 catalysts were examined by TEM and STEM-HAADF. TEM images in Figure 3a,b show the general feature of the catalyst surface. The particle size on the W_1/ZrO_2 catalyst is larger than that on the Zr_9W_1 catalyst. This result is consistent with the XRD data, as the crystallinity of the W_1/ZrO_2 sample is higher than that of the Zr_9W_1 sample. The STEM-HAADF image in Figure 3c reveals bright dots and nanoscale regions in Zr_9W_1 , which could be attributed to nanoclusters of WO_x bonded probably to ZrO_2 support through oxygen bonding. Meanwhile, the STEM-HAADF image of the W_1/Zr_9 sample, synthesized by the conventional impregnation method, reveals continuous bright domains corresponding to WO_x species in the form of polytungstates. The element mapping (Figure 3e–h) confirmed homogeneous distribution of W on the surface of Zr_9W_1 , demonstrating the

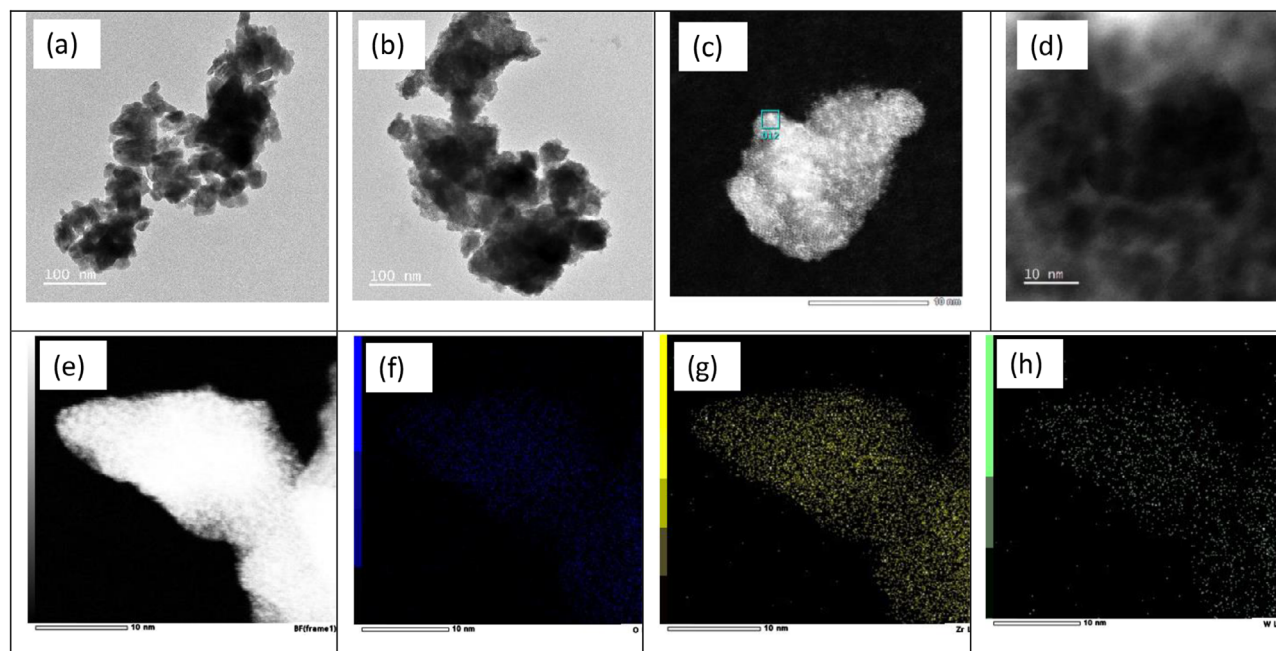


FIGURE 3 | (a) TEM image of W_1/ZrO_2 ; (b) TEM image of Zr_9W_1 ; (c) and (d) STEM-HAADF image of Zr_9W_1 and W_1/Zr_9 , respectively; (e–h) Element mapping of Zr_9W_1 .

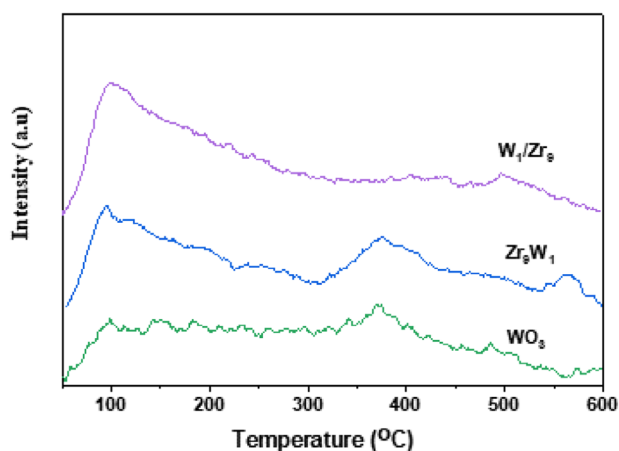


FIGURE 4 | NH_3 -TPD curves of WO_3 , Zr_9W_1 and W_1/Zr_9 .

benefits of the sol-gel method employed for the formation of WO_x nanoclusters.

The acidity of WO_3 , Zr_9W_1 , and W_1/Zr_9 catalysts was determined by NH_3 -TPD method, and the results are shown in Figure 4 and Table 2. In general, NH_3 -TPD curves can be divided into three regions, corresponding to the presence of weak acid sites (desorption temperature range of ca. 150–300°C), moderate acid sites (desorption temperature range of ca. 300–500°C), and strong acid sites (desorption temperature above 500°C) [33–35].

Regarding the mass density of acid sites, all three types of acid sites were observed in the synthesized catalysts investigated. In particular, Zr_9W_1 showed a larger desorption peak at around 380°C, which was attributed to a new type of moderate acid site that might be related to WO_x sub- and nanoclusters, which were abundantly observed by STEM-HAADF image (Figure 3). On the

other hand, in WO_3 and W_1/Zr_9 samples, only few amounts of this type of acid sites were observed. Thus, the mass density of acid sites was much higher in Zr_9W_1 prepared by the sol-gel method than in WO_3 and W_1/Zr_9 samples, prepared by the conventional impregnation method.

However, as only the acid sites on the catalyst surface could be determined by NH_3 -TPD, it is also meaningful to consider surface density of acid sites by taking into account their specific surface area. WO_3 presented the highest surface density of acid sites ($12.80 \mu\text{mol}_{NH_3}/\text{m}^2_{\text{catalyst}}$), followed by Zr_9W_1 ($7.26 \mu\text{mol}_{NH_3}/\text{m}^2_{\text{catalyst}}$), then W_1/Zr_9 ($5.96 \mu\text{mol}_{NH_3}/\text{m}^2_{\text{catalyst}}$). This is consistent with the observation of well-dispersed and uniformly distributed nanoclusters in the HRTEM and STEM images of the Zr_9W_1 in comparison to those of W_1/Zr_9 . Hence, the employment of the sol-gel method allowed increasing the acidity of the mixed oxides (Table 2), which is expected to be useful to improve the catalytic activity in the studied reaction of 5-HMF production.

To further evaluate the surface properties of the Zr_9W_1 material, SEM-EDS and XPS measurements were carried out. The EDS results are presented in Figure 5. The analysis shows that the molar ratio of W/Zr is approximately 0.126, which is close to the theoretical ratio of 0.111.

To estimate the oxidation state of elements on the catalyst's surface, one of the key factors influencing catalytic activity, XPS spectroscopy was performed on the Zr_9W_1 catalyst sample (Figure 6). Narrow scan W 4f and Zr 3d spectra (Figure 6a) were fitted under physically-meaningful constraints: within each spin-orbit doublet the area ratio was fixed to $4f_{7/2}:4f_{5/2} = 4:3$ (resp. $3d_{5/2}:3d_{3/2} = 3:2$ for Zr), the FWHM were identical for the two components, and the spin-orbit separations were constrained to $\Delta E(W\ 4f) = 2.2\text{ eV}$ and $\Delta E(Zr\ 3d) = 2.40\text{ eV}$, following best

TABLE 2 | Mass and surface densities of acid sites determined by NH₃-TPD measurements.

Catalyst	Mass density of acid sites (mmol _{NH₃} /g _{catalyst})				Surface density of acid sites (μmol _{NH₃} /m ² _{catalyst})			
	Weak	Moderate	Strong	Total	Weak	Moderate	Strong	Total
WO ₃	0.14	0.17	0.01	0.32	5.60	6.80	0.40	12.80
Zr ₉ W ₁	0.33	0.40	0.04	0.77	3.11	3.77	0.38	7.26
W ₁ /Zr ₉	0.19	0.10	0.05	0.34	3.33	1.75	0.88	5.96



FIGURE 5 | SEM-EDS spectrum of Zr₉W₁.

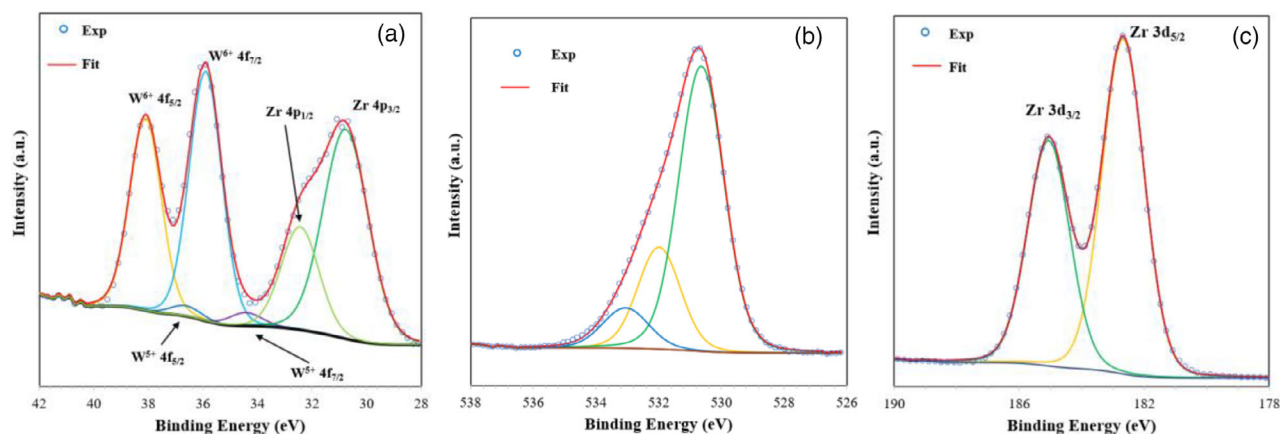


FIGURE 6 | Deconvoluted narrow scan XPS spectra of the Zr₉W₁ catalyst: (a) W 4f and Zr 4p region, (b) O 1s region, and (c) Zr 3d region.

practices for XPS curve-fitting [32]. The W 4f region is described by a dominant W⁶⁺ doublet at BE (4f_{7/2}) = 35.9 eV and BE (4f_{5/2}) = 38.1 eV, and a minor W⁵⁺ doublet at about 34.4/36.6 eV. The latter accounts for around 5% of the total W 4f area. The presence of a small amount of W⁵⁺ is consistent with previous works, which report that WO_x/ZrO₂ can host slightly reduced W species when WO_x domains interact with ZrO₂, especially near (sub)-monolayer to nanocluster regimes [36–38]. Because the W 4f window partially overlaps with zirconium photoemission, the Zr 4p envelope (28–34 eV) was also fitted (Figure 6a). This region contains only a single Zr⁴⁺ contribution and no additional shoulder that would indicate Zr³⁺ or reduced zirconium species. The Zr oxidation state was independently confirmed from the Zr 3d spectrum (Figure 6c), showing a clean Zr⁴⁺ doublet at 182.7 eV

(3d_{5/2}) and 185.1 eV (3d_{3/2}) with the expected 3:2 area ratio and ΔE ≈ 2.4 eV. No Zr³⁺ component (typically shifted 0.8–1.2 eV to lower binding energy) was detected, indicating that zirconium remains fully oxidized in the catalyst [39, 40].

The narrow scan O 1s spectrum (Figure 6b) consists of three components: the main peak at 530.7 eV assigned to lattice O²⁻ in oxides, a second contribution at 532.0 eV attributed to surface hydroxyl groups, and a weak high-binding-energy peak at 533.1 eV corresponding to physisorbed H₂O and/or carbonates. The relative abundance of –OH species agrees with the small W⁵⁺ fraction observed in W 4f, as surface protonation of WO_x sites is a known origin of Brønsted acidity in WO_x/ZrO₂ catalysts [39, 40].

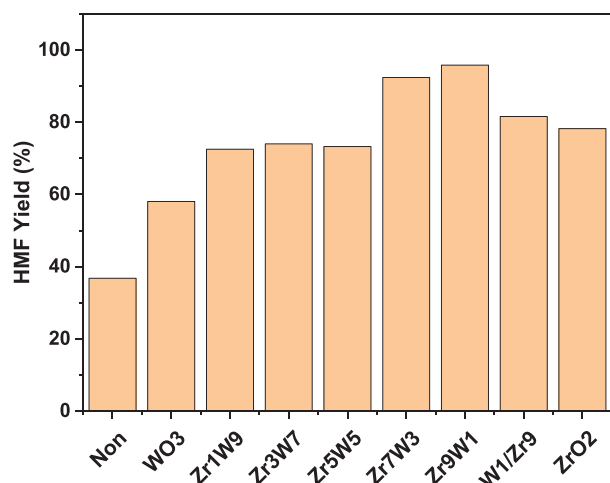


FIGURE 7 | Comparison of different catalysts in the catalytic conversion of fructose to 5-HMF under the same reaction conditions: an amount of 100 mg of catalyst, reaction temperature of 120°C, reaction time of 2 h, 100 mL of 5 wt.% of fructose in DMSO; Non = blank test. HMF, hydroxymethylfurfural.

3.2 | Catalytic Evaluation

The catalytic activity of the synthesized catalysts was evaluated in the conversion of fructose to 5-HMF at 120°C. Blank test (without catalyst) was also conducted for comparison.

Figure 7 shows that the 5-HMF yields obtained under the same conditions with ZrO₂, Zr₉W₁, Zr₇W₃, Zr₅W₅, Zr₃W₇, Zr₁W₉, W₁/Zr₉, and WO_x catalysts were 78.2%, 95.8%, 92.4%, 73.3%, 74.0%, 72.5%, 81.6%, and 58.1%, respectively. It is worth noticing that the 5-HMF yield notably increased in the case of Zr₇W₃ and Zr₉W₁ in comparison with the catalysts containing higher W content (Zr₅W₅, Zr₃W₇, and Zr₁W₉). In fact, it has been reported in the literature that, at low surface W density (0–4 W/nm²), WO_x could be found as isolated monotungstate species, whereas at moderate W content (about 4–8 W/nm²) and high W content (>8 W/nm²), nanoclusters and polytungstate/3D crystal of WO_x could be more favorably formed, respectively [28, 29]. In the case of the Zr₉W₁ sample, the surface tungsten content was quantified from XPS analysis using RSF-corrected W 4f and Zr (3d/4p) peak areas. A surface cationic ratio (W/Zr) XPS of approximately 0.07–0.08 was obtained, corresponding to a surface tungsten fraction of about 7%–8% among cations. Assuming a surface cation site density of ZrO₂ of ~5 sites/nm² (as commonly used in previous DFT studies of zirconia surfaces), this leads to an estimated surface tungsten density of ~0.35–0.40 W/nm², according to Ross-Medgaarden et al. [28]. This surface-sensitive quantification confirms the formation of WO_x nanoclusters and possibly isolated monotungstate species [28, 29].

Nanoclusters of WO_x and isolated monotungstate species have already been found as the most active structure of WO_x in dehydration reaction of different alcohols [41–44], and more specifically in dehydration of sugars (e.g., glucose, fructose, etc.) into 5-HMF [45–48]. This explains the highest catalytic activity of Zr₉W₁ among the different prepared catalysts in the production of 5-HMF from fructose as shown in Figure 7. Both the WO₃ and ZrO₂ single oxides were also active for the formation of 5-

HMF, but their activity was much lower than that of W₁/Zr₉ (Figure 7). Finally, the catalyst prepared by the conventional impregnation method (W₁/Zr₉) was also less active than its counterpart (Zr₉W₁) prepared by the sol-gel method (Figure 7). This once again highlighted the beneficial effect of the sol-gel preparation method in comparison with the conventional impregnation. The lower activity of W₁/Zr₉ could be tentatively attributed to the fact that the impregnation method usually led to the formation of nanoparticles of various size, with weak metal-support interaction.

On the basis of the results obtained in Figure 7, the factors which can affect the catalytic activity, including the fructose content, the reaction temperature, and the reaction time, were also investigated on Zr₉W₁ as the most active catalyst.

Figure 8a presents the impact of the reaction temperature. At 120°C, the HMF yield reached the highest value of 95.8% and decreased to 84.0% at 140°C and 81.0% at 160°C. This could be explained by side reactions, such as LA formation and oligomerization reactions, which are favored at 140°C and 160°C [49, 50]. At 100°C, the 5-HMF yield was only 41%, which could be explained by the kinetic limit. For the impact of the reaction time (Figure 8b), the duration of 2 h led to the maximum 5-HMF yield. Longer reaction times (3–4 h) could favor side reactions, such as LA formation and oligomerization, whereas shorter reaction time (1 h) was not enough to reach high yield. Finally, for the impact of the fructose content in the feed (Figure 8c), 5-HMF yield reached the highest value at 5 wt.%. Thus, the optimal operational conditions for the formation of 5-HMF from fructose over Zr₉W₁ catalyst were determined: reaction temperature of 120°C, reaction time of 2 h, 5 wt.% of fructose in the feed using DMSO as solvent, and catalyst loading of 10 g/L. Under these conditions, the 5-HMF yield could reach 95.8%. To evaluate the stability of the catalyst, it was reused three times. The results presented in Figure 8d show that the HMF yield decreased only slightly after three cycles of reuse, from 95.8% to 93.3%. The high yield and good stability of the catalyst indicate its potential as a promising candidate for further industrial scale-up.

4 | Conclusions

A series Zr-W-O mixed oxides were synthesized by the sol-gel method and compared with the counterpart prepared by the conventional impregnation method. The XRD patterns indicated that single oxides ZrO₂ and WO₃ exist as tetragonal and monoclinic crystalline phases, respectively, whereas most of the mixed oxide samples were found at the amorphous state, except for the Zr₉W₁ catalyst with the appearance of ZrO₂ tetragonal phase. These results demonstrated that the presence of the W element prevented the crystallization of both WO₃ and ZrO₂ crystal phases. The mixed oxides amorphous state was also consistent with the increasing specific surface areas in comparison with single oxides. In addition, the STEM-HAADF image and XPS analysis of Zr₉W₁ suggested the formation of Zr-stabilized WO_x nanoclusters, which are known as the most active sites of WO₃-based catalysts in the dehydration reaction. The NH₃-TPD measurement on the Zr₉W₁ sample revealed a large peak at around 380°C, which corresponds to the presence of moderate acid sites, which likely belonged to Zr-stabilized WO_x nanoclusters. XPS spectra of the

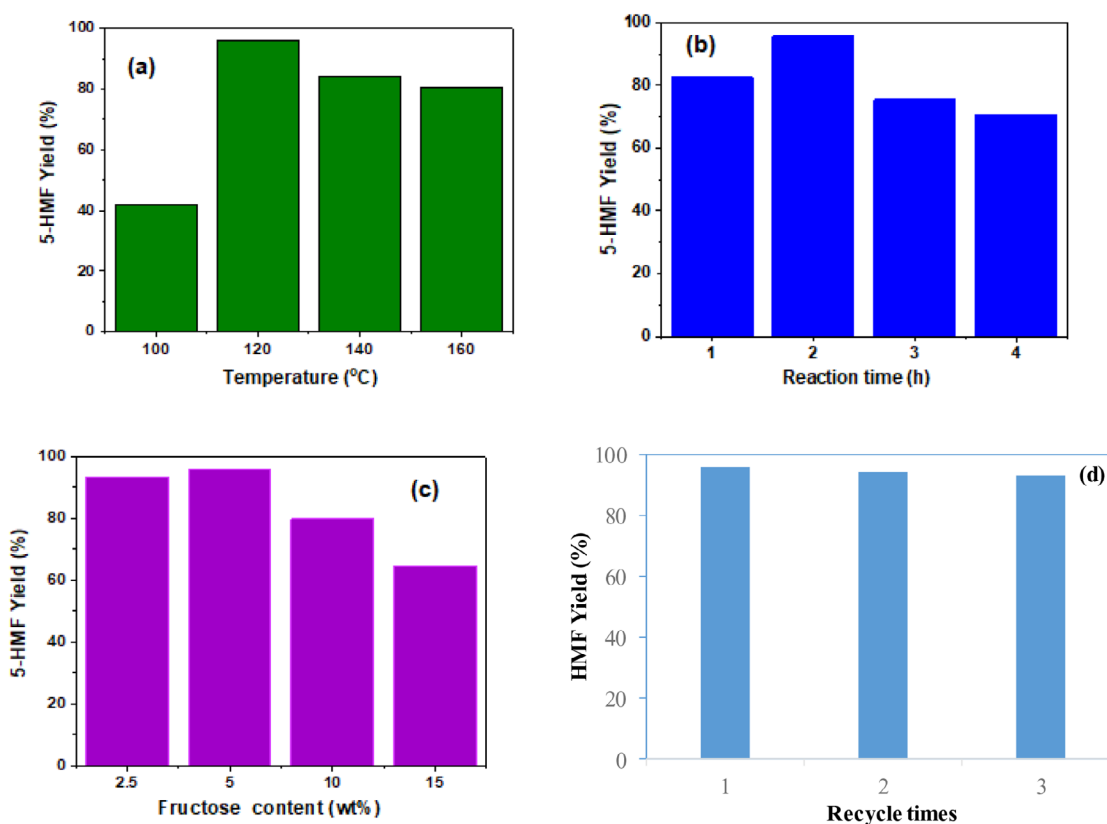


FIGURE 8 | (a) Impact of the reaction temperature on the 5-HMF yield. Reaction conditions: Zr_9W_1 catalyst, reaction time of 2 h, 5 wt.% of fructose in DMSO; (b) Impact of the reaction time on 5-HMF yield. Reaction conditions: Zr_9W_1 catalyst, reaction temperature of 120°C, 5 wt.% of fructose in DMSO; (c) Effect of initial substrate concentration on 5-HMF yield. Reaction conditions: Zr_9W_1 catalyst, reaction temperature of 120°C, reaction time of 2 h; (d) HMF yield over successive catalyst reuse cycles. Reaction conditions: Zr_9W_1 catalyst, reaction time of 2 h, reaction temperature of 120°C, 5 wt.% of fructose in DMSO.

Zr_9W_1 sample also showed the existence of oxidation states W^{6+} and W^{5+} , corresponding to the co-existence of Lewis and Bronsted acid sites. The results in the production of 5-HMF from fructose showed the remarkably high catalytic activity of the Zr_9W_1 sample, which might be tentatively explained by the presence of WO_x nanoclusters and possibly WO_x isolated monotonungstate species in this catalyst. Different factors affecting the 5-HMF yield, such as the reaction temperature, reaction time, and fructose content, were investigated. The highest 5-HMF yield reached 95.8% over Zr_9W_1 catalyst (10 g/L catalyst loading) at 120°C for 2 h from a mixture of 5 wt.% of fructose in DMSO solvent. This yield decreased by only 2.5% after three reuse cycles. This demonstrated the high potential application of Zr-W-O oxides synthesized by the sol-gel method for the conversion of fructose to 5-HMF.

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