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Microwave assisted rapid conversion of fructose into 5-HMF over solid acid catalysts

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This work, we investigated the dehydration of fructose into 5-hydroxymethylfurfural by using solid catalysts under microwave-assisted in dimethyl sulfoxide. Four kinds of solid catalysts such as ZrO_2 , WO_x/ZrO_2 , MO_x/ZrO_2 , $SO_4^{2'}/WO_x-ZrO_2$ and $SO_4^{2'}/MOO_x-ZrO_2$ were prepared and characterized by XRD, UV-DRS, FTIR, XPS, TEM, TPD, BET, Raman and the surface acid amount was obtained combining pyridine adsorption and UV spectrometry. The $SO_4^{2'}/WO_x-ZrO_2$ catalyst was found be the most active catalyst, and a fructose conversion of 95.80% with 83.90% of 5-HMF yield was obtained at 150°C for a relatively short reaction time of 5 min. The value of activation energy was comparable with previous values reported in the literature, this implies that the $SO_4^{2'}/WO_x-ZrO_2$ was efficient for the dehydration of fructose to 5-HMF and microwave irradiation heating had a remarkable accelerating effect on the fructose conversion.

1. Introduction

The decrease of fossil fuel reserves and deterioration of the social environment drive people to seek sustainable resources. As an abundantly available, cheap, renewable and low sulfur content resource, biomass not only can as fuels, but also can be converted into chemical intermediates for the production of various chemicals and liquid fuels. In the conversion of biomass, the study of dehydration of C₆-sugars into 5-hydroxymethylfurfural(5-HMF) has received considerable attention.¹⁻² 5-HMF has furan ring structure, aldehyde group, hydroxyl group and conjugated diene, therefore it can through hydrolysis, selective oxidation, hydrogenation and esterification, etc. methods to obtain a series of derivatives, such as 2,5-diformylfuran, levulinic acid,³ 2,5-furandicarboxylic acid,⁴ etc., which are widely used in the areas of drugs, fuels, and polymeric materials.⁵⁻⁶

Early times, many types of acid catalysts such as mineral acids(such as H_2SO_4 , HCl, H_3PO_4),⁷ organic acids(such as formic acid and acetic acid),⁸ strong acid cation exchange resins⁹⁻¹⁰ had been used for the dehydration of fructose. According to the earlier literature,¹¹⁻¹² the reaction mechanism for 5-HMF from fructose over acid catalysts as shown Scheme 1. In addition, ionic liquids were serving as both solvents and catalysts for the dehydration of fructose into HMF¹³⁻¹⁴ and had been proven effective, but its synthesis process complex and they had serious drawbacks in terms of separation and recycling. In contrast, heterogeneous catalysts showed superior behavior in terms of easy recovery and recyclability in dehydration of sugar.¹⁵ R. Kourieh et al. studied the WO_x/ZrO₂ surface acidic

properties for the aqueous hydrolysis of cellobiose, it revealed that WO_x/ZrO_2 catalysts, well known for their high acid surface chemistry and the presence of acidic sites of different natures(i.e. Lewis acid sites from zirconia and both Brönsted and Lewis sites from WO_x), could potentially be good candidates for the near-boiling water phase biomass reaction.¹⁶



Scheme 1 The reaction mechanism for 5-HMF from fructose

Several approaches had been reported for the dehydration of carbohydrates, such as Simeonov et al. synthesized 5-HMF by dehydration of fructose in either batch or flow chemistry conditions,¹⁷ Jadhav et al. carried out the dehydration reaction of sugar in superheated water in a stainless tubular reaction cell,¹⁸ De et al. used AlCl₃ as catalyst for fructose dehydration under microwave-assisted heating conditions.¹⁹ Above all, microwave technology had been applied by more and more researches, it had unique heating mode which could make organic reaction speed faster than traditional heating method and the reaction yield was high, it had fewer by-products. Qi et al. studied the catalytic conversion of fructose into 5-HMF by microwave heating and compared conventional sand bath heating with microwave heating, it revealed that the latter had a remarkable accelerating effect not only on fructose conversion, but also on 5-HMF yield, fructose conversion and HMF yields by microwave heating (91.7% and

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70.3%, respectively) were higher than those by sand bath heating (22.1% and 13.9% respectively).¹⁰

In this work, we introduced the W, Mo atom into ZrO_2 and prepared WO_x/ZrO_2 , MOO_x/ZrO_2 catalysts. Moreover, we prepared highly catalytic $SO_4^{2^-}/WO_x$ - ZrO_2 and $SO_4^{2^-}/MOO_x$ - ZrO_2 solid acid catalysts by wet impregnation. These catalysts were characterized via certain methods, such as X-ray diffraction (XRD), Fourier Transform infrared spectroscopy (FTIR), nitrogen adsorption-desorption measurement (BET), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), ammonia-temperature programmed desorption (NH₃-TPD), and the surface acid amount has been obtained combining pyridine adsorption and UV spectrometry. Furthermore, we investigated the dehydration of fructose into 5-HMF by using these catalysts under microwave-assisted in dimethyl sulfoxide (DMSO) in very short reaction time.

2. Experiment

2.1. Material

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All chemicals used were analytically grade: Fructose (99%, Aladdin[®]), 5-HMF (98%, Tianjin Fuchen Chemical Reagents Factory), n-butanol (99%, Beijing Chemical Works), zirconium (IV) propoxide (70wt.%, solution in 1-propanol, Sigma-Aldrich), Cyclohexane and Pyridine (99.5%, Xilong Chemical Co., Ltd.), ammonium molybdate(99%) and ammonium tungstate (85%~90%, Sinopharm Chemical Reagent Co., Ltd), cetyltrimethylammonium bromide (CTAB) and DMSO (99%, Tianjin Guangfu Fine Chemicals Research Institute), deionized water (H₂O, home-made).

2.2. Catalyst Synthesis

The synthesizing process of zirconia support was as follows. First, 2.5g CTAB dissolved in 20 ml n-butanol with stirring at 40°C for 10min to obtain a clear solution, then 0.02 mol of the zirconium (IV) propoxide solution was added to this solution with stirring about 10 min. In another container, 0.002mol of the transition-metal source (W, Mo) was dissolved in 10ml water, the formed solution was then added to the above-mentioned solution under vigorous magnetic stirring at room temperature. After stirring for 24h, the precipitate was transferred to a Teflon lined autoclave, and crystallization was carried out at 80°C for 24h, then filtered, washed with bi-distilled water several times. The obtained hydroxide precipitate was dried at 100°C for 5h and finally calcined at 550°C for 4h, the heating rate was controlled at 2°C /min.

As for $SO_4^{2^-}/WO_x$ - ZrO_2 and $SO_4^{2^-}/MoOx$ - ZrO_2 , these catalysts were prepared similar to the above-mentioned method. The only difference was that the obtained hydroxide precipitate was dried at 100°C for 5h and then was impregnated with 1mol/L H₂SO₄ for 30min(sample/ H₂SO₄=1g/10mL), then filtered, washed with hot distilled water at 80 °C several times and dried at 100°C ,and then was calcined at 550°C for 4h.

2.3. Catalysts characterization

XRD analyses were obtained on Rigaku D/MAX2500 instrument using Cu K α radiation. The scattering angle 20 was varied from 10° to 80°, with a step length of 0.02°. Fourier transform infrared (FT-IR) spectra were recorded on KBr pellets by a PerkinElmer (Spectrum Two) infrared spectrometer with the wavenumber from 4000 to 500cm⁻¹. The morphology of the catalytic materials were obtained by a transmission electron microscope(TEM: JEM-2000EX, JEOL). Instiu high pressure Raman measurements obtained using a spectrometer (focal length, 500 mm) combined with a liquid nitrogen-cooled CCD (Acton SP-2500 and PyLoN:100B, Princeton Instruments). A single-mode DPSS laser (power output, 50 mW) at 532 nm used as the excitation light source. XPS analyses were obtained on Theromo ESCALAB 250Xi instrument. The surface acid amount of samples were quantitatively measured via UV spectrometry with adsorbates of pyridine (Py) in cyclohexane solution on a Cary 5000 UV-Vis-NIR. The detailed steps were described previously by Sigian Zhang et al.²⁰ NH₃-TPD were performed on a Chembet Pulsar TPR/TPD. In a typical experiment for the TPD measurement, the sample were pretreated at 700°C for 30min in helium and then cooled to 100°C. A flow of 10% NH₃/He was then passed over the pretreated materials for 60min. Following this ammonia adsorption procedure, the reactor was purged with helium for 60min to remove residual/physisorbed ammonia, ammonia desorption was carried out 700°C with a heating rate of 10°C /min. Nitrogen physisorption studies were performed using Micromeritics ASAP 2010 model static volumetric adsorption instrument. The samples were dried in an oven at 80°C overnight prior to degassing. Prior to adsorption experiments, the catalysts were outgassed at 350°C for 8h. The pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method.

2.4. Procedure for catalytic degradation of fructose

The catalytic reaction for fructose dehydration to HMF was performed in a CEM Discover SP microwave reactor. 5mL fructose solution and catalyst were charged in a microwave tube. The tube was placed in the microwave reactor. The microwave power was set to 100W. Desired temperature and time were set. After the reaction, the tube was allowed to cool at room temperature. The conversion of fructose was analyzed with a LC98IIRI GPC with ZORBAX NH₂ column and the refractive index detector. The UV-visible spectrum of pure HMF solution has a distinct peak at 284nm. The yield of HMF was determined by measuring the absorbance of HMF product solution at 284nm using the standard curve method. Repeated measurement of the same solution showed the percentage of error associated with this measurement was $\pm 0.3\%$.²¹⁻²²

3. Results and discussion

3.1. Characterization of the catalyst 3.1.1. XRD patterns and FTIR measurement



Fig. 1. XRD patterns of different samples.

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Fig. 1 shows the XRD patterns of different catalysts, the samples showed diffraction peaks for 2θ =30.25°, 35.5°, 50.3° and 60°, it was estimated that zirconia essentially presented in the tetragonal form²⁴ and it had been generally accepted that the tetragonal phase was more important for the formation of acidic centers.²³ The bare nanosized ZrO₂ mainly existed in the monoclinic phase (m-ZrO₂), a stable phase under relatively high temperature; however, once WO_x was added, ZrO₂ dominantly crystallized in the tetragonal phase (t-ZrO₂), a metastable structure at low temperature.²⁴⁻²⁵ In addition, there was no diffraction line of the crystalline WO_x phase in the XRD patterns, implying that WO_x in these samples existed in a highly dispersed state on ZrO₂ surface and so do other samples else. The absorption spectra of UV-vis DRS are illustrated in ESI Figs.1, the band-gap energy (Eg) values of the samples are included in Table 1. The Eg of synthesized samples were lower than ZrO_2 , indicating that domain size became bigger and the transition-metal source existed in ZrO_{2}^{26-27} although the existence of the transitionmetal could not be analyzed by XRD.



The FT-IR spectra of the different catalysts are shown in Fig. 2. The band at 3438cm⁻¹ was attributed to O-H stretching vibrations of the physically absorbed water molecules, the band at 1632cm⁻¹ and 1388cm⁻¹ were attributed to HOH bending of water molecules associated with the sulfate group.²⁸ The band at 979cm⁻¹ was characteristic for stretching vibrations of W=O bond.²⁹ The band at 762cm⁻¹ was assigned to Mo=O stretching modes.³⁰ The sulfated samples exhibited strong bands at 1056, 1120, 1247cm⁻¹, which showed bidentate sulfate ion coordinated to the metal.³¹ These bands were absent in unsulfated samples. TEM images of samples are displays in ESI Figs.2, it revealed a globular structure. The average particles were obtained after calcination at 550°C. The size of the particles in the MO_x -ZrO₂ and SO_4^{2-}/MO_x -ZrO₂(M=W, Mo) samples were smaller than ZrO₂.





Fig. 3. Raman spectra of different samples

The Raman spectra of the different catalysts are shown in Fig. 3. All of them possessed the typical Raman signals of t-ZrO₂ at 641, 476, 312, and 274cm⁻¹ and only ZrO₂ showed obvious bands of m-ZrO₂,³² which conformed to the ZrO₂ phase detected by XRD characterization. A big Raman band from trace amounts of crystalline WO₃ NPS at 833 cm⁻¹ was present in the spectra for the WO_x-ZrO₂ catalyst sample, which reflected the good dispersion of the tungsten oxide phase on the ZrO₂ support;³³ the Raman band from trace amounts of crystalline MoO₃ NPS at 812 cm⁻¹ was present in the spectra for the MoO_x -ZrO₂ catalyst sample,³⁴ which reflected the good dispersion of the molybdenum oxide phase on the ZrO₂ support. The band at 962cm⁻¹ was attributed to the stretching vibration of M=O(M=W, Mo).^{23,35} The Raman spectra of SO₄²⁻/WO_x-ZrO₂ and SO₄²⁻/MoOx-ZrO₂ weren't measured, because they had a strong fluorescence effect.

The XPS spectra of the different catalysts are shown in Fig. 4. The O1s, Mo3d, Zr3d, S2p, W4f and Zr4p peaks of the samples demonstrated binding energies of 530.4, 232.6, 181.9, 168.7, 36.1 and 30.9eV, respectively.³⁶⁻³⁷ It directly confirmed the presence of W or Mo in the materials.







The NH₃-TPD profiles of the different catalysts are depicted in Fig. 5 to evaluate the acidity of the catalysts. The NH_3 -TPD profile of $SO_4^{2^2}$ /WO_x-ZrO₂ gave a wide region of stronger acid sites around 450°C and weak acid sites by the peak around 200°C. Although SO₄² /MoO_x-ZrO₂ showed a peak distributed at approximately 500°C but it was small. Nevertheless, other catalysts showed a broad peak of the amount max of acid sites around 200°C. It indicated that the acid strength of $SO_4^{2^-}/WO_x$ -ZrO₂ was much higher than others. The calculated amounts of acid sites via the UV spectrometry

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measurement were shown in Table 1, it was obvious that the sulfated samples exhibited higher surface acid amount than unsulfated samples, corresponding to the NH₃-TPD results. The highest acid amount of SO_4^{2-}/WO_x -ZrO₂ may be due to the enlargement of the surface area.³⁸⁻⁴⁰ Generally, the specific surface areas of the sulfated samples were slightly larger than the unsulfated samples, it may because the interaction between SO_4^2 and sample stabilized the sample against sintering producing thermally stable ZrO₂ structure.³⁸ Nitrogen adsorption-desorption isotherms and the average pore size distribution curves of the samples are shown in ESI Figs. 3-7. All the isotherms resemble the Type IV isotherms based on IUPAC classification with a large type H3 hysteresis loop, it indicated the presence of mesoporosity. The hysteresis loop was associated with the capillary condensation taking place in the mesopores signifying the preservation of the mesoporous structure even after crystallization at elevated temperature.⁴¹ The surface areas and pore size of samples measured by the BET method are included in Table 1. The specific surface area increased in the following order: $ZrO_2 < MoO_x/ZrO_2 <$ $SO_4^{2-}/MoO_y-ZrO_2 < WO_y/ZrO_2 < SO_4^{2-}/WO_y-ZrO_2$, this result proved that SO_4^{2}/WO_x -ZrO₂ may be an efficient catalyst, corresponding to the following reaction results.

Table 1 The physical properties of samples

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Catalyst	Surface area (m ² /g)	Pore size (nm)	Pore Volume (m²/g)	Qi (umol/g)	Eg (eV)
ZrO ₂	48.19	14.08	0.17	29.60	5.10
WO _x -ZrO ₂	139.70	7.59	0.22	131.42	3.75
MoO _x -ZrO ₂	64.23	4.74	0.08	76.36	3.19
SO4 ²⁻ /WOx-ZrO2	159.55	8.18	0.32	380.34	3.58
SO ₄ ²⁻ /MoO _x -ZrO ₂	82.75	5.35	0.11	256.71	2.91

All the findings presented above were consistent with the following general model (Scheme 2).⁴²⁻⁴⁴ The SO_4^{2-} was electron-withdrawing group, after it was introduced into material which could increased the formation of acidic centers.



3.2. Catalytic activities of various catalysts on fructose conversion and 5-HMF vield

3.2.1. The catalytic performances of different catalysts

The prepared samples were tested for fructose dehydration to 5-HMF at 140°C with the 5wt% fructose in DMSO for 5min. The reaction using 10wt%(catalyst amount with respect to fructose, g/g×100) of catalyst are shown in Table 2. It was found that all of the catalysts were active, furthermore, the addition of the heteroatom and the impregnation with H₂SO₄ influenced the catalytic activity. The yield increased in the following order: without catalyst<ZrO₂<MoO_x/ZrO₂<WO_x/ZrO₂<SO₄²⁻/MoO_x-ZrO₂<SO₄²⁻/WO_x-ZrO₂, corresponding to the specific surface area and surface acid amount. The activity of SO_4^{2-}/ZrO_2 was similar compared to SO_4^{2-} $/MoO_x$ -ZrO₂ and SO₄²⁻/WO_x-ZrO₂, but the reaction time was 20min. The addition of the heteroatom could shorten the reaction time, it may because the doped of heteroatom helped to stabilize the tetragonal phase of zirconia in the catalyst and inhibited the transformation from the metastable tetragonal phase to the monoclinic phase at the high calcination temperature,²⁴⁻²⁵ and the tetragonal phase was more important for the formation of acidic centers. The $SO_4^{2^-}/WO_x$ -ZrO₂ catalyst was found be the most active catalyst, it was attributed to the stable tetragonal phases and the amount of acidic sites in this catalyst. In addition, the SO_4^{2}/MoO_{x^-} ZrO₂ even had better catalytic effect, although the catalytic effect of SO_4^{2-}/MoO_x -ZrO₂ was poorer than SO_4^{2-}/WO_x -ZrO₂. Therefore, this work we mainly studied the dehydration of fructose into 5-HMF by using SO_4^{2-}/WO_x -ZrO₂ and SO_4^{2-}/MoO_x -ZrO₂ under microwaveassisted in dimethyl sulfoxide.

3.2.2. Effect of fructose concentration on the dehydration of fructose



Fig. 6. Influence of fructose concentration on the dehydration of fructose. (Reaction conditions: reaction temperature=140°C; catalyst amount=10wt%; reaction time=7min).

Table 2 Influence of the species of catalysts on the dehydration of fructose							
catalyst	Reaction solvent	Reaction time/min	Reaction temperature/°C	Fructose conversion/%	5-HMF yield/%	5-HMF selectivity/%	Ref.
无	DMSO	5	140	43.93	15.86	36.10	This work
ZrO ₂	DMSO	5	140	51.13	31.02	60.67	This work
WO _x -ZrO ₂	DMSO	5	140	67.66	53.03	78.38	This work
MoO _x -ZrO ₂	DMSO	5	140	61.74	47.26	76.55	This work
SO ₄ ²⁻ /WO _x -ZrO ₂	DMSO	5	140	87.52	70.88	80.99	This work
SO4 ²⁻ /MoO _x -ZrO ₂	DMSO	5	140	86.05	67.11	77.99	This work
SO ₄ ²⁻ /ZrO ₂	DMSO	20	140	93.60	72.80	77.78	[28]
TiO ₂	DMSO	5	140	-	54.10	-	[21]
AICI ₃	DMSO	5	140	-	71.30	-	[19]
ion-exchange resin	acetone-water	10	150	91.70	70.30	76.67	[10]

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Fig. 6 shows the effect of the fructose concentration on the dehydration of fructose. There was negligible effect on the dehydration of fructose when the fructose concentration was below 5wt%. The rate of fructose conversion had little effect when the fructose concentration was above 5wt%, but the HMF yield and the HMF selectivity decreased gradually with increasing initial fructose concentration. This was probably because self-polymerization of HMF or cross-polymerization between fructose and HMF would occur easily at higher initial concentration of fructose,¹⁰ giving rise to the formation of brown black soluble polymers and insoluble humins.¹⁹ In addition, it was obvious that the catalytic effect of SO_4^{-2}/MOA_x -ZrO₂ was poorer than SO_4^{-2}/WOx -ZrO₂, but the variation trend of the fructose conversion (the HMF yield and the HMF selectivity) was similar. So, in conclusion, we took 5wt% as the initial fructose concentration in this work.



Fig. 7. Influence of the catalyst amount on the dehydration of fructose. (Reaction conditions: fructose concentration=5wt%; reaction time=5min; reaction temperature=140°C).



Fig. 8. Influence of reaction time and temperature on fructose conversion and Arrhenius linearity fitting curve (a: SO_4^2/WO_x -ZrO₂,b: SO_4^2/MO_x -ZrO₂. Reaction conditions: catalys amount=10wt%; fructose concentration=5wt%)

3.2.3. Influence of the catalyst amount on the dehydration of fructose

Fig. 7 shows the effect of the catalyst amount with respect to fructose conversion, 5-HMF yield and 5-HMF selectivity. The amount of catalyst used were 5 wt%, 10 wt%, 20 wt% and 30 wt% (catalyst amount with respect to fructose, g/g×100) respectively. In the absence of catalyst, only 15.86% yield of 5-HMF yield were attained at 140°C for a reaction time of 5min in DMSO, nevertheless the 5-HMF yield reached to 61.06% (SO_4^{2-}/WO_x -ZrO₂) and 54.21% $(SO_4^{2^-}/MoO_x-ZrO_2)$ when 5wt% catalysts were added. It firmly indicated that SO_4^{2-}/WO_x -ZrO₂ and SO_4^{2-}/MoO_x -ZrO₂ showed excellent catalytic performance for the dehydration of fructose to 5-HMF. When the catalyst dosage increased from 5wt% to 10wt%, the 5-HMF yield still increased at 140°C for a reaction time of 5min, it was because that the catalytic sites increased with the increasing amount of catalyst, boosting the dehydration reaction. However, when we kept increasing the amount of catalyst, there was a smooth in fructose conversion and 5-HMF yield, this was probably

because the side reaction in the dehydration of fructose also accelerated under over-using of catalyst. Given the above discussion, it was evident that 10wt% of catalyst provided the best result for the model reaction.

3.2.4. Influence of different reaction time and temperature on the dehydration of fructose and Kinetics Analysis.

The Fig. 8 shows the influence of different reaction time and temperature on fructose conversion. It was obvious that the reaction temperature and time had a significant effect on the fructose conversion. While the reaction temperature increased, the fructose conversion increased. As the reaction proceeded, the fructose conversion also increased, when prolonging the reaction time to 5 min, fructose conversion was almost a constant at 160°C. When temperature was 140°C, fructose conversion was almost a constant for 7min, it showed that increased reaction temperature could shorten the reaction time. Many works reported a reaction order of one for the dehydration of fructose to 5-HMF. We performed a kinetic analysis of the dehydration of fructose

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Table 3 Comparison of Activation Energies and Pre-Exponential Factors for Acid-Catalyzed Fructose Dehydration to 5-HMF

Ea(KJ/mol)	A(min ⁻¹)	Reaction solvent	Catalyst	Ref
68.31	1.45×10 ⁸	DMSO	SO ₄ ²⁻ /WO _x -ZrO ₂	This work
69.31	1.80×10 ⁸	DMSO	SO ₄ ²⁻ /MoO _x -ZrO ₂	This work
99.20	2.10×10 ⁸	DMSO	[BMIM]OH	[45]
96.00	1.79×10 ⁸	Subcritical water	ZnSO ₄	[46]
60.40	4.80×10 ⁶	70:30(w/w) acetone/DMSO	ion-exchange resin	[47]
103.40	8.70×10 ¹¹	70:30(w/w) acetone/water	ion-exchange resin	[10]
80.00	3.10×10 ⁸	Supercritical methanol	H ₂ SO ₄	[48]
160.60	-	Aqueous solution	HCI	[49]

catalyzed by SO_4^{2-}/WO_x -ZrO₂ and SO_4^{2-}/MoO_x -ZrO₂ in DMSO. Values of ln(1-x) were plotted against reaction time(t) to obtain first-order kinetic constants. With those constants, an Arrhenius plot was generated, as shown in Fig. 8. This model had been employed in most of the kinetic studies and was found to give reasonable levels of agreement with experimental data.⁴⁵⁻⁴⁹ The activation energies and pre-exponential factors for acid-catalyzed fructose dehydration to 5-HMF obtained by different authors under different conditions are summarized in Table 3. The obtained activation energies and pre-exponential factors from this work were similar, it may depend on the same solvents and heating methods used, $^{\rm 47}$ on the other hand, considering the experimental error/standard deviation, we could know the SO_4^{2-}/MoO_x -ZrO₂ and SO_4^{2-}/WO_x -ZrO₂ exhibited similar catalytic activities. Compared to the previous values reported in the literature, it showed that the present process was more efficient than previous works as evident from the shorter reaction times.

The Fig. 9 shows the influence of different reaction time and temperature on the 5-HMF yield and 5-HMF selectivity. The 5-HMF yield and selectivity increased with reaction temperature, the temperature played a positive role on the dehydration of fructose. When the temperature increased up to 160° C, the yield of 5-HMF was slightly decreased, but the selectivity of 5-HMF was significantly declined. When the catalyst was SO_4^{-2}/WO_x -ZrO₂, it

showed the fructose conversion of 94.97% with 82.55% 5-HMF selectivity in 1min reaction time at 160°C. In addition, with the extending of reaction time, the 5-HMF yield and selectivity were improved consistently. When the reaction time was extended up to 7min and longer at 150°C, the 5-HMF yield decreased. But when the temperature was above 160°C, the 5-HMF yield and selectivity was decreased consistently. The variation trend of the HMF yield and selectivity for SO_4^{-2}/MOO_x -ZrO₂ were similar to SO_4^{-2}/WO_x -ZrO₂, it showed the fructose conversion of 95.33% with 81.64% 5-HMF selectivity in 3min reaction time at 160°C. In conclusion, it was generally noted that higher temperatures (>140°C) and longer reaction times (>5min) resulted in a loss of yield expectedly on account of by-product formation and/or decomposition of HMF.

4. Conclusions

Through this study, the ZrO₂, WO_x/ZrO₂, MOO_x/ZrO₂, SO₄²⁻/WO_x-ZrO₂ and SO₄²⁻/MOO_x-ZrO₂ solid catalysts were prepared and characterized by XRD, UV-DRS, FTIR, XPS, TEM, TPD, BET, Raman and the surface acid amount was obtained combining pyridine adsorption and UV spectrometry. These catalysts were employed in dehydration of fructose to 5-HMF under microwave-assisted in DMSO, the SO₄²⁻/WO_x-ZrO₂ catalyst was found be the most active catalyst, the fructose conversion of 95.80% with 83.90% of 5-HMF yield was obtained at 150°C for a relatively short reaction time of



Fig. 9. Influence of reaction time and temperature on 5-HMF yield and 5-HMF selectivity (a:SO₄²⁻/WO_x-ZrO₂,b:SO₄²⁻/MOO_x-ZrO₂.Reaction conditions: catalyst amount=10wt%; fructose concentration=5wt%)

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5min. The catalyst amount and fructose concentration were further optimized. The value of activation energy was comparable with previous values reported in the literature, this implied that the SO_4^{2-} /WO_x-ZrO₂ and SO_4^{2-} /MoO_x-ZrO₂ were efficient for the dehydration of fructose to 5-HMF under microwave-assisted in DMSO.

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