




# Role of Brønsted and Lewis acidic sites in sulfonated Zr-MCM-41 for the catalytic reaction of cellulose into 5-hydroxymethyl furfural

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## Abstract

A series of sulfonated Zr-MCM-41 samples were synthesized by the in-situ method followed by sulfonation using sulfuric acid for the catalytic study of cellulose to 5-hydroxymethyl furfural in batch condition. All synthesized catalysts were characterized by XRD, N<sub>2</sub> adsorption–desorption isotherm, FT-IR, TEM, EDX, and NH<sub>3</sub> temperature-programmed desorption analysis. The XRD and N<sub>2</sub> adsorption–desorption isotherm results have confirmed that incorporated Zr<sup>4+</sup> was substituted within the framework of silica MCM-41 with hexagonal pores. Similarly, the FT-IR and EDX results have proved that Zr-MCM-41 was sulfonated. The Brønsted acidic and Lewis acidic sites were identified by NH<sub>3</sub>-TPD analysis. Among the sulfonated Zr-MCM-41 catalysts, S-15Zr-MCM-41 has shown 70% cellulose conversion with 16.4% selectivity of 5-hydroxymethyl furfural at 170 °C for 2 h which was higher than other catalysts. It was attributed to the high ratio of Brønsted acidic to Lewis acidic sites.

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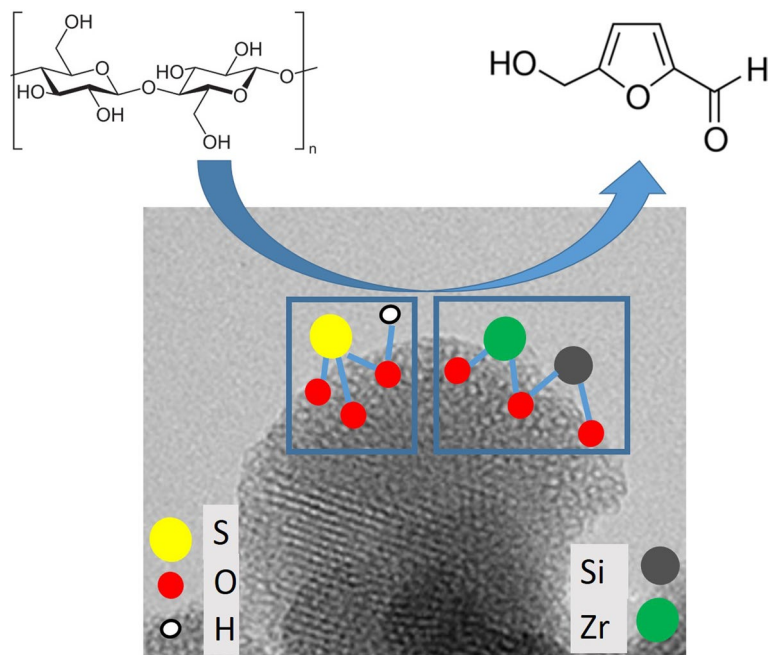
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## Graphic abstract



**Keywords** Zr-MCM-41 · Sulfonation · Brønsted & Lewis acidity · Cellulose · 5-HMF

## Introduction

5-Hydroxymethyl furfural (5-HMF) is a major important platform chemical that can be produced from cellulose and hemicellulose by hydrolysis in the acidic medium [1–3]. It is an intermediate in biomass-based carbohydrate chemistry and petroleum-based industrial chemistry to produce chemicals and fuels [4, 5]. Production of 5-HMF from cellulose involves 3 steps catalytic mechanism: hydrolysis of cellulose to glucose by Brønsted acid, isomerization of glucose to fructose by Lewis acid assistance, and dehydration of fructose to 5-HMF by Brønsted acid [6]. Few research groups have studied the conversion of cellulose to 5-HMF using homogeneous catalysts such as  $\text{H}_2\text{SO}_4$ ,  $\text{HCl-AlCl}_3$ ,  $\text{CrCl}_2\text{-CrCl}_3$ ,  $\text{ZrOCl}_2/\text{CrCl}_3$  [7–11]. However, they have reported some issues such as lack of separation of the catalyst, corrosion, and toxicity. These can be overcome by the use of solid acid catalyst [12–17].

As mentioned above, the conversion of cellulose to 5-HMF is catalyzed by Brønsted acidic and Lewis acidic sites. For this purpose, bifunctional solid acid catalysts have been developed and used. Mazzotta et al. have reported the effectiveness of  $\text{Ti(IV)-HSO}_3$  catalyst for the dehydration of cellulose, glucose, and fructose. They

depicted the dual role of Brønsted acidic and Lewis acidic sites for biomass conversion [18]. Similarly, Osatiashtiani et al. have used bifunctional sulfonated zirconia (S-ZrO<sub>2</sub>) catalyst for the conversion of glucose to 5-HMF [6]. The effectiveness of this catalyst was increased by impregnation on mesoporous silica, SBA-15 [19]. Mesoporous silica materials like SBA-15 and MCM-41 have been widely used as support due to high surface area 600–1200 m<sup>2</sup>/g and tunable pore size 2–50 nm [20–22].

Based on the above concept, in this article, we have studied the catalytic reaction of cellulose to 5-HMF in a batch reactor using sulfonated Zr-MCM-41 catalysts synthesized by in-situ method followed by sulfonation. Moreover, the role of Brønsted acidic and Lewis acidic sites presented in the synthesized catalyst useful for the catalytic reaction was also discussed.

## Experimental

### Materials

Analytical grade chemicals like zirconium (IV) sulfate (Zr(SO<sub>4</sub>)<sub>2</sub>), Tetraethyl orthosilicate (SiC<sub>8</sub>H<sub>20</sub>O<sub>4</sub>, TEOS), ammonium hydroxide (NH<sub>5</sub>O, 25wt%), cetyltrimethylammonium bromide (C<sub>19</sub>H<sub>42</sub>BrN, CTABr), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), cellulose ((C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>) and 5-hydroxy methyl furfural (C<sub>6</sub>H<sub>6</sub>O<sub>3</sub>) were purchased from the M/s. Sigma Aldrich Chemicals Pvt. Ltd., Vietnam, and used without purification.

### Synthesis of MCM-41 and sulfonated Zr-MCM-41

MCM-41 was synthesized by the soft template method using CTABr as a template. The desired quantities of TEOS, CTABr, and NH<sub>4</sub>OH were mixed in a glass beaker until a homogeneous solution was obtained. The mixture was transferred into a Teflon lined autoclave and kept at 100 °C for 24 h. A white precipitate was formed. It was filtered and washed with distilled water then dried at 100 °C for 12 h. Finally, it was calcined at 550 °C for 4 h in static air. We obtained MCM-41 [23]. Zr-MCM-41 was synthesized using the same procedure as that of MCM-41 with Zr/Si ratio (4, 8, 12, 15, 20 wt%). To sulfonate Zr-MCM-41, it was treated with 1 M H<sub>2</sub>SO<sub>4</sub> at room temperature for 1 h followed by filtration and washed with distilled water then dried at 100 °C for 12 h. We obtained sulfonated Zr-MCM-41 and labeled as S-xZr-MCM-41, where x represents the wt% of Zr loaded.

### Characterization

The X-ray diffractions were recorded using a D8 Advance X-ray diffractometer having Ni filtered Cu K<sub>α</sub> radiation in the range from 2θ=0.7–70° with a scan speed of 2°/min. The N<sub>2</sub> adsorption–desorption isotherms were measured using Micromeritics Tristar 3000 gas adsorption analyzer at 77 K. Before the isotherm measurement, 0.1 g of sample was activated at 200 °C for 3 h under vacuum to remove

moisture. The surface area was calculated by the multipoint BET method, total pore volume at  $P/P_0=0.99$ , and pore size by the BJH method. TEM images were recorded using FEI TECNAI G2 20 X-Twin high-resolution transmission electron microscopy operated at high voltage 200 kV. Energy-dispersive X-ray spectroscopy analysis was performed using Hitachi S-4700 scanning electron microscopy. FT-IR spectra were recorded on the JASCO FT-IR-4100 spectrometer in the range from  $4000 - 400 \text{ cm}^{-1}$  with a resolution of  $4 \text{ cm}^{-1}$  using the KBr disc method. Ammonia temperature-programmed desorption ( $\text{NH}_3$ -TPD) was measured using Micromeritics Autochem-II 2920 analyzer from  $100\text{--}600 \text{ }^\circ\text{C}$  with a heating rate of  $10^\circ/\text{min}$ .

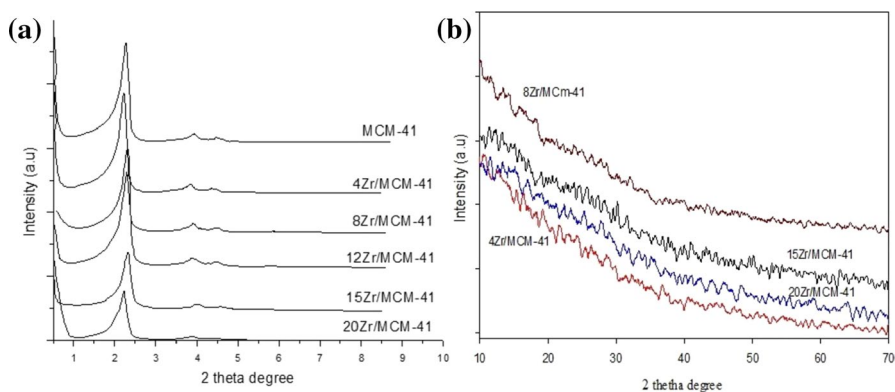
### Catalytic study of S-Zr-MCM-41

The catalytic reaction of cellulose to 5-HMF using S-Zr-MCM-41 catalysts was carried out in a Teflon-lined stainless steel reactor equipped with a mechanical stirring system. The reaction mixture, 2 g cellulose, 0.2 g catalyst, and 10 mL water were transferred into 50 mL reactor then the temperature was raised to  $170 \text{ }^\circ\text{C}$  with a heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$  and kept at this temperature for 2 h with a rotation speed of 400 rpm/min. The reaction products were collected by centrifugation and analyzed using GC-MS Agilent 7890A with MS detector.

## Results and discussion

### X-ray diffraction analysis

The low and wide-angle XRD patterns of MCM-41 and sulfonated Zr-MCM-41 were shown in Fig. 1. MCM-41 has shown 3 peaks at  $2\theta=2^\circ$ ,  $3.7^\circ$  and  $4.4^\circ$  with reflections planes (100), (110) and (200) respectively (JCPDS No. 00-049-1712) which were the main characteristic peaks of hexagonal mesoporous MCM-41 with a space group  $P6mm$  (Fig. 1a) [24]. Zr-MCM-41 catalysts have also shown



**Fig. 1** XRD of MCM-41 and sulfonated Zr-MCM-41: **a** low angle and **b** wide-angle

a low angle XRD pattern similar to bulk MCM-41. However, a decrease in the intensity of major peaks has been observed with an increase in the amount of Zr. In wide-angle XRD of MCM-41 and Zr-MCM-41 samples, no diffraction peaks have appeared (Fig. 1b) [25]. The lattice parameters  $d_{100}$  and  $a_0$  for all synthesized samples were presented in Table 1. The d-spacing ( $d_{100}$ ) and unit cell parameter constant ( $a_0$ ) were higher for higher loadings of Zr (12, 15, and 20 wt%) compared with bare MCM-41 because of the replacement of  $\text{Si}^{4+}$  by  $\text{Zr}^{4+}$  in the framework. Consequently, a change in lattice parameters has been observed.

## **N<sub>2</sub> adsorption–desorption isotherms**

The N<sub>2</sub> adsorption–desorption isotherms of MCM-41 and sulfonated Zr-MCM-41 at 77 K were shown in Fig. 2 and textural properties were presented in Table 1. For MCM-41, a hysteresis loop has been observed above the relative pressure  $P/P_0=0.85$  [26]. The isotherm curve of MCM-41 was similar to Type-IV with the H1 hysteresis loop of classification of the porous materials by IUPAC [27]. Therefore, it has mesopores. For sulfonated Zr-MCM-41 samples, a hysteresis loop has not appeared. It was due to the shrinkage of pore size by sulfonation. The calculated specific surface area, pore-volume, and pores size of MCM-41 was 1191 m<sup>2</sup>/g, 1.99 cm<sup>3</sup>/g, and 6.1 nm respectively. MCM-41 and S-4Zr-MCM-41 have shown surface area nearly the same. Further increase in Zr content, a change in textural properties has been observed. The surface area was reached to 874 m<sup>2</sup>/g, pore volume 0.74 cm<sup>3</sup>/g and pore size 3.6 nm. It was due to deformation effect of Zr ions incorporated into the structure of MCM-41.

**Table 1** The lattice parameters and textural properties of MCM-41 and sulfonated Zr-MCM-41

Sample	$d_{100}^a$ (nm)	$a_0^b$ (nm)	$S_{\text{BET}}^c$ (m <sup>2</sup> /g)	$S_{\text{mesopore}}^d$ (m <sup>2</sup> /g)	$V_{\text{total}}^e$ (cm <sup>3</sup> /g)	Pore size <sup>f</sup> (nm)
MCM-41	3.92	4.53	1191	826	1.99	6.1
S-4Zr-MCM-41	3.93	4.53	1243	825	1.27	3.7
S-8Zr-MCM-41	3.94	4.55	1040	664	0.91	3.5
S-12Zr-MCM-41	4.27	4.94	913	601	0.85	3.6
S-15Zr-MCM-41	4.34	5.01	1022	591	0.75	3.1
S-20Zr-MCM-41	4.23	4.89	874	575	0.74	3.6

<sup>a</sup>d-spacing at (100)

<sup>b</sup>unit cell parameter ( $a_0=2d_{100}/\sqrt{3}$ )

<sup>c</sup>BET surface area

<sup>d</sup>mesopore surface area

<sup>e</sup>total pore volume

<sup>f</sup>pore size by BJH method

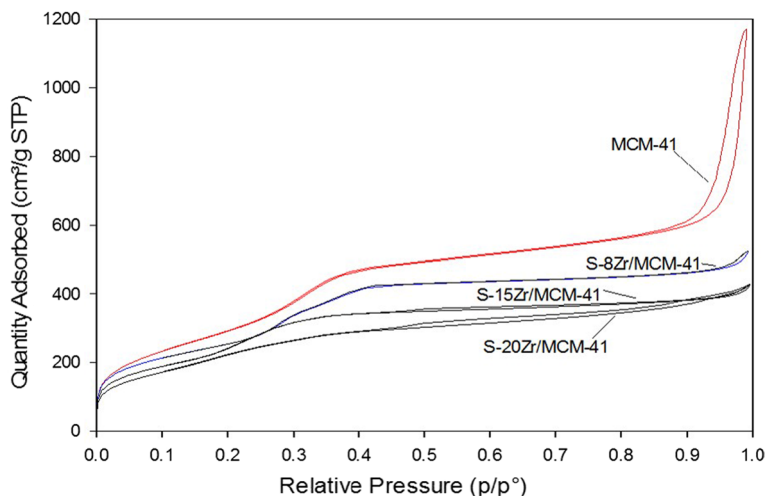


Fig. 2  $N_2$  adsorption–desorption isotherms of MCM-41 and sulfonated Zr-MCM-41

### FT-IR analysis

FT-IR spectra of MCM-41 and sulfonated Zr-MCM-41 catalysts were shown in Fig. 3. For MCM-41, the bands appeared at  $3450\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$  represented the stretching and bending vibrational bands of the O–H group of water. The symmetric and asymmetric vibrational bands of the Si–O–Si group have

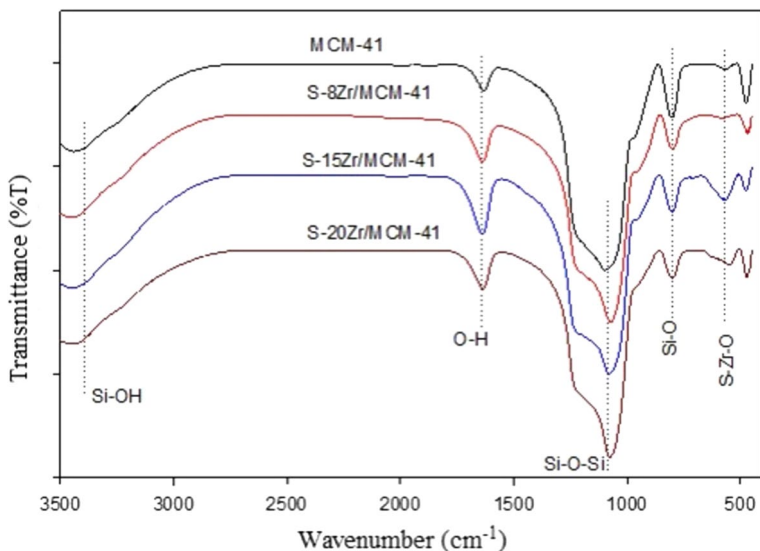
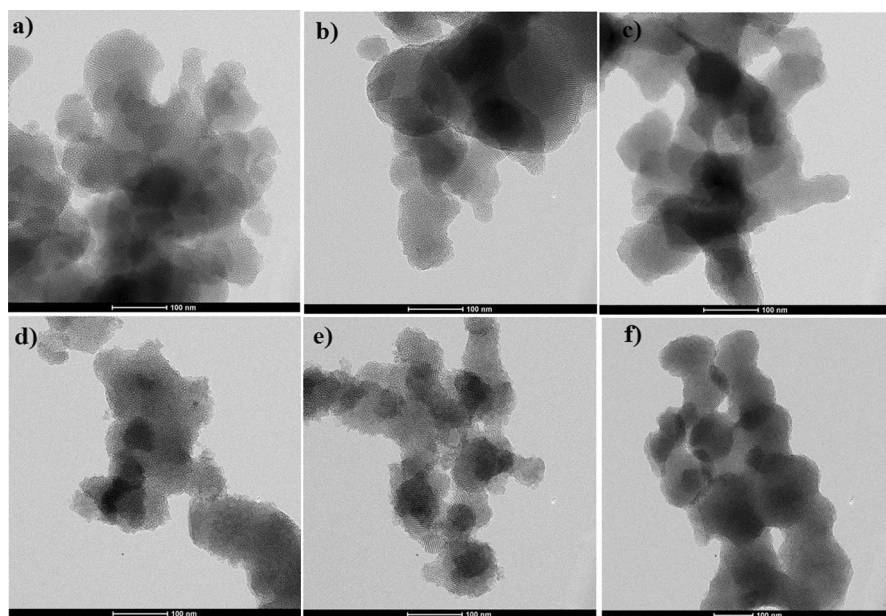


Fig. 3 FT-IR spectra of MCM-41 and S-Zr-MCM-41 samples

appeared at  $1084\text{ cm}^{-1}$  and  $826\text{ cm}^{-1}$  respectively. Moreover, the band appeared at  $465\text{ cm}^{-1}$  represented the bending vibrational band of Si–O–Si (or) Zr–O–Si [25, 28]. In sulfonated Zr-MCM-41 samples, the major vibrational bands of MCM-41 have been replicated. Along with this, the  $\text{SO}_2$  deformation band also appeared at  $550\text{ cm}^{-1}$  [29]. Hence, FT-IR analysis has confirmed that the sulfonate group has been attached to the walls of Zr-MCM-41.

### TEM and EDX analysis

Fig. 4 shows the TEM images of MCM-41 and sulfonated Zr-MCM-41. Ordered hexagonal pores were obtained for MCM-41 (Fig. 4a). For sulfonated Zr-MCM-41 samples, the same hexagonal pore structure was obtained. However, the particles correspond to zirconium oxide have not appeared. It confirmed that the incorporated zirconium was interconnected with the framework of MCM-41. The TEM analysis result was correlated with XRD. The content of zirconium in sulfonated Zr-MCM-41 samples was determined using energy-dispersive X-ray spectroscopy. Table 2 shows the elemental composition of sulfonated Zr-MCM-41 samples. Experimentally obtained Zr (wt%) was near to theoretically loaded amount. The amount of Sulphur in each sample was 10–12.5 wt%. It was also confirmed the presence of sulfur in the sulfonated Zr-MCM-41 samples.



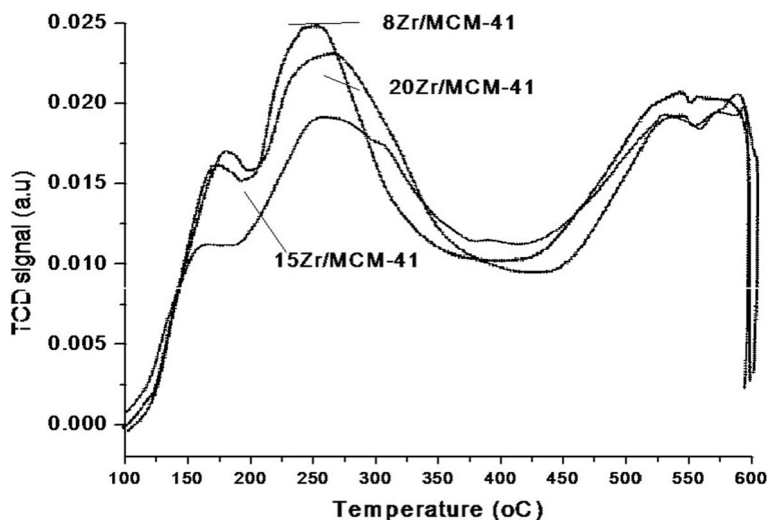
**Fig. 4** TEM images of **a** MCM-41, **b** S-4Zr-MCM-41, **c** S-8Zr-MCM-41, **d** S-12Zr-MCM-41, **e** S-15Zr-MCM-41, and **f** S-20Zr-MCM-41 (scale bar- 100 nm)

**Table 2** Elemental composition of sulfonated Zr-MCM-41 samples from EDX

Sample	Elements		
	Silicon (wt%)	Zirconium (wt%)	Sulphur (wt%)
S-4Zr-MCM-41	85.95	3.84	10.21
S-8Zr-MCM-41	81.27	7.23	11.50
S-12Zr-MCM-41	77.73	10.02	12.25
S-15Zr-MCM-41	73.44	14.78	11.78
S-20Zr-MCM-41	69.54	16.78	10.68

### Temperature programmed desorption of NH<sub>3</sub>

Ammonia temperature-programmed desorption profile of S-8Zr-MCM-41, S-15Zr-MCM-41, and S-20Zr-MCM-41 was shown in Fig. 5. The amount of NH<sub>3</sub> desorbed was presented in Table 3. Each sample has shown 3 desorption peaks in between the temperatures 140–170 °C, 250–270 °C and 470–570 °C which correspond to physisorbed ammonia, Brønsted acidic and Lewis acidic sites respectively [30]. By substitution of Si<sup>4+</sup> by Zr<sup>4+</sup> created Lewis acidic sites whereas sulfonated Zr-MCM-41 sample has generated Brønsted acidic sites (SO<sub>3</sub>H<sup>-</sup>). The total amount of NH<sub>3</sub> desorbed was 1.807 mmol/g for S-8Zr-MCM-41, 1.809 mmol/g for S-15Zr-MCM-41, and 1.259 mmol/g for S-20Zr-MCM-41. The catalyst S-8Zr-MCM-41 has shown high Lewis acidic sites whereas S-15Zr-MCM-41 has shown high Brønsted acidic sites. The order of the ratio of Brønsted acidic site to Lewis acidic site was S-15Zr-MCM-41 > S-8Zr-MCM-41 > S-20Zr-MCM-41. The synergetic of the skeleton

**Fig. 5** NH<sub>3</sub> temperature-programmed desorption of S-Zr-MCM-41 samples



**Table 3** Amount of NH<sub>3</sub> desorbed for S-Zr-MCM-41 samples

Sample	NH <sub>3</sub> desorbed (mmol/g)			Total NH <sub>3</sub> desorbed (mmol/g)	Ratio of B/L <sup>a</sup>
	T <sub>max</sub> 140–170 °C	T <sub>max</sub> 250–270 °C	T <sub>max</sub> 470–570 °C		
S-8Zr-MCM-41	0.415	0.799	0.593	1.807	1.347
S-15Zr-MCM-41	0.404	0.986	0.419	1.809	2.353
S-20Zr-MCM-41	0.385	0.490	0.384	1.259	1.276

<sup>a</sup>Ratio of Bronsted acidic/Lewis acidic sites

structure, Zr loading and Sulphur surface concentration lead to variation in the type of acidic site strength.

### Catalytic conversion of cellulose to 5-HMF

MCM-41 and sulfonated Zr-MCM-41 catalysts have been used for the catalytic conversion of cellulose to 5-HMF in the Teflon lined stainless steel reactor. The results were presented in Table 4. The conversion of cellulose without catalyst was 1.3% at 170 °C for 2 h. For MCM-41, the conversion was increased to 15.2% and S-Zr-MCM-41 catalysts 63.3–70.2%. The selectivity and yield of 5-HMF were higher with the increase in the amount of Zr. Yayati et al. have studied silica-supported tin catalyst for the catalytic reaction of glucose. It has converted glucose into fructose by isomerization because of the Lewis acidic nature of the catalyst [31]. In this article, the synthesized catalyst sulfonated Zr-MCM-41 has both Brønsted acidic and Lewis acidic sites. So, it converted cellulose into 5-HMF. Among the synthesized sulfonated Zr-MCM-41 catalysts, high conversion of cellulose and 5-HMF selectivity was obtained for S-15Zr-MCM-41 because of the high ratio of Brønsted acidic to Lewis acidic sites (NH<sub>3</sub>-TPD analysis). Therefore, the catalyst which has Brønsted acidic and Lewis acidic properties are useful for the hydrolysis of cellulose and

**Table 4** Catalytic reaction of cellulose to 5-hydroxymethyl furfural at 170 °C for 2 h

Catalyst	Conversion of cellulose (%)	Selectivity of 5-HMF (%)	Yield of 5-HMF (%)
No catalyst	1.3	0.8	0.01
MCM-41	15.2	1.3	0.2
S-4Zr-MCM-41	63.3	3.0	1.9
S-8Zr-MCM-41	64.5	10.6	6.8
S-12Zr-MCM-41	69.5	11.4	9.0
S-15Zr-MCM-41	70.2	16.4	11.5
S-20Zr-MCM-41	68.6	9.4	6.4

cellulose derivatives. In the forthcoming article, we want to study the optimization of catalyst quantity, temperature, reaction time, and recyclability.

## Conclusion

In this work, we have systematically studied the catalytic conversion of cellulose to 5-hydroxymethyl furfural using MCM-41 and sulfonated Zr-MCM-41 catalysts in a batch reactor. The characterization results have stated that replacement of  $\text{Si}^{4+}$  with  $\text{Zr}^{4+}$  in MCM-41 by in-situ synthesis, the existence of hexagonal mesopores, attachment of sulfate groups to the walls of Zr-MCM-41, and the presence of Bronsted acidic and Lewis acidic sites. The high catalytic conversion of cellulose and selectivity of 5-HMF was obtained for S-15Zr-MCM-41 at 170 °C, for 2 h because of the high ratio of Brønsted acidic to Lewis acidic sites.

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