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Volume 40 | Number 1 | January 2016 | Pages 1–846

NJC

New Journal of Chemistry
www.rsc.org/njc

A journal for new directions in chemistry

ISSN 1144-0546

ROYAL SOCIETY OF CHEMISTRY

PAPER
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DOI: 10.1039/C9NJ01311C

Sulfated Zirconia an Efficient Catalyst for the Friedel-Crafts Monoalkylation of Resorcinol with Methyl tertiary butyl ether to 4-Tertiary butylresorcinol

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View Article Online
DOI: 10.1039/C9NJ01311C

Abstract

Friedel-Crafts alkylation of resorcinol with methyl tertiary butyl ether was carried out over sulfated zirconia (SZ) catalysts in the liquid phase. The SZ catalysts were synthesized by impregnation method with different sulfur amounts and characterized by XRD, FT-IR, Nitrogen sorption, XPS, SEM, Pyridine-FTIR, and NH_3-TPD. The effect of sulfur loading on the total acidity and catalytic activity was investigated. The influence of the nature of the solvents on the alkylation reaction was inspected in terms of their acceptor and donor numbers. The sulfur loading, amount of solvent, temperature, catalyst amount, mole ratio and reusability of catalyst were examined. The SZ catalyst synthesized by impregnating 1N sulfuric acid was found to be highly selective for the monoalkylation to 4-tertiary butyl resorcinol (72%) with the resorcinol conversion of ~70%. The catalyst was recycled thrice with a negligible decrease in the yield for 4-tertiary butylresorcinol. The SZ exhibited the best performance at low temperature (60 °C) among the different types of solid acid catalysts studied so far.

Keywords: sulfated zirconia; resorcinol; 4-tertiary butyl resorcinol, Friedel-Crafts reaction

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1. Introduction

Alkylation of aromatics is one of the important reactions in organic chemistry due to its wide application in the petrochemicals, fine chemical, perfume, dye and pharmaceutical industries.[1-2] Among them, Friedel-Crafts butylation of resorcinol to produce mono-*tert* butylated products is of the most significant due to its involvement in the synthesis of antioxidants, polymer stabilizers, therapeutics, and organic synthetic applications.[2-4] The alkylation of resorcinol with methyl tertiary butyl ether (MTBE) gives mixture of alkylated benzenediols and ethers. Being thermodynamically favoured, the dialkylated 4,6-di-*tert*-butyl resorcinol (4,6-DTBR) is usually the major product.[5] However, the 4-tert-butylresorcinol(4-TBR) is of particular interest as antioxidants in food preservative and in treatment of skin diseases. Therefore, selective synthesis of 4-TBR at high conversion of resorcinol is a difficult and challenging task for the catalyst designer.[6]

Traditionally, homogeneous Lewis ($AlCl_3$, $FeCl_3$) and Brönsted acids (H_2SO_4, H_3PO_4) catalysed the reaction.[4] However, the limitation and hazardous nature of these conventional acid catalysts have been replaced by the use of heterogeneous catalysts. There are few solid acid catalysts that have been studied for the reaction such as montmorillonite clay, zeolites, ZrO_2 supported phosphotungstic acid, dodecatungstophosphoric acid supported on K-10, sulfated mesoporous Al_2O_3 and heteropolyacid supported mesoporous materials.[1-6] However, the reactions over these catalysts were carried out at high temperature and/or pressure, with moderate yields for 4-TBR .

Over the past two decades, application of anion modified metal oxides for catalysis have received more attention.[7-8] ZrO_2 has been commonly utilized as a support. However, robust acid sites can also be generated on ZrO_2 by modifications with WO_4^{2-}, SO_4^{2-} and MoO_4^{2-} ions.[8] Among these, SO_4^{2-} modified ZrO_2 catalyst attracted much attention because of its high activity

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in alkane isomerization at low temperature.[9] The H_2SO_4 treatment of ZrO_2 generates Brönsted and Lewis acid sites on it, and these active sites induce a super acidity in the resulting sulfated zirconia (SZ). Thanks to their acidic nature, SZ were further exploited in bulk petrochemical processes like alkylation, acylation, isomerization and cracking. Simple synthesis procedure, excellent thermal stability, resistance to thermal extrusion, and low cost offer several advantages over other solid acid catalysts. Thus, continuous development of this catalyst generated interest in the synthesis of fine and specialty chemicals like nopol, 1.4-dioxane, coumarins, organic esters, N, N'-diphenylene diamines etc.[7, 10-13] The SZ catalyst was utilized as an acid catalyst for the various Friedel-Crafts alkylation reactions such as alkylation of diphenyl oxide with benzyl chloride, alkylation of guaiacol and *p*-Cresol with cyclohexene, alkylation of 4-methoxyphenol with MTBE and alkylation of benzene with benzyl chloride.[7] The alkylation of catechol and anisole with MTBE was also studied over SZ catalyst but a low catalytic activity was observed.[4] However, to the best of our knowledge, SZ catalyst has not been studied so far for alkylation of resorcinol with MTBE to produce 4-TBR.

Recently, we reported heteropolyacid supported silica as an active catalyst for the alkylation of resorcinol.[6] In continuation of our investigation of simple, efficient and active catalyst for this reaction, herein we report the application of SZ as a solid acid catalyst for the conversion of resorcinol to 4-TBR. In this study, SZ catalyst with different sulfur loadings was synthesized and studied for the alkylation reaction. The effect of sulfation, the nature of the solvent used and the recyclability of the catalysts were investigated. The physicochemical properties of the catalysts were correlated with the activity of the alkylation reaction.

2. Materials and Methods

2.1. Catalyst Preparation

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SZ catalysts were prepared by the method as reported in the literature.[12] $Zr(OH)_4$, from the MEL Chemicals, Manchester, UK, was treated with different concentrated solutions of H_2SO_4 and calcined at high temperature. In a typical procedure, 10 g of $Zr(OH)_4$ was stirred into the 100 ml of a H_2SO_4 solution of the desired concentration (0.5N, 1N, 2N, 3N, 4N). After stirring for 60 min, the catalyst was filtered, washed with water, dried and finally calcined at different temperatures (500 and 650 ˚C) for 4 h. Obtained catalysts are indicated by the term SZ-X-T, where X stands for the concentration of H_2SO_4 used and T stands for the calcination temperature. SZ-T indicates the whole series of catalysts treated with different concentrations of H_2SO_4 but all calcined at the same temperature T. For comparison purpose, 10% Ga-BEA zeolite and 20% DTP/K10 catalysts were synthesized by the literature method.[2-4]

2.3. Catalyst characterization

The phase purity and crystalline properties of all SZ catalysts were determined by the X-ray diffraction on a Siemens D5000 diffractometer equipped with a Cu Kα source. The samples were analysed in the 2 theta range of 5 and 80° with a scan rate of 0.02°/s. The sulfur present on the catalyst was determined by the CHNS analysis using Thermo Finnigan FLASH EA 1112 CHNS analyzer.[14]

Specific surface area, pore volume, and pore size distributions were obtained through N_2 sorption experiments performed using a Micrometrics Tristar 3000. Before the measurements, catalysts were degassed overnight under vacuum (6 Pa) at 150 °C. The measurements were performed at −196 °C and with relative pressures in the range of 0.01–1.00 (p/p_0). The specific surface area was calculated from the adsorption isotherm in the p/p_0 relative pressure range of 0.05–0.30 using the Brunauer–Emmett–Teller method (BET). The pore size distribution, mean

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pore diameter, and pore volume were calculated by the Barrett–Joyner–Halenda method (BJH) using the data from the isotherm desorption branch.[6]

Surface acidity measurements of the SZ catalyst were done by pyridine adsorption technique as reported earlier.[6] The wafers of SZ catalyst were prepared, weighed and then placed in a sample holder inside a Pyrex cell specially designed for the controlled heating of the sample under vacuum and equipped with an optical NaCl window. In a typical measurement, the catalyst was pre-treated at 300 °C under vacuum (between 10^{-4} and 10^{-5} Pa) for 2 h in order to remove impurities from the surface. After cooling under vacuum, 1000 Pa of pyridine was sent at room temperature in the cell and adsorption was allowed for 30 min. The sample was then outgassed at 10^{-5} Pa at 100 °C. FT-IR spectra were taken in transmission mode before and after pyridine adsorption, using a spectrometer IFS55 Equinox (Bruker) equipped with a DTGS detector. The spectra were recorded with 100 scans between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1}.

NH_3 adsorption and subsequent temperature-programmed desorption (NH_3-TPD) were performed in a Hiden CATLABPCS combined micro reactor and mass spectrometer (MS) system as reported earlier.[15] Experiments were performed according to the following three steps: (1) stabilization of a flow of pure He (30 mL/min) at 50 °C for 25 min in order to check the sensitivity factor of He and therewith to determine that of NH_3 during the later TPD (through the previously calibrated He/NH_3 sensitivity factors ratio) and subsequent heating to 150 °C (still under 30 mL/ min of pure He); (2) adsorption of NH_3 at 150 °C for 1.5 h from a 95:5 He/NH_3 flow (25 mL/min) mixed with a flow of pure He (5 mL/min); (3) flush at 100 °C under pure He (30 mL/min) for 2.5 h in order to eliminate physisorbed NH_3 and subsequent TPD from 100 to 650 °C (10 °C/min, still under 30 mL/min of pure He) in order to desorb chemisorbed NH_3**.** XPS measurements were carried out with a SSX 100/206 spectrometer from Surface Science

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Instruments as reported earlier.[15] The pressure within the analysis chamber was about 10^{-6} Pa. The zone analysed was about 1.4 mm^2, and the pass energy was set at 150 eV for the general spectrum and at 50 eV for the elementary spectra. An electron gun set at 8 eV and a nickel grid placed 3 mm above the surface of the samples were used to stabilize the charge. The following sequence of spectra was recorded: general spectrum, C 1s, O 1s, S 2p and Zr 3d. The C-(C, H) component of the C 1s peak of adventitious carbon was fixed at 284.8 eV to set the binding energy scale. When required, spectra were decomposed with the Casa XPS program (Casa Software Ltd., UK) with a Gaussian/Lorentzian product function after subtraction of a nonlinear baseline. For the quantification of the elements, the sensitivity factors and acquisition parameters provided by the manufacturer were used.

2.4. Catalyst activity studies

The alkylation of resorcinol with MTBE was carried out in the liquid batch reactor. In a typical reaction, 2.2 g of resorcinol was dissolved in 4.8 ml of MTBE, 0.9 ml of o-xylene (internal standard) and 2 ml of solvent in a 100 mL two neck round bottom flask fitted with the condenser. The reactor was placed in an oil bath under magnetic stirring (1200 rpm) and heated at 60 °C under atmospheric pressure. Then, 0.22 g of catalyst was added. The reaction was monitored by GC–FID analysis. For the sampling, 10 μl of the reaction mixture was mixed with 1.8 mL of methanol and was analysed by gas chromatography (Shimadzu-2041, FID detector) equipped with RTX-5 column (0.25 mm I.D and 30 m length). The oven temperature programme was 60 °C (1 min), 60–180 °C (10 °C/min), 180 °C (5 min). All the products were identified by injecting the standard sample followed by the NMR analysis as done in our previous work.[6] The conversion and selectivity were directly calculated from GC peak areas in mol% using a multi-point calibration curve through the internal standard method. The mass balance was also calculated after the reaction and was found to be in the range of 95-98 %.

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3. Results and discussion

3.1. Characterization of catalyst

The SZ catalyst calcined at 500°C shows no crystalline phases, whereas the catalyst calcined at 650 °C exhibits some crystallinity in the XRD analysis. (**Figure S1 and Figure 1**) The low crystallinity of sample calcined at 500°C is due to the presence of amorphous sulfate that has dispersed in the matrix.[16] The XRD pattern of ZrO_2 and SZ catalysts calcined at 650 °C are shown in **Figure 1.** The ZrO_2 displayed peaks at $2\theta = 24, 28.2, 31.5$ and $30.2, 34.5, 35.4, 50.2, 60.2, 62.9$ due to the presence of monoclinic and tetragonal phases, respectively. However, the SZ catalysts exhibited predominant peaks only due to the tetragonal phase, indicating the strong influence of sulfation on the modification of thermodynamically stable monoclinic to tetragonal phase, as observed in the literature.[7, 10]

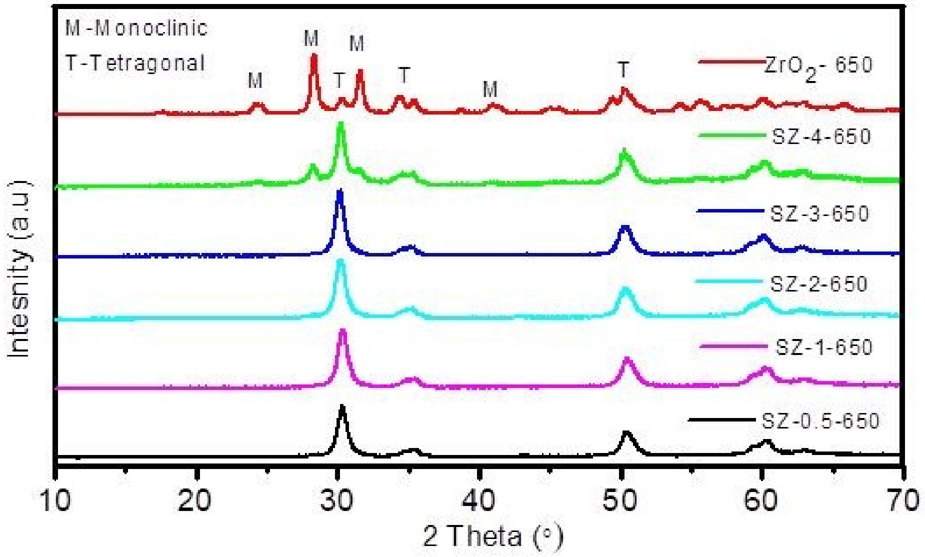

Figure 1. XRD patterns of ZrO_2 and sulfated zirconia catalysts calcined at 650 °C.

The amount of sulfur in all the SZ catalysts was determined by the CHNS analysis and are tabulated in **Table 1.** There is a linear correlation between the concentration of H_2SO_4 used and the amount of sulfur present on ZrO_2 calcined at 650 °C, however no correlation existed for the

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catalyst calcined at 500 °C. This could be because SZ catalyst calcined at a lower temperature of 500 °C

Table 1. Physio-chemical properties and catalytic activity of SZ catalysts in alkylation of resorcinol.

Catalyst	S (wt. %)	S/Zr (At %)	Specific Surface area (m^2/g)	Average Pore size (Å)	Average Pore volume cm^3/g)	Acidity (μ mol/g)	Conversion of resorcinol (mol %)	Selectivity				TON (10^{-3})
								4-TBR	4,6-DTBR	R-MTBE	Others	
SZ-0.5-500	4.79	0.25	191	52	0.162	406	61	79	16	2	2	9
SZ-1-500	4.73	0.25	184	52	0.107	404	64	77	20	2	2	8
SZ-2-500	5.12	0.26	154	46	0.119	358	53	76	8	10	6	12
SZ-3-500	5.82	0.26	155	61	0.144	340	44	77	9	9	5	15
SZ-4-500	4.40	0.29	34	158	0.098	148	43	75	6.	13	6	35
SZ-0.5-650	1.06	0.11	109	51	0.141	182	57	71	27	1	1	21
SZ-1-650	1.15	0.14	119	52	0.154	176	58	72	25	1	1	22
SZ-2-650	1.34	0.13	113	53	0.146	165	57	75	22	2	1	24
SZ-3-650	1.39	0.13	103	61	0.165	152	55	75	21	2	2	27
SZ-4-650	1.53	0.12	68	67	0.105	115	51	79	10	6	5	38
ZrO_2-650	0.0	0.0	30	120	0.095	0	0	0	0	0	0	0
$Zr(OH)_4$	0.0	0.0	306	49	0.168	0	0	0	0	0	0	0

Reaction Conditions: Catalyst amount = 0.22-gram, Temperature = 60 °C; Resorcinol= 2.2-gram, MTBE = 7.2 ml, time= 10 h, * TON is calculated by mmol of resorcinol converted per acid site determined byTPD-NH3.

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contained both physically and chemically adsorbed sulfur in large quantity (4-5 wt %), whereas SZ calcined at a high temperature of 650 °C exhibited lower sulfur content (1-2 wt %), with the sulfur in majority likely present in a chemically adsorbed state. The surface S/Zr ratio determined by the XPS analysis further supports the fact that SZ-500 catalysts possess double amount of sulfur in comparison to SZ-650 catalysts. (**Table 1**) Moreover, for SZ-650 series of catalysts (SZ-0.5N to SZ-4N) the S/Zr ratio (determined by XPS) - almost remained the same, but CHNS analysis reveals an increase of the total sulfur content from SZ-0.5N to SZ-4N, indicating the presence of extra sulfur in the bulk phase.[12]

The N_2 adsorption-desorption isotherm of the SZ catalysts calcined at 650 °C showed the type-IV isotherm with H_2 type hysteresis loop confirming the presence of mesopores. (**Figure 2**)

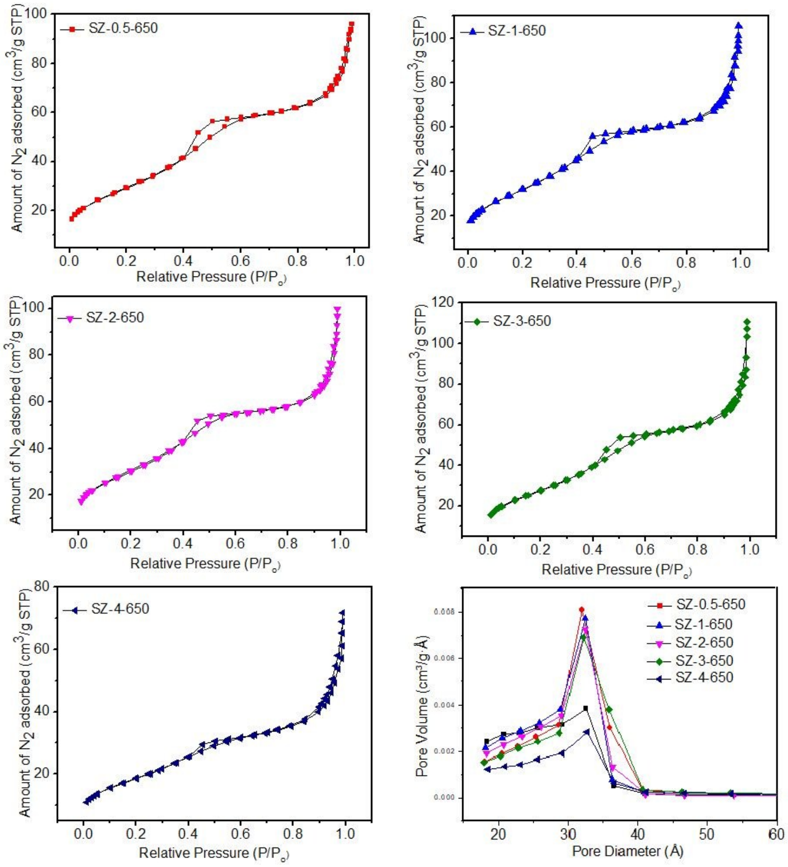

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Figure 2. Nitrogen adsorption-desorption isotherms and pore size distribution of SZ catalysts calcined at 650 °C.

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The SZ calcined at 500 °C did not exhibit any hysteresis indicating the absence of mesopores. (**Figure S2**) These above results indicate that high temperature is required for the generation of mesoporosity in the ZrO_2. The surface area of ZrO_2 increased considerably after sulfation due to the change in its textural properties. However, SZ catalyst showed lower surface area compared to $Zr(OH)_4$, due to the sulfate loading.(**Table1**) The specific surface area of SZ-650 catalysts decreased with the increase in the sulfur amount, except for the SZ-0.5N. This decrease in surface area and change in porosity could be due to a sulfate migration into the bulk phase of ZrO_2.[17] The average pore diameter increased with the increase in the sulfate loading as reported by other researchers. [18-19]

FT-IR analysis of all the SZ catalysts, revealed the presence of sulfate ions and bonding of sulfate ions with ZrO_2 as shown in **Figure 3.** (**Figure S3**) The FT-IR analysis in the fingerprint region showed the presence of 997 cm^{-1} peak due to the symmetric (υ1) vibrations of S-O whereas

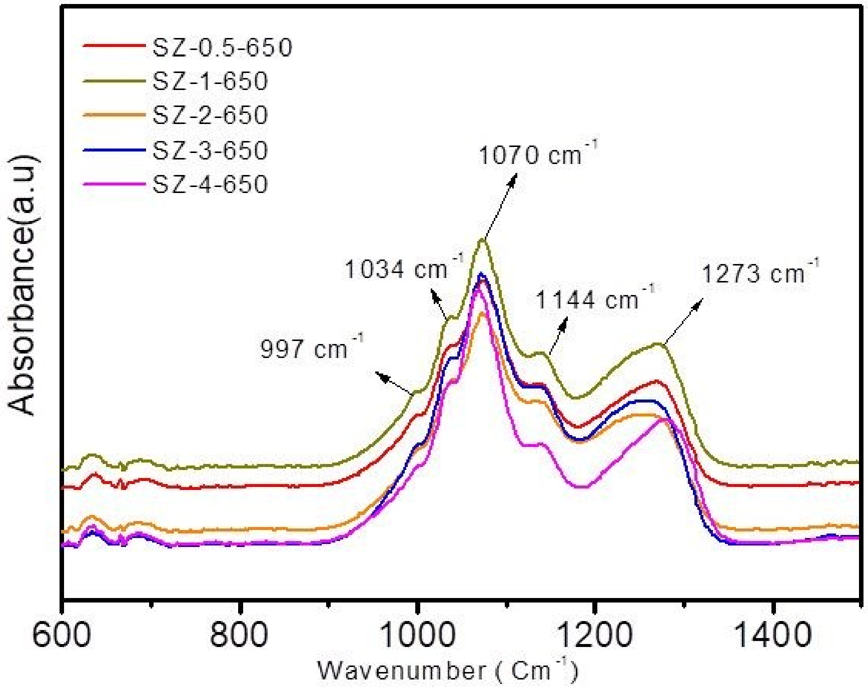

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Figure 3. FT-IR spectra of sulfated zirconia catalysts calcined at 650 °C.

1034, 1070, 1144 and 1273 cm^{-1} peak were observed due to the antisymmetric (υ3) vibrations of O- S-O bonds. The results indicate the presence of sulfate ions on the surface of ZrO_2 in a bidentate fashion.[12]

XPS analyses were performed for all SZ catalysts to verify the presence of sulfate species, to estimate the S/Zr ratio at the surface and the oxidation state of S. The values are presented in **Table 1**. No impurities were found, except the contamination carbon inherent to the analysis. All the SZ catalysts show the peak associated to the $S2p_{3/2}$ (Binding energy = 169.3 eV) and $S2p_{1/2}$ (Binding energy =170.4 eV), confirming the presence of sulfur with an oxidation state +6 as observed for sulfate moieties. **(Figure S4)** The binding energies of Zr peaks $3d_{3/2}$ and $3d_{5/2}$ in ZrO_2

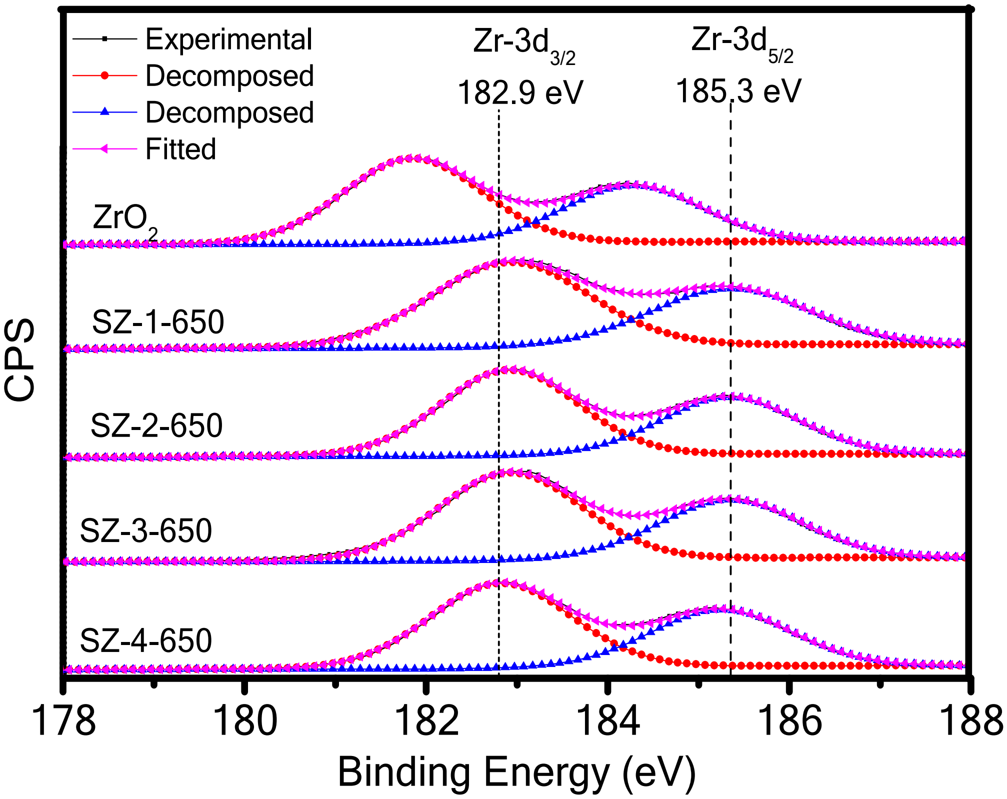

Figure 4. Zr $3d_{5/2}$ and $3d_{3/2}$ XPS spectra of the SZ-650 catalysts.

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are typically of 181.8 eV and 184.2 eV, respectively. Whereas Zr doublet in SZ catalysts appeared at binding energies of 182.9 eV ($3d_{3/2}$) and 185.3 eV ($3d_{5/2}$).(**Figure 4**) The shift of around 1.1 eV toward higher binding energy observed for SZ catalysts is due to inductively withdrawal of electron density from ZrO_2 by sulfate groups.[20]

The use of IR spectroscopy to detect adsorbed pyridine allows distinguishing the Brönsted and Lewis acidity present on the SZ catalysts.[21] The intensity of Brönsted (B) and Lewis (L) acid sites obtained from the absorbance at 1541 and 1446 cm^{-1} respectively and corresponding B/L ratios were measured. FTIR pyridine adsorption spectra of SZ catalysts calcined at 650 ˚C are as shown in **Figure 5.**

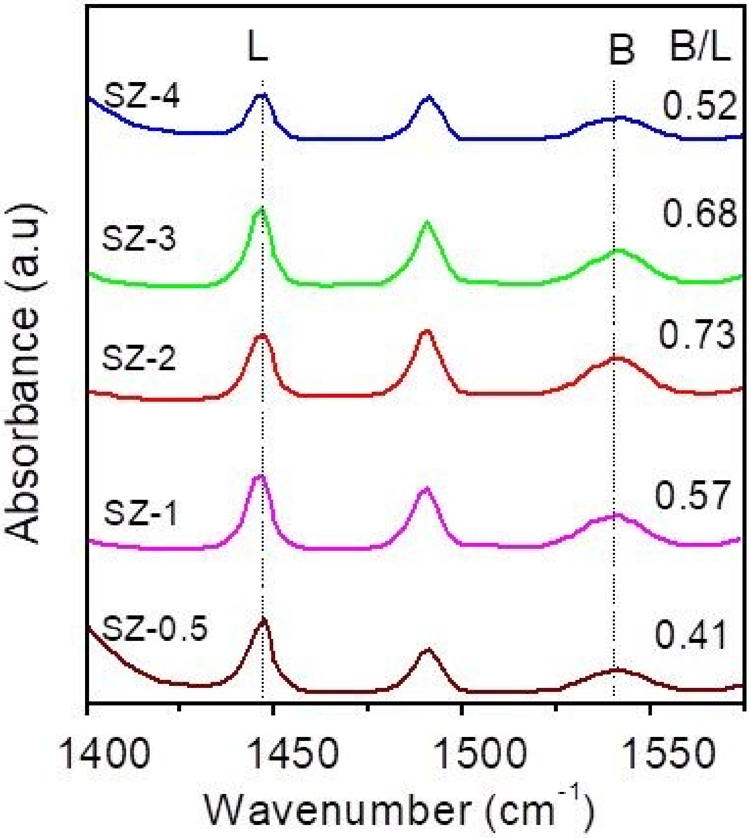

Figure 5. Acidity measurement of SZ catalysts calcined at 650 °C by pyridine FT-IR analysis (B-Brönsted acid site, L-Lewis acid site).

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The SZ showed a peak at 1541 cm^{-1} and 1446 cm^{-1} indicating the presence of both Brönsted and Lewis acidity. It is well known that sulfate groups inductively withdraw the electron density from ZrO_2, as a result Lewis acid sites are created on ZrO_2. The Brönsted acid sites are due to protons generated by sulfate groups. The B/L ratio of the SZ-650 catalysts increased from SZ-0.5N to SZ-2N and later decreased as seen on **Figure 5.** (**Table S1**) The decrease of B/L ratio for SZ-3N and SZ-4N could be due to the formation of polysulfate groups by the excessive sulfur on the ZrO_2.[12]

To find the amount and strength of acid sites, a temperature programmed desorption NH_3 profile of all the SZ samples was measured as shown in **Figure 6.** The marked initial desorption in the temperature range 150-300 °C is due to the NH_3 with medium acid sites. The desorption peak of NH_3 in the range 300-500 °C is due to the strong acid sites. The total amount of acid

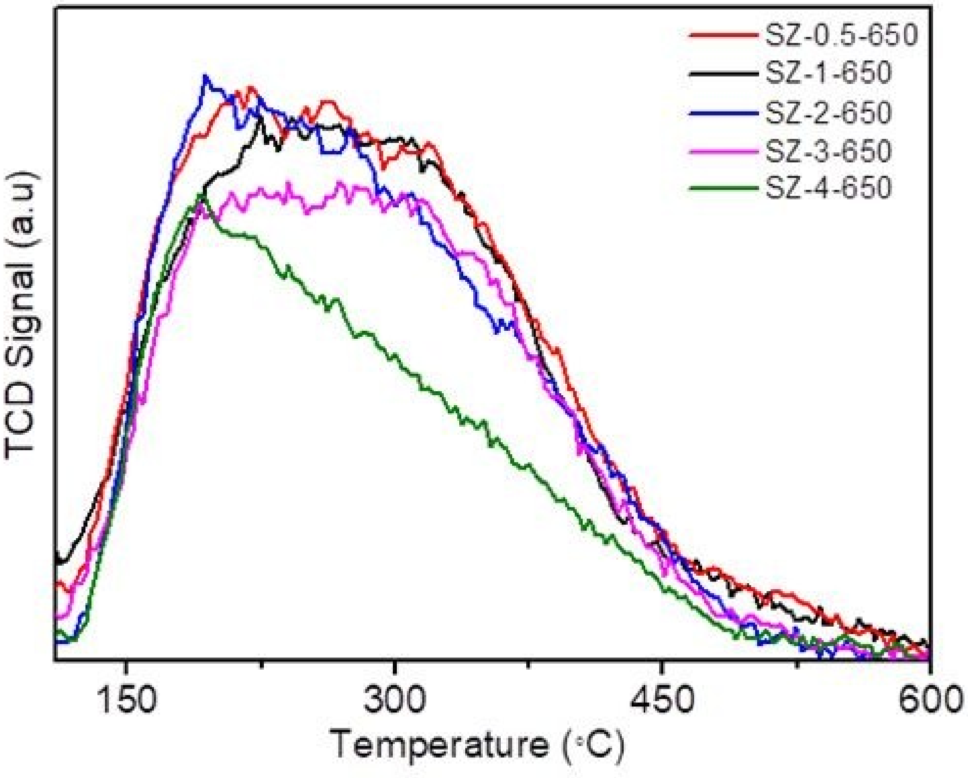

Figure 6. TPD-NH_3 profiles of sulfated zirconia catalysts calcined at 650 °C.

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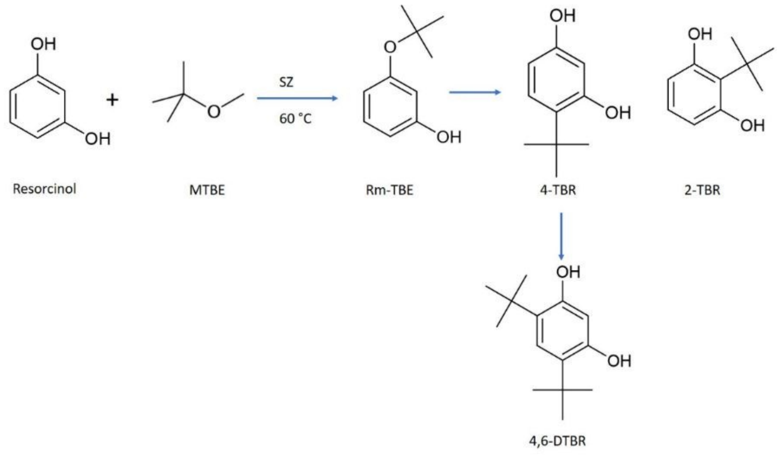
sites measured were tabulated in **Table 1**. The SZ-500 catalysts exhibited higher acidity compared to the SZ-650 catalysts due to their higher surface area. (Figure S5) The number of total acid sites decreased from SZ-0.5N to SZ-4N. (**Table 1**) For SZ catalysts with low sulfur content (SZ-0.5), the sulfation takes place on the O-Zr-O sites where both Brönsted and Lewis acidities are generated by sulfate and -Zr- sites respectively resulting in high acidity.[22] As the sulfur content increased (SZ-4N), greater number of sulfate groups masks the Lewis acidic sites (O-Zr-O); the migration of sulfate to the bulk of the catalyst also contributes decreasing the total acidity as measured by pyridine adsorption. Excess sulfate groups on the surface of zirconia in the form of isolated and poly-sulfates do not contribute to acidity.[22] To check the morphology of the synthesized SZ-1-650 catalyst SEM images were taken as shown in **Figure S6**. The images of SZ-1N-650 showed the presence of large bunches of particles with average size of 1-2 µm; high resolution of these particles exhibits agglomerated small crystallites of 80-100 nm in size.

3.2. Catalytic activity studies

3.2.1. Catalytic activity over different SZ catalysts.

Alkylation of resorcinol to 4-TBR is a two-step reaction. The first step is the formation of R-mTBE; in the second step R-mTBE isomerizes to the 4-TBR. (**Scheme1**)



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Scheme 1. Schematic presentation of resorcinol alkylation with methyl tertiary butyl ether with different products.

In this reaction pathway, R-MTBE acts as an intermediate. The formed 4-TBR is more reactive than the resorcinol and hence further undergoes alkylation to 4,6-DTBR. 2-TBR is also formed in small amount due to the steric hindrance at the C_2 position of resorcinol making the carbocation attack difficult. (**Scheme1**)

The resorcinol alkylation was investigated for SZ catalysts with different sulfur loadings and compared with its precursor. $Zr(OH)_4$ and ZrO_2 showed no activity due to the absence of any strong acid sites. The catalytic activity of SZ catalysts with different amounts of sulfur and calcination temperatures are shown in **Table 1**. The SZ-650 catalysts with low sulfur content, low surface area and low acidity exhibited almost similar activity compared to the SZ-500 catalysts having high surface area, acid sites and sulfur content. (**Table 1**) This could be due to the more marked presence of crystalline phase in SZ-650 catalysts than that of amorphous phase in SZ-500 ones. This confirms that conversion of resorcinol is influenced by the structural and surface properties of the catalyst. The presence of crystalline tetragonal ZrO_2 phase in the SZ-650 catalyst has a major influence on the activity. The SZ-500 catalysts with amorphous ZrO_2 are not Lewis acidic and possess only Brönsted acidity due to the sulfates; whereas SZ-650 with their crystalline ZrO_2 possess both Lewis and Brönsted acidity. Hence, SZ-500 even with high surface area, sulfur content and total acidity possess almost similar catalytic activity as that of SZ-650. All the SZ-650 catalysts almost showed similar activity after the 10 h of reaction time. Therefore, comparing their initial catalytic activity was more practical and is tabulated in **Table S1**. The resorcinol conversion determined after 2 h of reaction time decreases with the increase of sulfur content and decreases with total acidity from SZ-0.5N to SZ-1N.This indicates that the conversion of resorcinol mainly depends upon the total number of acid sites. The TON were also

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higher for SZ-650 catalysts compared to the SZ-500 catalysts.(**Table 1**) The decrease in resorcinol conversion with the decrease of total acidity was observed from SZ-0.5 to SZ-4 as seen from **Figure 7**. Furthermore, the proportion of Brönsted and Lewis acidities of SZ-650 catalysts did not correlate well with the activity or selectivity in the alkylation reaction. (**Table S2**) This indicates that both Brönsted and Lewis acid sites catalyse the reaction. The SZ-1-650 catalyst showed 58 % resorcinol conversion with 72 % of 4-TBR selectivity and 25% selectivity for 4,6-DTBR. Hence, further, optimization studies were done using SZ-1-650 catalyst.

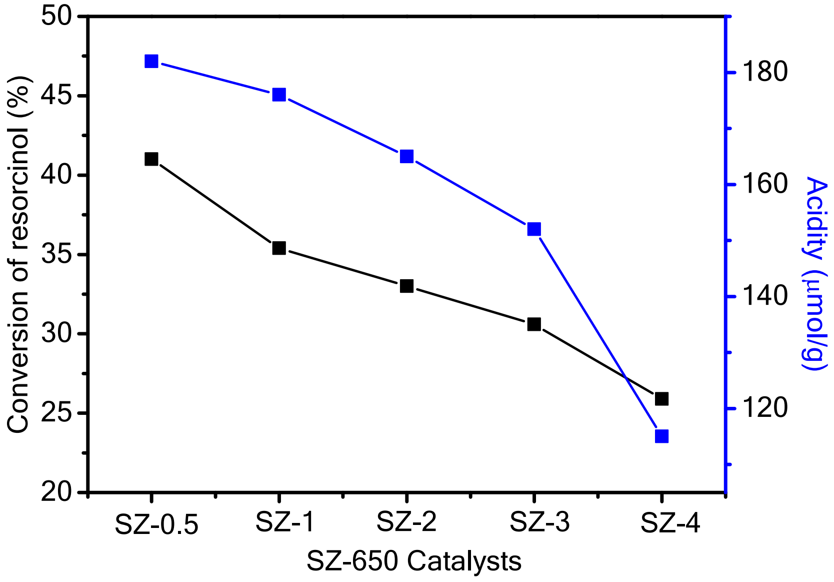

Figure 7. Correlation of acidity of SZ-650 catalysts with conversion of resorcinol in alkylation reaction.

3.2.3. Study on nature of solvents

The effect of different solvents in the alkylation of resorcinol over SZ catalysts was examined. The reaction with SZ-1N catalyst without solvent gave a conversion of 58%. The use of solvent was necessary in order to dissolve the solid resorcinol during the reaction. Hence, reaction was carried out in different solvents. Results are shown in **Table 2.**

In order to correlate the solvent properties with the catalytic activity, the conversion of resorcinol with the dialectic constant was plotted as seen in the **Figure S7**. Dielectric constant of

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solvent was varied from 2.0 (cyclohexane) to 36.7 (N, N-dimethyl formamide) but did not correlate well with the catalytic activity. The solvent N,N-dimethyl formamide (DC=36.7) and nitrobenzene (DC=34.8) with almost similar DC showed different conversion for resorcinol as shown in **Table 2.**

Table 2. Effect of solvent on resorcinol alkylation reaction.

Solvent	**Dielectric constant (DC)**	**Acceptor Number (AN)**	**Donor number (DN)**	**Conversion of Resorcinol (%)**	**Selectivity (%)**				
					RmTBE	**2-TBR**	**4-TBR**	**4,6-DTBR**	**Others**
No solvent	--	--	--	57	0.5	0.3	72	26	0.6
MTBE	--	--	--	58	0.6	0.5	72	26	0.6
Cyclohexane	2.0	0	0	52	0.7	0.5	77	21	0.5
Benzene	2.2	8.2	0	62	0.6	0.4	76	22	0.4
1,2-Dicholoroethane	10.3	16.7	0	70	0.5	0.3	72	25	0.4
Nitrobenzene	34.8	14.8	4.4	63	0.5	0.4	72	27	0.4
1,4-dioxane	2.2	10.3	14.3	47	1.1	3.2	85	10	0.3
1,2-dimethoxyethane	7.2	10.2	20.0	25	4.3	10	80	4	0.8
N,N-Dimethyl formamide	36.7	16	26.6	0	0	0	0	0	0

Reaction Conditions: catalyst =SZ- 1-650, catalyst amount = 0.22 g, temperature = 60 °C; resorcinol= 2.2-gram, MTBE=4.8 ml =, solvent = 2 ml, time =10h.

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A further study on the effect of the solvent properties via their AN and DN led to a better understanding of the role of the solvent in the reaction. AN and DN of different solvents were reported by Gutman[23]. They are a measure of the acidic or basic nature of solvents. Subsequently, these values have been accepted and used by several researchers.[12-13, 24-26] **Table 2** reveals that an increase in the AN of the solvent (at constant DN = 0) from cyclohexane to 1,2-dichloroethane, increases the resorcinol conversion from 52 to 70 %. At the opposite, an increase in DN (keeping AN in its best range = 10-20) of the solvent from nitrobenzene to N,N-dimethylformamide, decreased the conversion from 63 % to 0.

From the above results, it is clear that solvents with high AN and low DN give a high resorcinol conversion. A high AN for solvent represents a marked presence of Lewis acidic properties, which improve the catalytic activity without affecting the acid sites of the catalyst. The solvents with high DN are Lewis basic in nature, making that these solvents tend to interact with the acidic sites of the SZ catalyst.[27] As a consequence, solvents with high DN like N,N-dimethylformamide and 1,2-dimethoxyethane preferentially adsorb on the acid sites of SZ resulting in blockage of active sites. The other reason for the lower activity obtained in high donor number (Lewis basic) solvents could be due to the stabilization of tertiary butyl carbocation during the reaction. Stabilization of these carbocation will essentially lead to decline the rate of reaction. Among all the solvents, 1,2-dichloroethane with high AN and low DN thus showed excellent performance.

Furthermore, the effect of varying the amount of solvent was also carried out with the 1,2-dicholoroethane. As the amount of solvent increased from 0 to 8 ml the conversion of resorcinol dropped from 58 to 49 % likely due to the dilution effect but the selectivity for the 4-TBR increased from 72 to 84 %. (**Figure 8**)

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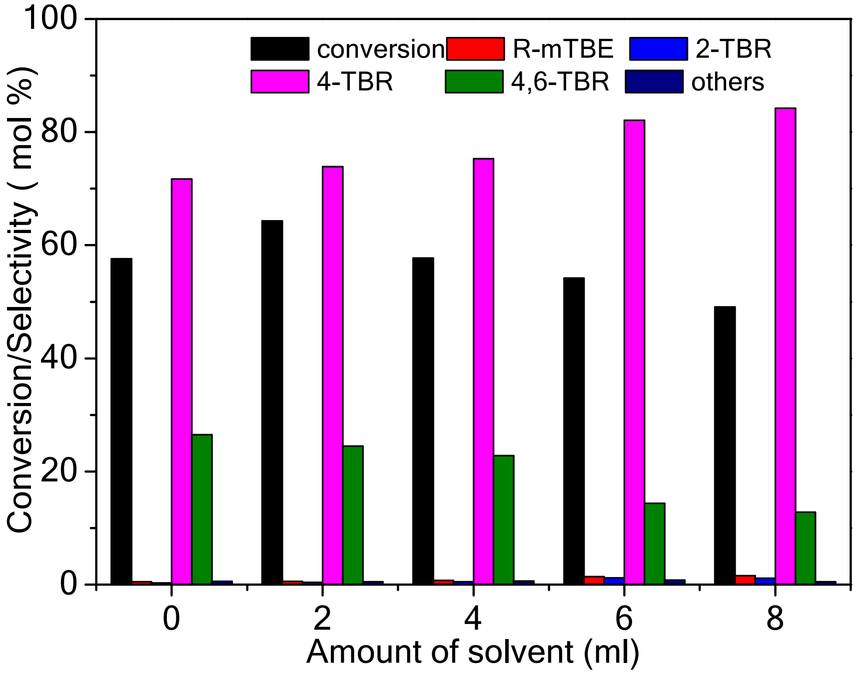

Figure 8. Effect of amount of solvent (1,2-dichloroethane) on resorcinol alkylation.

3.2.2. Influence of reaction conditions

The effect of molar ratio resorcinol to MTBE during the catalytic reaction was studied at 60 °C using SZ-1N catalyst. The ratio resorcinol to MTBE was varied from 1:4 to 1:1 as shown in **Figure 9a.** The conversion of resorcinol remained almost constant whatever the MTBE concentration. However, as the Resorcinol: MTBE ratio decreased from 1:4 to 1:1, the selectivity for the 4-TBR decreased at the same time selectivity for 4,6-DTBR increased. This indicates the further alkylation of 4-TBR occurs more markedly at lower MTBE concentration. Based on the above results, 1:3 mole ratio was selected for this reaction to get high conversion of resorcinol (58 %) with good (72 %) selectivity for 4-TBR.

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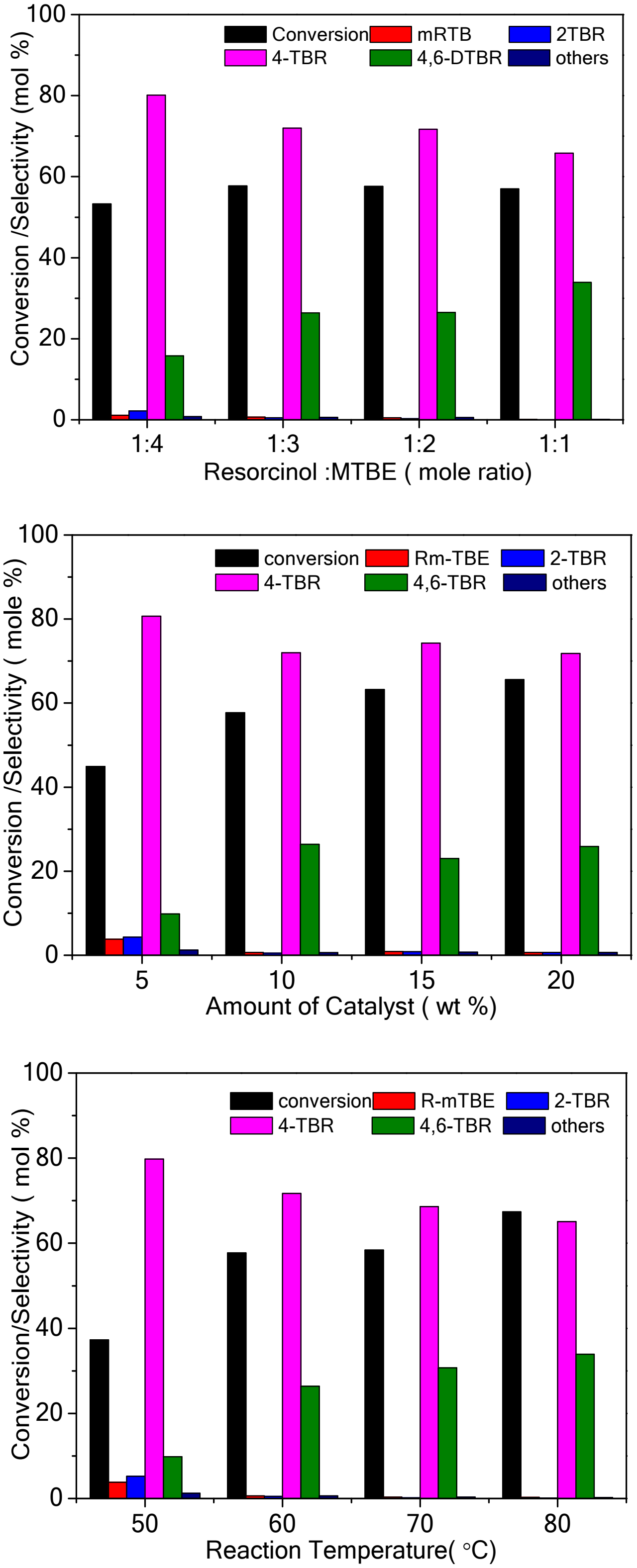

Figure 9. Influence of reaction conditions. a) Effect of resorcinol: MTBE mole ratio: conditions: catalyst = SZ-1N, catalyst amount = 10 wt%, temperature = 60 °C, time =10 h.(b) Effect of catalyst amount: conditions: catalyst = SZ-1N, resorcinol = 2.2 g, MTBE =4.8 ml, temperature = 60 ◦C, time = 10 h. (c) Effect of reaction temperature: conditions: catalyst = SZ-1N, catalyst amount = 10 wt%, resorcinol = 2.2 g, MTBE =4.8 ml, temperature = 60 ◦C, time = 10 h.

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The study of the effect of the catalyst amount on alkylation was conducted by taking different weight % of SZ-1N catalyst with respect to resorcinol weight. As the catalyst amount was increased from 5 to 20 wt%, the conversion of resorcinol increased from 45 to 66 % and selectivity for 4-TBR dropped from 81 to 72 % respectively. (**Figure 9b**) The use of more catalyst increased the secondary alkylation reaction. The 10 wt. % of catalyst was good enough to produce selectively 4-TBR with good conversion of resorcinol.

The effect of reaction temperature was also studied using SZ-1N catalyst with resorcinol to MTBE mole ratio of 1:3 using 10 wt% of catalyst. The conversion of resorcinol increased with the increase of reaction temperature as shown in **Figure 9c**. The selectivity for 4,6-DTBR increases at higher temperature above 70 °C due to the predominant secondary alkylation reaction.

An attempt to use different butylating agents such as tertiary butanol (TBA) and di tertiary butyl dicarbonate (DTBDC) was finally made and are tabulated in the **Table S3**. The TBA produces water as by product, which resulted in a lower conversion likely as due to the blockage of the catalyst acidity. Whereas MTBE and DTBDC produce methanol and CO_2 as by-products, respectively, without influencing the catalyst, hence relatively good conversion of resorcinol was observed over these alkylating agents.

3.2.6. Leaching and recycling test

Leaching test was carried out for alkylation reaction to investigate the stability of the active sites at the surface of the catalysts into the reaction conditions. The reaction was carried out using SZ-1N catalyst at reaction temperature of 60 °C with resorcinol to MTBE mole ratio of 1:3. Reaction was stopped after 2 h (35 % conversion) and the hot reaction mixture was filtered. The reaction was continued with the filtrate; the conversion remained unchanged along the next

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10 hours, indicating that no leaching of active sites into the reaction medium had occurred during the first part of the experiment**. (Figure S8)**

As a recycling test, the catalyst SZ-1 was filtered after the reaction, washed with acetone followed by drying in static air for 1 h at 120 °C and finally calcined in static air at 500 °C for 2 h. It was then used in the alkylation reaction with a fresh reaction mixture. The catalyst showed good recyclability with a minimal decrease in activity after 3 cycles. **(Figure 10)**.

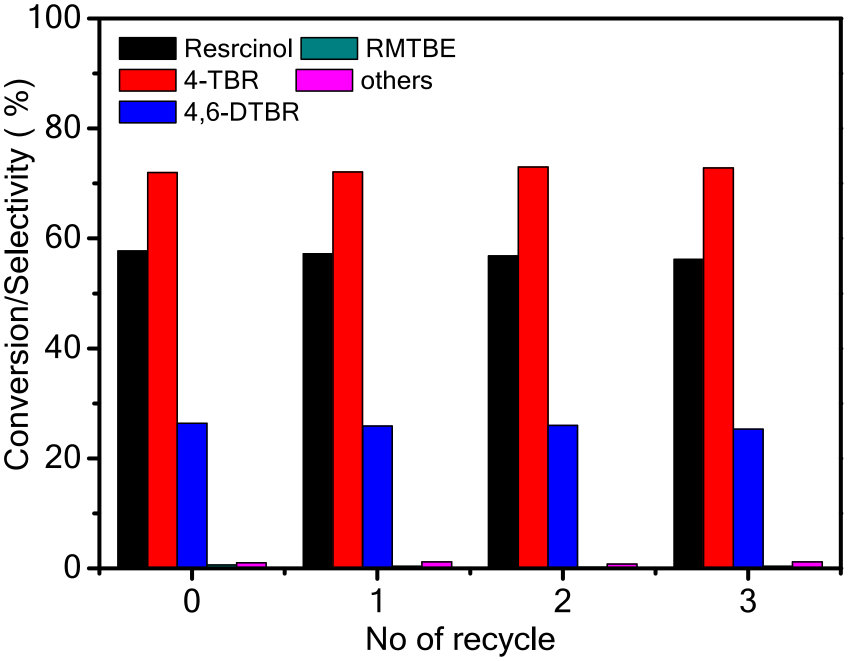

Figure 10. Recycle study of SZ catalyst in resorcinol alkylation reaction. Reaction Conditions: catalyst amount = 0.22-gram, temperature = 60 °C; resorcinol= 2.2 g, MTBE = 7.2 ml, time= 10 h.

XRD of the catalyst after the third cycle revealed the still intense unchanged pattern of tetragonal phase indicating the structural integrity of the catalyst (**Figure S9). **Furthermore, the XPS spectra of fresh SZ-1N catalyst and after the third recycle showed a similar surface S/Zr ratio (0.15), surface area (113 m^2/g) and sulfur content (1.10 wt %), indicating that no leaching of the sulfur from the surface and textural changes has occurred during none of the steps of the experiment. **(Figure S10 and Figure S11)**

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Table 3 shows the comparison of catalytic activity of SZ-1N with other reported solid acid catalysts from the literature.[1-6] The 10% Ga-BEA zeolite and 20% DTP/K10 are the only catalysts to exhibit 100 % selectivity for 4-TBR. However, for 20% DTP/K10 and Ga-Beta catalysts, the

Table 3 Comparison of catalytic activity of the SZ catalyst with other reported solid acid catalysts.

Catalysts	Conversion of Resorcinol (%)	Selectivity (%)					References
		RmTBE	2-TBR	4-TBR	4,6-DTBR	Other	
SZ-1-650	70	0.5	0.3	72	25	0.4	Present work
10%Ga-BEA	4	17	35	54	0	0	Present work
Acidified Montmorillonite K10	17	4	9	85	2	0	Present work
ZrO_2-PTA	67	13	--	55	26	6	[5]
10%Ga-BEA	59	--	--	100	--	--	[2]
Acidified Montmorillonite K10	100	--	--	25	75	--	[1]
20% DTP/K10	97	--	-	100	--	--	[4]
ITQ-6 zeolite	45	--	--	78	--	--	[3]
HPW/SBA-15	35	3	4	52	26	15	[6]

reaction was carried out at high temperature of 150 °C and 80 °C, respectively.[2-4] Furthermore, the use of less abundant thus more costly metal like Ga is less attractive process. The 10% Ga-BEA zeolite and 20% DTP/K10 catalysts exhibited lower resorcinol conversion compared to SZ-1N-650 in the present reaction conditions. ITQ-6 zeolite showed a 45 % resorcinol conversion with a 78% selectivity to 4-TBR at 100 °C.[3] The other catalysts such as ZrO_2 supported phosphotungstic acid (PTA), acidified montmorillonite K-10 and heteropolytungstate (HPW) supported SBA-15 exhibited lower activity and selectivity in the alkylation reaction compared to SZ-1N.[1,5-6] SZ in the present work exhibited a good resorcinol conversion of 70% with 72.5% of selectivity to 4-TBR at lower temperature (60 °C) than most of the previously reported catalysts tabulated in **Table 3**. The SZ catalyst designed in the current study being simple, efficient and easily scalable, it makes it an attractive catalyst for alkylation reaction.

4. Conclusions

Application of sulfated zirconia (SZ) as highly selective and reusable catalyst for the synthesis of 4-tertiary butyl resorcinol from resorcinol and methyl tertiary butyl was reported. The SZ showed the best catalytic performance at low temperature among different types of acid catalysts. SZ calcined at 650 °C showed higher catalytic activity compared to the SZ-500 °C. The total acidity of SZ optimized by different concentrations of H_2SO_4 treatment influences the acidity and the conversion of resorcinol. Treating ZrO_2 with high concentration of H_2SO_4 decreased the total number of acid sites in SZ. The presence of solvent with high acceptor and low donor numbers is necessary for SZ catalyst to show high activity and selectivity in alkylation reaction. The SZ synthesized by treating 1N H_2SO_4 was found to be highly active (~70 %), selective (72.5%) and reusable catalyst for the alkylation reaction.

Acknowledgement

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The authors thank the FRS-FNRS for the Projet de recherche n° T.0064.16, and the Postdoctoral position allocated to VSM from it. The authors also thank Francois Devred for the technical support.

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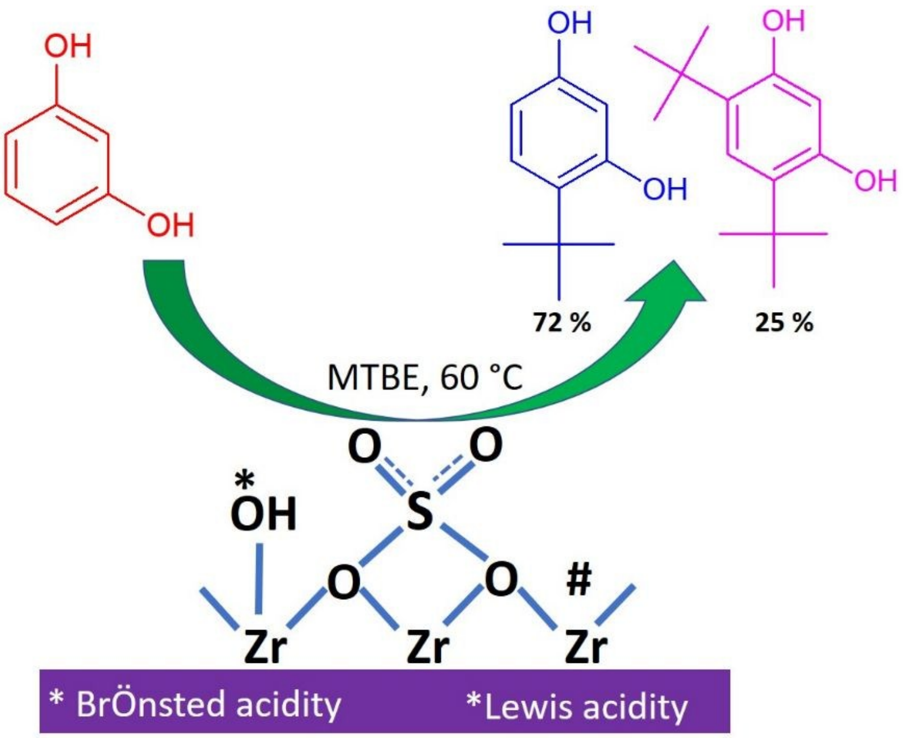

Sulfated zirconia (SZ) is an efficient and recyclable catalyst in the selective monoalkylation of resorcinol with MTBE to 4-tertiary butyl resorcinol at low temperature (60 °C)