Novel zirconium containing cage type silicate (Zr-KIT-5): An efficient Friedel–Crafts alkylation catalyst

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ABSTRACT

Zirconium was successfully incorporated into cubic KIT-5 mesoporous silicate by direct hydrothermal synthesis employing F127 triblock copolymer as the structure-directing agent. The Zr-KIT-5 materials exhibit relatively high specific surface area ($\sim 1000 \text{ m}^2/\text{g}$) and pore volumes ($0.7\text{--}0.8 \text{ cm}^3/\text{g}$), with an average cage diameter of approximately 8.8 nm as evidenced from N_2 sorption and HR-TEM results. Diffuse reflectance UV–Vis spectroscopy and XPS studies reveal framework Zr^{4+} species that result in the formation of predominantly Lewis acid sites and some Brønsted acid sites, both of which increase with Zr content. The Zr-KIT-5 materials are shown to be highly active and stable catalysts for anisole benzylation with benzyl alcohol (BzOH) forming monobenzylation products (mainly ortho- and para-). It is shown that the benzylation activity depends mainly on the number and nature of the acid sites. Zr-KIT-5 material is thus a promising and environmentally benign Friedel–Crafts alkylation catalyst with many potential applications.

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1. Introduction

The Friedel–Crafts alkylation/acylation of aromatic compounds, an important reaction in organic synthesis, is commonly carried out in the presence of homogeneous acid catalysts (e.g. AlCl_3 ,

BF_3 , H_2SO_4 , HF, H_3PO_4 etc.) [1]. To overcome the acid handling and waste disposal problems associated with these catalysts, solid acid catalysts, most notably zeolites, [2] have been pursued as environmentally superior alternatives. Although zeolites have been shown to be highly active in the alkylation and/or acylation of aromatics with lower alcohols [3–6], their microporous nature creates diffusion limitations during the benzylation of aromatics and eventually leads to catalyst deactivation [7]. It has been shown that introducing redox functionality [8] or generating mesoporosity [9,10] in these zeolites dramatically increases the benzylation

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activity [11]. However, the synthetic procedures associated with the formation of mesoporosity in zeolites are tedious. Ordered mesoporous silicate materials with tunable acidity are relatively easier to synthesize and have been shown to be active for benzylation reactions. For example, SBA-15 type materials containing Al [12] and Fe [13] have been reported to show facile benzylation activity. Interestingly, Fe-SBA-15 was found to be superior to Al-SBA-15 indicating that the redox functionality of Fe-based catalysts imparts surprisingly remarkable activity for this type of reaction [14].

In recent years, we have been engaged in the preparation of catalytic materials based on cubic ordered mesoporous silicates such as KIT-6 [15], KIT-5 [16] and SBA-16 [17]. Zirconium containing KIT-6 catalysts were shown to possess, almost exclusively, Lewis acid sites that are highly active and stable for the dehydration of isopropanol [18] and ethanol [19]. In this paper, we extend our synthesis methodology to incorporate Zr into KIT-5 material, presenting a detailed characterization of the structural properties and the nature of zirconium coordination within the KIT-5 framework. Like Zr-KIT-6 materials, these materials are also shown to possess Lewis acid sites that can be tuned with Zr loading. Unlike Zr-KIT-6 however, the Zr-KIT-5 materials also exhibit Brønsted acidity at higher Zr content.

Anisole benzylation is often deployed as a test reaction to understand the nature of acid sites in a catalyst system. In general, benzylation is carried out using benzyl chloride or benzyl alcohol as alkylating agent, the latter being environmentally advantageous as it produces water as side product. In the presence of Lewis acid sites, benzyl alcohol forms predominantly dibenzyl ether (DBE) [20]. In contrast, Brønsted acid sites [21–25] are reported to be responsible for the formation of alkylated products. The synthesized Zr-KIT-5 materials show facile and stable activity for anisole benzylation with benzyl alcohol. The effect of acidity on conversion and product selectivity are presented.

2. Materials and methods

2.1. Synthesis of Zr-KIT-5

The synthesis of Zr-KIT-5 materials was carried out with molar Si/Zr ratios of 100, 50 and 25, designated as Zr-KIT-5(100), Zr-KIT-5(50) and Zr-KIT-5(25) respectively, were synthesized following an analogous procedure reported for the synthesis of tungsten incorporated KIT-5 materials [16] employing tetraethyl orthosilicate (TEOS 98%, Aldrich) and required amounts of Zirconium(IV) oxychloride octahydrate (99.5% Sigma–Aldrich) as the Si and Zr sources, respectively. Under the synthesis condition used, a high loading of Zr (Si/Zr = 10) resulted in a highly viscous gel that upon drying and calcination yielded a heterogeneous material that was unlike the OMS materials obtained at lower Zr loadings. This suggests a non-homogenous dispersion of ZrOx species at such high Zr loadings that is undesired and hence was not considered for further studies.

2.2. Characterizations of Zr-KIT-5

Small Angle X-ray Scattering (SAXS) patterns were recorded on a Rigaku system with a S-MAX 3000 instrument using a Bede Scientific microfocus tube source operating at 45 kV and 0.66 mA. Powder X-ray diffraction patterns were collected on a Rigaku MiniFlex diffractometer with a Cu K α irradiation source. The textural properties were evaluated from N₂ physisorption isotherms at –196 °C on a Quantachrome NOVA 2000e instrument. Scanning Electron Micrographs (SEM) and Transmission Electron Micrographs (TEM) were carried out on a Versa 3D dual beam

Scanning Electron Microscope/ Focused Ion Beam (FEI, Hillsboro, OR, USA) with a silicon drift EDX detector (Oxford Instruments, X-Max, UK) and FEI Tecnai F20 G2 X-Twin instruments respectively. Elemental analysis was performed on a Horiba Jobin Yvon JY 2000 ICP-OES instrument. Diffuse reflectance UV–Vis spectra were recorded in the 200–800 nm range at room temperature, using Spectralon (Labsphere, Inc) as the reference, with a PerkinElmer (Lambda 850) spectrophotometer equipped with a diffuse reflectance integrating sphere. X-ray photoelectron spectroscopy (XPS) data were recorded on a Physical Electronics PHI 5800 ESCA system with standard non-monochromatic Al X-rays (1486.6 eV) operated at 250 W and 15 kV in a chamber pumped down to a pressure of approximately 1.0×10^{-8} Torr. The curve fitting was done using XPSPEAK with constraints applied to peak position, area as well as FWHM (full width at half maximum). Temperature programmed ammonia desorption (NH₃-TPD) was carried out in a Micromeritics Autochem 2910 instrument equipped with a Thermal Conductivity Detector (TCD). Pyridine FTIR spectra of Zr-KIT-5 samples were acquired by saturating the Zr-KIT-5 samples with pyridine, drying the samples at 100 °C in vacuum to remove physisorbed pyridine and analyzing them in the DRIFT mode at 120 °C using a TENSOR-27 FTIR system with PIKE diffuse IR attachment.

2.3. Benzylation of anisole with benzyl alcohol

In a typical reaction, benzyl alcohol (1.08 g, 10 mmol), anisole (10.8 g, 100 mmol), dodecane (0.34 g, 2 mmol, internal standard) and Zr-KIT-5 (100 mg) were charged into a 25 mL two-necked round bottom flask fitted with a reflux condenser. The reaction mixture was stirred with a magnetic stir bar under nitrogen atmosphere (50 std cc/min) at the desired temperature (maintained with an oil-bath) for a period of 6 h. Samples were withdrawn periodically and analyzed on a Varian CP-3800 GC equipped with ZB-Wax capillary column (25 m $\times$ 0.32 mm $\times$ 0.2 μ m) and FID. The C balance based on analysis of liquid phase products was nearly $100 \pm 2.5\%$

3. Results and discussion

3.1. Characterization of Zr-KIT-5

SAXS patterns of Zr-KIT-5 samples as compared to a purely siliceous Si-KIT-5 are shown in Fig. 1. Reflections characteristic of face centered close-packed cubic lattice with *Fm3m* symmetry (111), (200) and (220) were observed for Si-KIT-5 and Zr-KIT-5 samples, with no significant changes in the intensity of these peaks up to Si/Zr ratio of 50 [16,26–28]. However, a drastic decrease in the peak intensity (with peak broadening) was observed at increasing

Fig. 1. SAXS patterns of Zr-KIT-5 materials compared with Si-KIT-5.

Table 1

Physicochemical characteristics of calcined Zr-KIT-5 samples with different zirconium content.

KIT-5 (Si/Zr) ^a	Si/Zr ^b	Zr (wt%)	a_0^c (nm)	S_{BET}^d (m ² /g)	V_{tp}^e (cc/g)	V_{mp}^f (cc/g)	$d_{\text{p, NLDFT}}^g$ (nm)
Si-KIT-5	–	–	19.7	1056	0.81	0.29	8.8
Zr-KIT-5(100)	96	1.6	20.4	1018	0.71	0.28	8.8
Zr-KIT-5(50)	51	2.9	20.9	1011	0.73	0.19	8.8
Zr-KIT-5(25)	25	5.7	20.3	971	0.81	0.03	8.8

^a Molar ratio in the synthesis gel.^b Actual molar ratio in sample determined by ICP-OES.^c $a_0 = d_{111} \sqrt{3}$.^d S_{BET} = specific surface area determined using Brunauer–Emmett–Teller (BET) equation from adsorption isotherm at P/P_0 between 0.05 and 0.30.^e V_{tp} = total pore volume at 0.99 P/P_0 .^f V_{mp} = micropore volume.^g $d_{\text{p, NLDFT}}$ = determined using NLDFT kernel developed for silica exhibiting cylindrical/spherical pore geometry.

Zr contents [e.g. Zr-KIT-5(25)] suggesting some decrease in long range ordering in this sample. Unit cell parameters derived from (111) reflections (Table 1) are typical of those previously observed for KIT-5 type materials [16,28–30]. A slight increase in the unit cell parameter was observed for Zr-KIT-5 samples as compared to Si-KIT-5 [16]. This increase is attributed to Zr incorporation in these samples, resulting in the replacement of Si^{4+} ions by Zr^{4+} ions with higher atomic radius. Elemental analysis (via ICP OES) showed that the Si/Zr ratios in the calcined Zr-KIT-5 samples are almost identical to those in the initial synthesis gel.

Nitrogen physisorption isotherms of Zr-KIT-5 and Si-KIT-5 samples are shown in Fig. 2a. Textural properties obtained from N_2 physisorption studies are summarized in Table 1. All KIT-5 samples showed type IV adsorption isotherm with sharp capillary condensations occurring between 0.60 and 0.70 P/P_0 and a broad H2-type hysteresis loop with desorption occurring at $\sim 0.47 P/P_0$. Results are in good agreement with those reported for KIT-5 type materials [16,28–30]. The shifted onset of desorption to much lower P/P_0 values is attributed to the presence of smaller pore windows. Such isotherms are typical of ordered mesoporous materials possessing large uniform cage-like pores. A significant change in the slope of the capillary condensation step was evidenced at increased Zr

content. This is reflected in the micropore volume measurement by the t-plot method (Table 1), which decreased at increasing Zr content. The high specific surface area observed for the parent Si-KIT-5 sample similarly decreased progressively with an increase in Zr loading.

The pore size distribution (estimated using NLDFT adsorption branch kernel developed for silica materials exhibiting either cylindrical or spherical pore geometry available in the Autosorb software) showed a bimodal distribution for all the KIT-5 samples [16,31] (Fig. 2b). The cage diameter of the primary mesopore is estimated to be approximately 8.8 nm. The presence of additional mesopores centered at approximately 2.4–2.8 nm is attributed to the entrance channels to the primary mesopore cages. Similar observation was also made in W-KIT-5 samples reported earlier by us [16].

Transmission electron microscopy images for representative Zr-KIT-5 samples are shown in Fig. 3. Cubic three-dimensional mesoporous structures with a high degree of long-range ordering, typical of $Fm3m$ structures, are clearly observed [16,31]. In addition, a homogeneous distribution of Zr species in Zr-KIT-5(25) sample can be seen in the electron mapping of a TEM image (see Fig. 4). The weight percentage of Zr estimated from this image is approximately 5.6, which is very close to that measured from ICP-OES (5.7%, see Table 1). We also performed the dispersion of Zr species in a fairly larger area in dual beam FIB/SEM and the results are presented in Fig. 5. A good agreement of 6.3 wt% Zr was obtained from the EDX analysis and a homogeneous dispersion of Zr was also noticed from electron mapping.

XRD patterns of calcined Zr-KIT-5 and Si-KIT-5 samples in the high angle region ($2\theta = 10\text{--}80^\circ$) were compared with ZrO_2 nanopowder (Aldrich) as depicted in Fig. 6. The broad diffraction peak centered at 2θ values of approximately $18\text{--}22^\circ$ corresponds to the amorphous silica walls of Zr-KIT-5 materials, as also observed in Si-KIT-5. No characteristic reflections corresponding to bulk zirconia could be observed in Zr-KIT-5 (100, 50 and 25) samples, suggesting a homogenous dispersion of Zr species in samples with low Zr loading, confirming the TEM and SEM analyses.

The diffuse reflectance UV–Vis spectra of Zr-KIT-5 materials are shown in Fig. 7. Distinct absorption bands around 203 nm and 209 nm were observed for the Zr-KIT-5(100 and 50) and Zr-KIT-5(25) samples, respectively. In addition, weak absorption bands around 230 nm and 280 nm were observed in all Zr-KIT-5 samples. In general, the absorption band around 205–215 nm, previously observed for Zr-containing mesoporous silicates, is attributed to ligand-to-metal charge transfer (LMCT) from an O^{2-} to an isolated Zr^{4+} ion in a tetrahedral configuration [32–36]. Based on these findings, we conclude that most of the Zr is incorporated as Zr^{4+} ion in a tetrahedral configuration in Zr-KIT-5 materials. The weak absorption band at 230 nm is attributed to LMCT of O^{2-} to Zr^{4+} typically present in ZrO_2 or Zr(IV) silicate [32–34,36] and the band at 280 nm samples may be attributed to the presence of

Fig. 2. (a) Nitrogen physisorption isotherms, and (b) pore size distributions, for Zr-KIT-5 and Si-KIT-5.

Fig. 3. Representative transmission electron microscopy images of Zr-KIT-5 (Si/Zr).

Fig. 4. STEM image of Zr-KIT-5(25) and its corresponding electron mapping and EDX analyses.

homogeneously distributed ZrO_2 nanoparticles [32–36]. The absence of reflection peaks due to crystalline ZrO_2 clusters in the wide angle XRD for Zr-KIT-5(100, 50 and 25, Fig. 6) suggests that either the particle size and/or the concentration of ZrO_2 clusters might be relatively low in these samples. Further, FTIR spectra of Zr-KIT-5 in the region of $1800\text{--}600\text{ cm}^{-1}$ (Fig. S1) reveal vibration bands associated with asymmetric and symmetric stretching vibrations of Si–O–Si bond at 1228 , 1082 and 804 cm^{-1} respectively. The bending vibration mode of Si–O–H is observed at

1650 cm^{-1} . Besides, the formation of Si–O–Zr units is confirmed by the characteristic vibration band at 966 cm^{-1} [37].

Fig. 8 shows the XPS spectra of Zr-KIT-5(25) for Zr3d lines ($3d_{3/2}$ and $3d_{5/2}$). The binding energy (BE) obtained for Zr $3d_{5/2}$ is 183.3 eV which is higher than the values reported for ZrO_2 (182.5) [38]. Bosman et al. reported an increase in BE of Zr $3d_{5/2}$ of about $0.6\text{--}1.2\text{ eV}$ with a decrease in Zr loading (in $\text{SiO}_2\text{--ZrO}_2$ mixed oxides) compared to pure ZrO_2 [38]. The observed BE values for Zr-KIT-5 are found to be close to those reported for Zr^{4+}

Fig. 5. Dual beam FIB/SEM image of Zr-KIT-5(25) and its elemental mapping and EDX analyses.

Fig. 6. Wide angle XRD of Zr-KIT-5 samples compared with commercial ZrO₂.

Fig. 7. Diffuse reflectance UV-Vis spectra of Zr-KIT-5.

Fig. 8. The XPS spectra of Zr-KIT-5(25) suggesting Zr incorporation as Zr^{4+} ions in KIT-5 silica framework.

Fig. 9. Ammonia TPD profiles of Zr-KIT-5 and Si-KIT-5.

incorporated TUD-1 silicates [32,34], providing further evidence of Zr incorporation as Zr^{4+} ions in the KIT-5 silica framework.

To measure the acidity of Zr-KIT-5 samples, temperature programmed ammonia desorption studies (NH_3 -TPD) were performed, benchmarking the results with Zr-free Si-KIT-5 sample. Ammonia TPD profiles are shown in Fig. 9. No significant ammonia desorption was observed for Si-KIT-5 (0.02 mmol NH_3 /g). However, the total acidity increased significantly to 0.22 mmol NH_3 /g for Zr-KIT-5(100) upon incorporation of a small amount (1.6 wt%) of Zr into KIT-5. The total number of acid sites increases with Zr content (see Table 2). FTIR spectra of adsorbed pyridine (measured at 120 °C) on Zr-KIT-5 samples (Fig. 10) confirmed the predominant presence of Lewis acid sites. The observed absorbance bands at around 1580 and 1440 cm^{-1} are attributed to pyridine adsorbed on Lewis (L) sites while those at 1480 cm^{-1} are assigned to a combination of Brønsted and Lewis (B + L) acid sites. Protonated pyridine species, typically observed on Brønsted acid sites around 1545 cm^{-1} , were weakly evident at low Zr loading [Zr-KIT-5(100)] and appear to increase with Zr content (see also Table 2). It has also been reported that the substitution of Zr^{4+} for Si^{4+} in the silica

Fig. 10. FTIR spectra of adsorbed pyridine over Zr-KIT-5 at 120 °C.

framework can result in Brønsted acidity at the bridging oxygen due to differences in the charge density of the two ions [39].

3.2. Benzylation of anisole over Zr-KIT-5

In general, the liquid phase benzylation of anisole with benzyl alcohol (BzOH) over Zr-KIT-5 catalysts results in the formation of only monobenzylation compounds such as ortho-benzylanisole (*o*-BA) and para-benzylanisole (*p*-BA) as major products (Scheme 1). The initially formed dibenzyl ether (DBE) is further consumed for the formation of *o*-BA and *p*-BA. Only very minor amount of meta-benzylanisole (*m*-BA) is observed. No significant BzOH conversion was noted when the reaction was performed without any catalyst (at 170 °C) and also with Si-KIT-5 (at 130 °C).

Fig. 11a shows temporal BzOH (limiting reactant) conversion profiles at different temperatures using 100 mg of Zr-KIT-5(25) catalyst. The corresponding product selectivities are given in Fig. 11b. At 110 °C, the BzOH conversion is only approximately 18% after 1 h and near complete conversion of BzOH is achieved after nearly 6 h. Further increases in reaction temperature (130–170 °C) markedly enhance the conversion rates, resulting in nearly total BzOH conversion within 30 min at 170 °C. Moreover, the selectivities towards benzylation products increase with reaction temperature (Fig. 11b). A significant amount of DBE is observed at lower reaction temperature (lower BzOH conversion), which also acts as an alkylating agent at higher temperatures thus improving selectivities towards *o*-BA and *p*-BA. The rate of DBE consumption (as an alkylating agent) is dictated by temperature. At lower temperatures (90 and 110 °C), the consumption rates are slow enough that it is possible to see its gradual evolution and consumption. At higher temperatures (130 °C and beyond), the consumption rate (as an alkylating agent) increases to such an extent that the DBE produced is totally consumed during the run with corresponding increases in the alkylated product. A figure reflecting the temporal DBE consumption profiles at various temperatures is presented in the ESI (see Fig. S1). Interestingly, at all temperatures, the ratio of *o*-BA/ *p*-BA was observed to be between 1.07 and 1.12.

Table 2

Variation of Lewis and Brønsted Acidities of Zr-KIT-5 samples with Zr content.

Sample	Total acidity ^a NH_3 mmol/g	Lewis (L) ^b	Brønsted (B) ^b	L/B ratio ^c
Zr-KIT-5(100)	0.22	0.53	0.02	47.8
Zr-KIT-5(50)	0.35	1.10	0.11	20.9
Zr-KIT-5(25)	0.59	1.27	0.26	10.4

^a From ammonia TPD measurements.

^b Relative areas estimated from FTIR spectra of adsorbed pyridine.

^c Calculated using absorption coefficients (bands at 1461 and 1454 cm^{-1} , $\epsilon = 0.165$ cm^2 μmol^{-1} ; band at 1545 cm^{-1} , $\epsilon = 0.078$ cm^2 μmol^{-1}).

Scheme 1. Benzylation of anisole with benzyl alcohol over Zr-KIT-5.

Fig. 11. Effect of temperature on (a) temporal BzOH conversion profiles, and (b) product selectivities at 6 h over Zr-KIT-5(25). Reaction conditions: anisole = 100 mmol, BzOH = 10 mmol, dodecane = 2 mmol, catalyst = 100 mg.

Fig. 12. Effect of Zr-KIT-5(25) catalyst amount on (a) temporal BzOH conversion profiles, and (b) product selectivities at 6 h, at 130 °C. Reaction conditions: anisole = 100 mmol, BzOH = 10 mmol, dodecane = 2 mmol, $T = 130\text{ }^\circ\text{C}$.

Similarly, catalyst amount has a significant effect on conversion of BzOH. With 25 mg of Zr-KIT-5(25) catalyst at 130 °C, about 45% BzOH conversion is observed after 6 h of reaction (Fig. 12a). However, doubling this catalyst amount (to 50 mg) yields nearly total BzOH conversion in 6 h. With 100 mg, complete conversion of BzOH is achieved in 2 h at 130 °C. The variation in catalyst amount also has an appreciable effect on product distribution (Fig. 12b). Although 100% BzOH conversion is achieved with 50 and 100 mg of catalyst, ~17% DBE (unreacted) is observed with 50 mg of catalyst. With 25 mg of catalyst, the amount of DBE (~28%) is similar to that of *p*-BA (~34%). These results demonstrate the importance of the availability of acid sites to convert not only BzOH but also the DBE.

The conversion rate of BzOH decreases with increasing BzOH concentration (decreasing anisole excess) in the feed (Fig. 13a). Similar conversion profiles are observed for molar feed anisole/BzOH ratios of 10 and 5, reaching ~100% BzOH conversion in 2 h and 4 h min respectively. For anisole/BzOH ratio of 2.5, only ~75% BzOH was converted after 6 h. The DBE formation (Fig. 13b) also increased with BzOH concentration (i.e. lower anisole/BzOH ratios), suggesting that the DBE formed by etherification is the primary product that acts as alkylating agent. Indeed, it was shown that DBE was preferentially formed over Lewis sites [20] and that formation of the ether is a faster reaction compared to the benzylation reaction [40].

The Si/Zr ratio and the acidity of Zr-KIT-5 materials play a crucial role in the BzOH conversion and product distribution (Fig. 14a). Zr-KIT-5(100), having a lower number of acid sites (22 mmol NH_3/g), yields only ~40% BzOH conversion in 6 h with DBE as the major product (~51% selectivity, see Fig. 14b). In contrast, ~98% BzOH conversion is observed with Zr-KIT-5(50) and ~15% DBE still remains after 6 h (Fig. 14b). The higher conversion rate of BzOH and DBE to form monobenzylated products over Zr-KIT-5(25) catalysts is clearly due to presence of a greater number of acid sites (both B and L sites) as compared to the other Zr-KIT-5 catalysts. As the Zr content is increased from 1.6 to 5.7 wt%, the L/B ratio decreases due to a steeper increase in the Brønsted acid sites relative to the Lewis acid sites. Similarly, the BzOH conversion normalized with respect to the total acid sites also increases as the Zr loading is varied (see Table 3, entries in rows 3–5). This clearly suggests that the nature of the acid sites plays a role in the observed conversion and selectivity profiles.

Comparison of the performance with literature reports (Table 4) clearly shows the superiority of Zr-KIT-5 over other microporous materials (HZSM-5 and H-Beta). The Zr-KIT-5 materials show higher catalytic activity at much lower temperature compared to Brønsted acidic catalysts such as Nb_2O_5 , niobium phosphate or mesoporous ZrPW. It also should be noted that at similar reaction temperature, complete conversion of BzOH was observed in shorter duration. Heteropoly acid catalysts are reported to catalyze

Fig. 13. Effect of initial anisole to BzOH mole ratio on (a) temporal BzOH conversion profiles, and (b) product selectivities, at 130 °C over Zr-KIT-5(25) catalyst.

Fig. 14. Effect of Si/Zr mole ratio on (a) temporal BzOH conversion profiles, and (b) product selectivities at 6 h at 130 °C; Reaction conditions: anisole = 100 mmol, BzOH = 10 mmol, dodecane = 2 mmol.

Table 3

Dependence of anisole benzylation over Zr-KIT-5 catalysts on total number of acid sites. Reaction conditions: anisole = 100 mmol, BzOH = 10 mmol, dodecane = 2 mmol, $T = 130$ °C.

Zr-KIT-5(Si/Zr)	Cat. amt	X_{BzOH}	$X_{\text{BzOH}}/\text{acid sites}^a$
25	25	5.4	36.7
25	50	10.5	35.7
25	100	22.2	37.6
50	100	14.4	32.1
100	100	8.1	21.8

^a Number of acid sites per g catalyst is listed in Table 2.

Table 4

Performance comparison of Zr-KIT-5 catalyst with literature data for anisole benzylation with benzyl alcohol.

Catalyst	T , °C	t , min	X_{BzOH}	Selectivity (%)		
				o-BA	p-BA	DBE
Zr-KIT-5(25)	130	240	100	51.8	47.3	0.7
Zr-KIT-5(25)	170	~40	100	52.6	46.9	0
H ₃ PO ₄ -WO ₃ -Nb ₂ O ₅ [22]	80	180	100	94	—	0.3
25% TPA/SnO ₂ [40]	120	90	95.12	33.56	42.26	24.17
ZSM-5 (HT) [11]	100	60	~30	—	—	—
MesoZSM-5(SO ₃ H-CTAB)-MW [11]	100	60	~100	—	—	—
Nb ₂ O ₅ /Al ₂ O ₃ [20]	160	90	100	29.2	44.9	20.3
Nb ₂ O ₅ [20]	160	180	100	27.4	41.2	16.6
Niobium phosphate [41]	160	<360	100	34.3	53.1	5.2
M-ZrPW-20 [42]	170	120	100	~87	—	—
H-Beta [42]	170	120	~63	~83	—	—
H-ZSM5 [42]	170	120	~17	~65	—	—

Fig. 15. (a) Recycle activity and hot-filtration studies, and (b) product selectivities at 6 h, for Zr-KIT-5(25) catalyst at 130 °C; reaction conditions: anisole = 100 mmol, BzOH = 10 mmol, dodecane = 2 mmol.

anisole benzylation at even lower temperature (80–120 °C) possibly due to higher number of Brønsted acid sites. Nevertheless, the Zr-KIT-5 catalyst can be recycled multiple times without loss of activity (Fig. 15a). Although the temporal BzOH conversion profiles for the different recycle runs are similar, a mild increase in

DBE was noted after the 3rd cycle (Fig. 15b). Also only mild variations in the textural properties were noticed for both the fresh and recycled catalysts (see Fig. S3 and Table S1). Further, when the reaction mixture was hot-filtered after 20 min, no significant

changes in BzOH conversion was noticed in the filtrate. The foregoing results clearly demonstrate that the Zr-KIT-5 catalysts are reusable and stable under the reaction conditions.

4. Conclusions

Successful Zr incorporation into the framework of KIT-5 was achieved via a one-step direct hydrothermal synthesis procedure. The structural ordering and Zr incorporation were confirmed from complementary analytical techniques such as SAXS, N₂ sorption, TEM, DRS-UV-Vis and XPS. Homogenous Zr dispersion was observed both from SEM and TEM analyses. All Zr-KIT-5 catalysts possess predominantly Lewis acid sites, with both the Lewis and Brønsted acid sites increasing with Zr content. The Zr-KIT-5 materials show facile and stable activity for anisole alkylation with benzyl alcohol leading mainly to mono-alkylated products, outperforming other acidic mesoporous catalysts reported in the literature. Our results suggest that the alkylation activity is dependent on both the number and nature of the acid sites. Thus, Zr-KIT-5 materials show promise as environmentally superior alternatives to conventional Friedel–Crafts alkylation catalysts.

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