Chemical Engineering Journal 278 (2015) 113–121

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

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

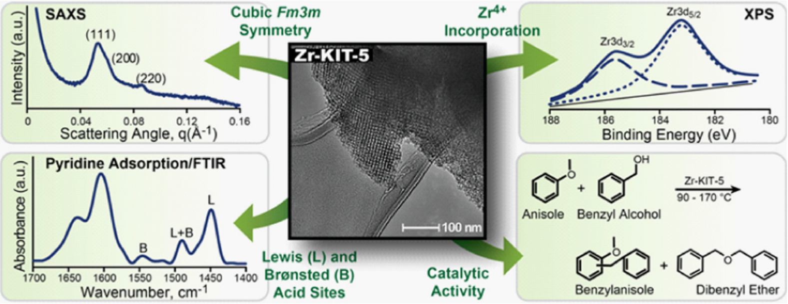
Anand Ramanathan [a], Hongda Zhu [a,b], Rajamanickam Maheswari [a,c], Bala Subramaniam [a,b,*]

[a] Center for Environmentally Beneficial Catalysis, The University of Kansas, Lawrence, KS 66047, USA
[b] Department of Chemical and Petroleum Engineering, The University of Kansas, Lawrence, KS 66045, USA
[c] Department of Chemistry, Anna University, Chennai 600025, India

HIGHLIGHTS

- New type of Zr-incorporated cage type *Fm3m* silicates, Zr-KIT-5, synthesized.
- Zr incorporation as Zr^{4+} evident from both UV–Vis and XPS results.
- Zr-KIT-5 materials exhibit dominant Lewis acidity that increases with Zr content.
- Zr-KIT-5 highly active and stable for anisole benzylation with benzyl alcohol.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Available online 3 December 2014

Keywords:
KIT-5
Zirconium
Friedel–Crafts alkylation
Anisole
Benzyl alcohol

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 (~1000 m^2/g) and pore volumes (0.7–0.8 cm^3/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 monobenzylated 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.

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

---

* Corresponding author at: Department of Chemical and Petroleum Engineering, The University of Kansas, Lawrence, KS 66045, USA. Tel.: +1 785 864 2903; fax: +1 785 864 6051.
E-mail address: bsubramaniam@ku.edu (B. Subramaniam).

http://dx.doi.org/10.1016/j.cej.2014.11.099
1385-8947/

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 N_2 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 (NH_3-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 × 0.32 mm × 0.2 μm) and FID. The C balance based on analysis of liquid phase products was nearly 100 ± 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 (1 1 1), (2 0 0) and (2 2 0) 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

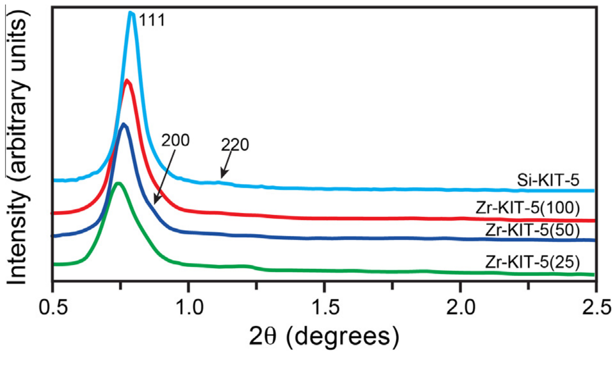


Fig. 1. SAXS patterns of Zr-KIT-5 materials compared with Si-KIT-5.