CATALYTIC ESTERIFICATION OF BENZYL ALCOHOL WITH ACETIC ACID BY ZIRCONIA –LOADED ON MESOPOROUS MATERIAL

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ABSTRACT

This research focuses on the synthesis and characterization of metal-containing mesoporous silica for catalytic esterification of benzyl alcohol with acetic acid. In this study Zr-containing MCM-41 (Zr-MCM-41) with different molar ratios were synthesized successfully, and the influence of the Si/Zr molar ratio on the crystalline structure, textural properties, morphological features and surface acidity of Zr-MCM-41 mesoporous molecular sieves was investigated by X-ray diffraction (XRD), N_2 adsorption-desorption measurement, SEM and FTIR (Fourier transform infrared) Spectroscopy, UV-Vis diffuse reflectance (UV-Vis DR), spectroscopy and single point BET. It is observed that the structural ordering of Zr-MCM-41 varies with the Si/Zr ratio, and highly ordered mesoporous molecular sieves could be earned for a Si/Zr molar ratio larger than 5. Calcination may significantly improve the structural regularity. After impregnation with 15 wt % of $H_3PW_{12}O_{40}$ (denoted as HWP hereafter),in esterification reaction of benzyl alcohol with acetic acid, the benzyl alcohol conversion over all the HPW/Zr-MCM-41catalysts linearly increases with increasing the reaction temperature, and selectivity to benzyl acetate was 100 %. The molar ratios of reactants also were investigated for final product yield; the molar ratio of acetic acid to benzyl alcohol can be 2:1 for high yield. The presence of zirconium in tetrahedral coordination was indicated by UV-Vis DR spectra, which shows an absorption band around 220 nm in Zr-MCM41. The catalyst had more active sites than pure Si-MCM-41 due to enhanced hydrophobicity properties and the presence of framework zirconium species as Lewis active sites. Kinetics studies have shown that the esterification reaction follows the Eley-Ridel mechanism. The energy of activation for the reaction follows the order: HPW/Zr-MCM-41(Si/Zr=5) > Zr-MCM-41(Si/Zr=10) > Zr-MCM-41(Si/Zr=20).

ABSTRAK

Penyelidikan ini adalah terfokus pada sintesis dan pencirian silika mesoliang yang mengandungi logam bagi pemangkinan pengesteran benzil alkohol dengan asid asetik. Dalam kajian ini MCM-41 yang mengandungi Zr dengan nisbah molar yang berbeza-beza telah berjaya disintesis, dan pengaruh nisbah molar Si/Zr terhadap struktur hablur, ciri-ciri tekstur, morfologi dan keasidan permukaan penapis molekul mesoliang Zr-MCM-41 mesoporous telah dikaji menggunakan pembelauan sinar-X (XRD), penjerapan-penyahjerapan N_2, SEM, spektroskopi FTIR (inframerah Fourier-transform), spektroskopi ultra-lembayung nampak pemantulan difusi (UV-Vis DR), dan analisis BET titik tunggal. Didapati bahawa keteraturan struktur Zr-MCM-41 berubah mengikut nisbah Si/Zr, dan penapis molekul mesoliang bertertib julat jauh dapat dihasilkan bagi sampel yang bernisbah molar Si/Zr lebih besar daripada 5. Proses pengkalsinan secara jelas boleh meningkatkan keteraturan struktur. Setelah pengisitepuan dengan $H_3PW_{12}O_{40}$ 15 wt% (diwakili sebagai HWP), dalam tindak balas pengesteran benzil alkohol dengan asid asetik, penukaran benzil alkohol bermangkinkan kesemua HPW/Zr-MCM-41 meningkat secara linear dengan peningkatan suhu tindak balas, dan peratus pemilihan terhadap benzil asetat adalah 100%. Nisbah molar reaktan juga dikaji terhadap penghasilan produk tindak balas, di mana nisbah molar asid asetik kepada benzil alkohol 2:1 telah menunjukkan peratusan hasil paling tinggi. Kehadiran zirkonium dalam koordinatan tetrahedral telah ditunjukkan oleh jalur serapan pada sekitar 220 nm dalam spektrum UV-Vis DR bagi Zr-MCM-41. Mangkin tersebut adalah lebih aktif berbanding Si-MCM-41 tulen kerana peningkatan sifat hidrofobik dan kehadiran spesies zirkonium bingkaian sebagai tapak aktif Lewis. Kajian kinetik telah menunjukkan bahawa tindak balas pengesteran benzil alkohol dengan asid asetik berlaku menurut mekanisme Eley-Rideal. Tenaga pengaktifan bagi tindak balas tersebut adalah mengikut tertib: HPW/Zr-MCM-41 (Si/Zr = 5) > Zr-MCM-41 (Si/Zr = 10) > Zr-MCM-41 (Si/Zr = 20).

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AAS	-	Atomic absorption spectroscopy
AA	-	Acetic acid
BA	-	Benzyl alcohol
CTABr	-	Cetyltrimethylammonium bromide
ER	-	Eley-Ridel
FTIR	-	Fourier transformer infrared spectroscopy
HPW	-	Tungsten phosphoric acid
KBr	-	Potassium bromide
LH	-	Langmuir-hinshelwood
MCM	-	Mobil composition of matter
RHA	-	Rice husk ash
SI – MCM – 41	-	Purely siliceous MCM-41
TEOS	-	Tetraethylorthosilicate
DR UV – Vis	-	Diffuse reflectance ultraviolet-visible Spectroscopy
XRD	-	X-ray diffraction
Zr – MCM - 41	-	Zirconia containing MCM-41

LIST OF APPENDICES

Solid acid catalysts as zeolites are convenient alternatives to such conventional acids which have been used as catalysts since 1960s in petrochemicals manufacture, further expanding into areas of speciality and fine chemical synthesis [6]. But zeolites are microporous materials and meet with diffusional resistance both for reactants and products as well as applicable only for smaller molecular organic compound.

Mesoporous silica possesses high specific surface areas, tunable pore channels from 16 to 100Á and high specific pore volumes, which show that mesoporous silica is considerable to overcome the limitation of zeolites. Since, mesoporous materials do not have efficient catalytic properties due to absence of catalytically active sites, so MCM-41 is often modified by incorporating certain active materials such as metal oxides, metal complexes and others. therefore, the research is conducted in order to synthesize the zirconia loaded MCM-41 and the resulting material tested in the esterification of benzyl alcohol with acetic acid. Figure 1.1 gives the reaction scheme for esterification of benzyl alcohol with acetic acid.

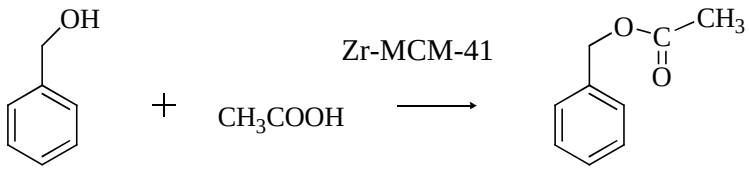

Figure 1.1 Esterification of benzyl alcohol with acetic acid

1.2 Objectives of Study

The research objectives are listed as below:

(a) To synthesize high quality zirconia loaded on MCM-41

(b) To characterize the physicochemical properties of the catalyst by, Fourier-Transform Infrared (FTIR) spectroscopy, Diffuse reflectance UV-Visible (DRUV-Vis) spectroscopy, X-ray diffraction (XRD), and nitrogen adsorption desorption measurement.

(c) To investigate the catalytic properties of Zr-MCM-41 in the esterification of benzyl alcohol with acetic acid

(d) To study the chemical kinetics of the esterification of benzyl alcohol with acetic acid.

1.3 Scopes of Research

The scopes of the research are listed as below:

(a) Direct synthesis of zirconia loaded on MCM-41(Zr-MCM-41) with various content of zirconium.

(b) Characterization of physicochemical properties of Zr-MCM-41 using XRD, nitrogen on adsorption desorption isotherm, DR UV-Vis and FTIR spectroscopies.

(c) Optimization of the reaction parameters such as temperature, reaction time and molar ratio of reactants.

(d) Investigation on the chemical kinetic of reaction of benzyl alcohol with acetic acid.

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