DEVELOPMENT OF MODIFIED MCM-41 CATALYST SYSTEM TOWARDS EPOXIDATION OF 1-OCTENE AND METHYL OLEATE

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Declaration

I hereby declare that the work reported in this thesis is my own, unless specified and acknowledged by quotation.

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ABSTRACT

The discovery of mesoporous molecular sieves has created a tremendous interest in the synthesis of these materials, particularly MCM-41 and its analogue, because of their very high surface areas and possibility of precisely tuned pore sizes (20-100 Å). These mesoporous materials have a wide range of potential applications starting from selective adsorption to heterogeneous catalysis, particularly for bulky molecules. Ti-MCM-41 has been widely developed as a catalyst for olefin epoxidation because of the active sites of Ti can acts as a very reactive compound for this reaction besides MCM-41 plays an important role as a support which is in the mesopore range. The research done provides an optimal reaction condition for epoxidation of Methyl Oleate using Ti-MCM-41 samples, based on the study of epoxidation of model compound, 1-Octene. The optimized reaction conditions lead to a maximum of epoxide selectivity and yield and also alkene conversion.

In this study, a series of mesoporous titanosilicate Ti-MCM-41 molecular sieves with various Si/Ti ratios, 25, 55, 66, 80 and 100 have been hydrothermally synthesized at 100^{O}C for 48 hours, using surfactant namely hexadecyl-trimethylammonium bromide as template and tetramethylammonium hydroxide as mineralizer. Chemical and physical properties of products obtained were characterized using powder X-ray diffraction (XRD), FTIR spectroscopy, DRUV-visible spectroscopy, nitrogen sorption measurements, differential thermal analysis (TGA-DTG), and scanning electron microscopy (SEM). XRD analysis shows that Ti-MCM-41 is a semicrystalline material with ordered mesoporous hexagonal structure which is indicated by a reflection peak at 2θ in the range of 1.6˚ to 2.6˚. The crystallinity of

Ti-MCM-41 after calcinations was almost two-fold higher than that of the as-synthesized one. Calcination in nitrogen leads to desorption of organic templates from the pores of Ti-MCM-41 in contrast to template burning in air. The crystallinity and surface area of Ti-MCM-41 both decrease with an increase of titanium content. Nitrogen sorption measurements exhibit BET surface area of Ti-MCM-41 are in the range of 880 m^2g^{-1} to 1075.163 m^2g^{-1}. Quite high BET surface areas with isotherms of type IV of the samples are typical for hexagonal MCM-41 type ordered mesoporous materials. The results of XRD and FTIR show that the solid products have the MCM-41 structure and contained only atomically dispersed titanium, consistent with framework titanium in Ti-MCM-41. All of the materials had a uniform pore size distribution which is around 3.0 nm. DRUV-visible analysis shows that Ti-MCM-41 has two types of titanium species; one species is titanium isolated tetrahedral which is active to catalyze epoxidation of alkenes and the other is titanium isolated octahedral. Catalytic activities of Ti-MCM-41 were tested in the epoxidation of 1-Octene and methyl oleate using tert-butyl hydroperoxide as peroxide in a batch reactor. Catalyst with high titanium content (Si/Ti = 25) is prone to deactivate due to high side compounds although at one hand, the hydrophobicity is improved. The titanium sites in MCM-41 catalysts are buried on the silica walls, being non-accessible to the reactants, thus lower the catalytic activity and turnover. The best is to use catalysts with average amount of titanium (Si/Ti = 80). When comparing between silylated and non-silylated samples, it was found that silylated samples exhibit higher catalyst activity, and the conversion and TON increased three times as compared to non-silylated samples. Silylation increases greatly the hydrophobicity of Ti-MCM-41 catalysts and therefore, water concentration on the surface of catalyst is reduced, and subsequent glycol formation which is one of the side products is nearly avoided. Silylation also decreases the number of silanol groups (and very probable Ti-OH groups) in the catalyst whereby these groups posses a weak acid character, but strong enough to catalyze the undesired reaction of oxirane ring opening.

ABSTRAK

Dengan penemuan pengayak molekular mesoporos menyedarkan perhatian yang khusus diberikan kepada sintesis bahan ini terutamanya MCM-41 dan analognya kerana sifat luas permukaannya yang tinggi dan kebolehan melaras saiz liang dengan tepat (20-100 Å). Bahan mesoporos ini merangkumi bidang aplikasi yang luas dan berpotensi besar bermula daripada sebagai penjerapan selektif sehingga kepada mangkin heterogenous, khususnya bagi molekul bersaiz besar. Mangkin Ti-MCM-41 telah banyak dikembangkan untuk tindak balas pengepoksidaan olefin disebabkan sifat titanium yang reaktif bagi tindak balas ini manakala MCM-41 bertindak sebagai penyokong yang bersifat mesoporos. Kajian ini menyediakan suatu keadaan tindak balas yang optimum bagi tindak balas pengepoksidaan metil oleat menggunakan sampel Ti-MCM-41 berdasarkan kepada kajian pengepoksidaan bahan model, 1-oktena. Keadaan tindak balas optimum yang diperolehi terarah kepada peningkatan secara maksimum di dalam keselektifan untuk hasil epoksida dan penukaran alkena.

Di dalam ujikaji ini, satu siri titanosilikat mesoporos, pengayak molekular Ti-MCM-41 dengan pelbagai nisbah mol Si/Ti 25, 55, 66, 80 dan 100 disintesis secara hidroterma pada suhu 100^{O}C selama 48 jam, menggunakan surfaktan seperti heksadesiltrimetilammonium bromida sebagai *templat* dan tetrametilammonium hidroksida sebagai bahan mineral. Sifat kimia dan fizikal mangkin terbentuk dicirikan menggunakan teknik seperti pembelauan sinar-X (XRD), spektroskopi FTIR, spektroskopi DRUV-vis, ukuran penjerapan/ penyerapan nitrogen, analisis terma pembezaan (TGA-DTG) dan mikroskopi imbasan elektron (SEM). Analisis XRD menunjukkan Ti-MCM-41 yang dihasilkan bersifat semi-kristal dengan aturan

struktur heksagonal mesoporos seperti yang ditunjukkan oleh puncak pembelauan pada sudut 2θ antara 1.6˚ hingga 2.6˚. Mangkin Ti-MCM-41 selepas pengkalsinan menunjukkan penghabluran dua kali ganda lebih tinggi berbanding mangkin tanpa pengkalsinan. Ini disebabkan pengkalsinan di dalam nitrogen dapat mengeluarkan templat organik yang terdapat di dalam liang Ti-MCM-41 sementara pembakaran templat berlaku di dalam udara semasa proses pengkalsinan. Pembentukan hablur dan luas permukaan berkurang dengan penambahan kandungan titanium. Daripada ukuran penjerapan/ penyerapan nitrogen, luas permukaan Ti-MCM-41 adalah dalam julat 880 m^2g^{-1} to 1075 m^2g^{-1}. Sampel menunjukkan luas permukaan BET yang agak tinggi dengan isoterma jenis IV, merupakan parameter biasa bagi unsur aturan mesoporos jenis MCM-41 heksagonal. Keputusan XRD dan FTIR menunjukkan pepejal yang terhasil mengandungi struktur MCM-41 dan juga titanium terlarut secara atomik, selari dengan kerangka titanium di dalam Ti-MCM-41. Kesemua sampel mempunyai penyerakan saiz liang yang seragam iaitu dalam lingkungan 3.0 nm. Analisis DRUV-visible menunjukkan Ti-MCM-41 mempunyai dua spesis titanium; iaitu titanium terisolasi secara tetrahedral yang aktif di dalam tindak balas pengepoksidaan alkena dan titanium terisolasi secara oktahedral. Aktiviti pemangkinan Ti-MCM-41 ditentukan di dalam tindak balas pengepoksidaan 1-oktena dan metil oleat di dalam reaktor sekumpul dengan menggunakan tert-butil hidroperoksida sebagai agen peroksida. Mangkin dengan kandungan titanium yang tinggi (Si/Ti = 25) cenderung untuk mengalami penyahaktifan, akibat pertambahan produk sampingan walaupun pada masa yang sama, sifat kehidrofobikan diperbaiki. Kawasan titanium di dalam mangkin MCM-41 tertanam pada dinding silika, menyebabkan ia tidak dapat bertindak balas dengan reaktan, seterusnya merendahkan aktiviti pemangkinan. Komposisi titanium terbaik ialah menggunakan kuantiti titanium yang sederhana (Si/Ti = 80). Apabila membandingkan sampel yang tersililat dan tidak tersililat, didapati sampel yang tersililat menunjukkan peningkatan sebanyak tiga kali ganda aktiviti pemangkinan berbanding sampel yang tidak tersililat. Pensililan sangat membantu meningkatkan sifat kehidrofobikan mangkin Ti-MCM-41 kesan daripada pengurangan kepekatan air pada permukaan mangkin dan seterusnya menghindar penghasilan glikol yang merupakan salah satu produk sampingan. Proses pensililan dapat mengurangkan jumlah kumpulan silanol di dalam mangkin (besar kemungkinan kumpulan Ti-OH) yang mana kumpulan ini memiliki ciri-ciri asid lemah, tetapi cukup kuat untuk menjadi pemangkin bagi tindak balas pembukaan gelang oksiran yang tidak diperlukan pada peringkat ini.

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