

SYNTHESIS AND CHARACTERIZATION OF TIN-MODIFIED MESOPOROUS
SILICA MCM-48 FOR SELECTIVE OXIDATION OF ALCOHOL TO ALDEHYDE

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Amitabha
To my beloved parents
Lam Ah Lin and Wong Heng Hoong
for their love that made me firm and resolute

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PREFACE

This thesis is the result of my work carried out in the Department of Chemistry; Universiti Teknologi Malaysia between November 2004 to September 2006 under supervision of Assoc. Prof. Dr. Salasiah Endud. Part of my work described in this thesis has been reported in the following publications or presentations:

1. Wong, K.-L. and Endud, S. Synthesis, Characterization, and Catalytic Properties of Tin Containing MCM-48 in Oxidation of Alcohols. *Proceedings of Annual Fundamental Science Seminar 2005*. July 4-5, 2005. Johor, Malaysia: Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia. 2005. 87-95.
2. Wong, K.-L. and Endud, S. Tin-containing Mesoporous MCM-48 in Oxidation of Benzyl Alcohol to Benzaldehyde. Poster presentation at the *18th Symposium Kimia Analisis Malaysia (SKAM-18)*. Universiti Teknologi Malaysia, Skudai, Johor, Malaysia. September 12-14, 2005. P-90.
3. Wong, K.-L. and Endud, S. Mesoporous Silica MCM-48 Molecular Sieve Modified with SnCl₂ in Alkaline Medium for Selective Oxidation of Alcohol. Oral presentation at the *International Symposium on Zeolites and Microporous Crystals (ZMPC 2006)*. Yonago, Tottori Pref., Japan. July 30- August 2, 2006.

4. Wong, K.-L. and Endud, S. Nanostructured Tin Oxide Catalysts Prepared by Molecularly Designed Dispersion: An Oxidation System for Green Chemistry. Exhibitor in the *8th Industrial Art and Technology Exhibition (INATEX 2006)*. Universiti Teknologi Malaysia, Skudai, Johor, Malaysia. August 29-September 4, 2006. Gold Medal Winner.

5. Endud, S. and Wong, K-L. Mesoporous Silica MCM-48 Molecular Sieve Modified with SnCl₂ in Alkaline Medium for Selective Oxidation of Alcohol. *Micropor. Mesopor. Mater.*, 2007. 101: 256-263.

ABSTRACT

Tin-modified mesoporous silica MCM-48 with various Si/Sn ratios has been prepared by post synthesis modification in alkaline medium. Local rice husk ash (RHA) has been used as Si precursor in the synthesis of Si-MCM-48 samples while SnCl₂ was used as the tin source in the modification. The tin-modified MCM-48 samples were characterized by using powder X-ray diffraction (XRD) analysis, Fourier transform infrared (FTIR) spectroscopy, ultraviolet-visible diffuse reflectance (UV-Vis DR) spectroscopy, nitrogen physisorption measurement, field emission scanning electron microscopy (FESEM) and temperature-programmed reduction (TPR) analysis. Surface acidity of the prepared samples was determined by using pyridine adsorption-desorption measurement followed by FTIR spectroscopy. In addition, thermal and hydrothermal stability testing for the tin-modified samples were carried out. The FTIR, UV-Vis DR and XRD results show that tetrahedral tin species can be introduced into the mesoporous material without destroying the framework structure of the molecular sieves. Surface acidity studies confirm that Lewis acid sites had been generated on the mesoporous silica MCM-48 by post-synthesis modification. The generation of Lewis acid sites could be due to the introduction of tin species and/or because of defect sites that had been created during post-synthesis modification. Tin-modified sample SnM60 (Si/Sn = 60) possessed highest amount of Lewis acidity. In oxidation of benzyl alcohol, all the tin-modified samples gave 100% selectivity to benzaldehyde in reaction time under 22 hours. The catalytic activity can be correlated with the Lewis acid sites generated by post-synthesis modification. Purely siliceous MCM-48 and physically mixed tin-containing MCM-48 samples that possesses no Lewis acidity gave poor performance in the catalytic reaction. With the increase in the amount of oxidant in the reaction mixtures, the conversion of benzyl alcohol increased significantly but the selectivity for benzaldehyde was reduced. For reusability test, the catalytic performance of the re-used samples was maintained within 5-10% after two cycles of reuse without significant loss of activity. Comparison of the catalytic performance of SnM60 in the oxidation of unsaturated primary alcohols and saturated aliphatic primary alcohol towards the corresponding aldehydes showed higher % conversion of the unsaturated primary alcohols than that of the saturated aliphatic primary alcohol.

ABSTRAK

Silika berliang meso MCM-48 yang terubahsuai dengan timah dalam pelbagai nisbah Si/Sn telah disediakan melalui pengubahsuaian pasca-sintesis dalam medium alkali. Abu sekam padi tempatan telah digunakan sebagai sumber Si dalam sintesis sampel Si-MCM-48, manakala SnCl_2 telah digunakan sebagai sumber timah dalam pengubahsuaian tersebut. Sampel MCM-48 yang mengandungi timah telah dicirikan dengan kaedah pembelauan sinar-X (XRD), spektroskopi inframerah transformasi Fourier (FTIR), spektroskopi pemantulan difusi ultralembayung-nampak (UV-Vis DR), penyerapan nitrogen, mikroskopi elektron pengimbasan pancaran medan (FESEM) dan analisis penurunan dengan suhu teraturcara (TPR). Keasidan permukaan bagi sampel yang telah disediakan telah diperolehi melalui penyerapan-penyahjerapan piridina diikuti dengan spektroskopi inframerah. Ujian kestabilan termal dan hidrotermal juga telah dijalankan ke atas sampel. Hasil XRD, FTIR and UV-Vis DR menunjukkan bahawa spesies timah dapat diselitkan dalam bahan berliang meso tanpa memusnahkan struktur kerangka penapis molekul tersebut. Kajian keasidan permukaan mengesahkan bahawa tapak asid Lewis telah dapat dihasilkan pada silika berliang meso MCM-48 dengan pengubahsuaian pasca-sintesis. Penghasilan tapak asid Lewis tersebut mungkin disebabkan oleh penyelitan sepsis timah atau tapak kecalaan yang terbentuk semasa pengubahsuaian pasca-sintesis. Sampel terubahsuai dengan timah SnM60 (Si/Sn = 60) mempunyai keasidan Lewis yang tertinggi. Dalam ujian pemangkinan, semua sampel terubahsuai dengan timah memberikan kepilihan 100% terhadap benzaldehid dalam masa tindak balas bawah 22 jam. Aktiviti pemangkinan dapat dikaitkan dengan tapak asid Lewis yang terhasil dengan pengubahsuaian pasca-sintesis. MCM-48 bersilika tulen dan sampel MCM-48 terkandung timah yang disediakan secara campuran fizikal memberikan prestasi yang rendah dalam tindak balas pemangkinan. Dengan peningkatan kandungan ejen pengoksidaan dalam campuran tindak balas, nyata sekali bahawa penukaran benzil alkohol juga meningkat, tetapi kepilihannya terhadap benzaldehid telah menurun. Dalam ujian penggunaan semula, prestasi pemangkinan bagi sampel terpakai masih dapat dikekalkan setelah dipakai semula sebanyak dua kali dengan hanya perbezaan aktiviti sebanyak 5-10% berbanding dengan yang asal. Perbandingan aktiviti pemangkinan SnM60 dalam penukaran alkohol primer tak tepu dan alkohol primer alifatik tepu kepada aldehid sepadan menunjukkan % penukaran alkohol primer tak tepu lebih tinggi daripada alkohol primer alifatik tepu.