ABSTRACT

A series of $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}$ oxide catalysts were prepared using a standard recipe, with modifications to the method, i.e. addition of oxalic acid and diluents. These catalysts were subjected to activation process comprised of two different steps of calcination. The calcined samples were subjected to further modification by leaching processes in three different types of leaching media, i.e. water, nitric acid and ammonia solution. The structural, chemical, and thermal properties of the as-synthesized phase and surface modification catalyst were investigated with various characterization techniques, including X-ray diffraction (XRD),, BET surface area, X-ray fluorescence (XRF), scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX), thermogravimetric analysis coupled to mass spectroscopy (TG-MS), as well as differential scanning calorimetry (DSC). The reactivity studies have been done by temperature programmed reaction spectroscopy (TPRS) and temperature programmed reduction spectroscopy (TPR). In order to induce the catalytic activity of oxidation of propane to acrylic acid, all catalysts were further investigated for propane oxidation using high-throughput fixed bed reactor system or commonly referred to as Nanoflow.

The BET surface areas for undiluted system are in the typical range of $1.0 - 10.0 \ m^2g^{-1}$ for the MoVTeNb oxide and diluted in the range $30.0 - 50.0 \ m^2g^{-1}$. Addition of oxalic acid enhanced the surface area and catalytic activity. Different surface morphology of the catalyst obtained by low-magnification SEM images from the calcined and leaching samples indicates that leaching perturbed the surface morphologies of the catalysts. XRD result shows the calcined and leached sample to be constituted by M1 phase and M2 phases in the ratio of 50-60% and 20-30%, respectively. This also indicates that when leaching

process occurs in oxide phase, the structure or chemical bonds were strong enough to resist breakage and thus could not be leached out easily. High-resolution TGA-MS and DSC analysis played a key role to the relevant material synthesis process. Their ability to identify the solid state of the material will further illustrate the kinetic differences of the ligand removal and gases evolved during calcination. It was proven that the preparation method, post-precipitation treatment, post calcination treatment and the activation procedure would affect the physico-chemical nature of the MoVTeNb oxide catalyst and subsequently its performance as a selective oxidation catalyst for propane to acrylic acid. Reducing agent such as oxalic acid is a good surface redox for the catalyst. Following that, a structure-activity correlation was attempted. No significant correlation was found between catalytic performance (conversion and selectivity) and M1/(M1+M2) ratios.

ABSTRAK

Beberapa siri $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}$ oksida telah dihasilkan dengan resipi standad, penambahan asid oksalid dan 'diluent'. Mangkin-mankin ini telah mengalami proses pengaktifan melalui dua langkah pengkalsinan yang berbeza. Mangkin yang telah dikalsinasi kemudiannya mengalami proses basuhan dengan menggunakan agen basuhan seperti air, nitrik asid dan larutan ammonia. Sifat-sifat struktur, kimia, dan terma bagi sistem dua fasa tulen telah dicirikan dengan menggunakan pelbagai kaedah pencirian termasuk kaedah pembelauan sinar-X (XRD), penjerapan dan penyahjerapan gas nirrogen (BET), pendaflour sinar -X (XRF), mikroskop electron imbasan dan taburan tenaga sinar-X (SEM-EDX), termagravimetrik-jisim spektroskopi (TGA-MS), dan perbezaan imbasan tenaga (DSC). Pembelajaran reactiviti mangkin telah menggunakan pemprograman suhu reaksi spektroskopi (TPRS) dan pemprograman suhu reductif (TPR). Bagi merealisasikan aktiviti pengoksidaan propana kepada asid akrilik, kesemua mangkin telah menjalani process aktiviti menggunakan 'high-throughput' fixed bed reaktor atau Nanoflow.

Analysis BET untuk system yang tidak dilarutkan mempunyai luas permukaan antara 1.0 hingga 10.0 m^2/g manakala mangkin MoVTeNb oksida yang dilarutkan mempunyai luas permukaan antara 30-50 m^2/g. Pnamabahan asid oksalid telah Berjaya meningkat luas permukaan. Pelbagai morphologi dapat dihasilkan menaggunakan gambar dari SEM beresolusi rendah untuk sampel yang telah dikasinasi dan dibasuh menaggunakan pelarut di mana sampel yang dibasuh menunjukkan permukaan mangalami perubahan. XRD tealh menunjukkan terdapat dua struktur fasa telah dihasilkan iaitu M1 dan M2 di mana komposisinya adalah 50-60 % dan 20-30 % untuk fasa yang lagi satu. Ini menunjukkan bahawa, proses basuhan bagi sampel yang telah dikalsinasi tidak menagubah struktur

dalaman sampel tersebut. Teknik TGA dan DSC dapat menunjukkan perubahan kinetic semasa pemabuangan ligan dan gas semasa kalsinasi berlaku di mana ia menunjukkan perubahan dari fasa tak stabil kepada fasa stabil. Ini membuktikan bahawa proses penghasilan, roses pembasuhan, proses pengkalsinan dan proses pengaktifan telah memberi kesan kepada struktur magkin MoVTeNb oksida terhadap process selektif propane kepada asid akrilik.Agen penurunan seperti asid oksalid telah memeberikan kapasiti penurunan terhadap mangkin. Tiada korelasi di anatara perhubungan sturktur mangkin dengan bilangan M1/(M1+M2).