

SYNTHESIS OF SULFONIC ACIDS MODIFIED SILICA COATED ON MAGNETITE AND ENVIRONMENTAL CONTROL WITH ORGANOSILANES FOR CATALYST OF ETHYL ACETATE HYDROLYSIS

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ABSTRACT

Sulfonic acids modified silica coated on magnetite has been prepared, characterized and tested as catalysts for the hydrolysis of ethyl acetate. Coating was carried out through the sol-gel process by mixing magnetite, tetraethoxysilicate and 2-propanol as a solvent. In the modification of silica coated magnetite, (3-mercaptopropyl)trimethoxysilane (MPTMS) was used as a source of thiol (-SH) groups with various sulfur densities. These thiol groups then were oxidized with concentrated nitric acid to obtain sulfonic acid groups. The organosilane graftings for synthesizing sulfonic acid catalysts were triethoxyethylsilane, triethoxyphenylsilane and triethoxyoctylsilane as precursors of organosilane compounds. The acidity of these catalysts was examined using an ion exchange method with NaCl solution. The sodium and chloride ions which were not exchanged were analyzed with Ion Chromatography (IC). The products of the catalytic reaction were examined using Gas Chromatography (GC).

XRD data confirmed that the coating of magnetite and oxidizing of thiol groups maintained the crystallite size of magnetite. XPS showed that all magnetite surfaces were properly coated with silica. From ICP-AES analysis, the Si/Fe ratio of coated and uncoated magnetite did not change significantly. The success of MPTMS coating and organo-grafting was proved with the CHN and S analysis. It was obtained the highest and lowest sulfur densities were 1.7 nm^{-2} and 0.2 nm^{-2} , respectively. For the series sulfonic acid catalysts, the IC analysis results gave the maximum and minimum acid content of 0.89 and 0.18 mmol $\text{H}^+ \text{g}^{-1}$, respectively. Octyl-grafted catalyst generated the higher activity twice than phenyl, ethyl and non-grafted catalyst in the hydrolysis of ethyl acetate where water participated as a reactant. In addition, the increase of the surface density of acid sites resulted in an enhancement of the overall catalytic activities. The type of organosilane and the amount of MPTMS loading are the important factor to enhance the catalytic activity in the hydrolysis reactions. Organo-grafted catalyst is a magnetically separable and reusable water-tolerant solid acid catalyst.

Key words: magnetite, silica, sulfonic acid, acid catalyst, ethyl acetate.

SINTESIS SILIKA TERMODIFIKASI ASAM SULFONAT TERLAPIS MAGNETIT DAN KONTROL LINGKUNGAN DENGAN ORGANOSILAN UNTUK KATALIS HIDROLISIS ETIL ASETAT

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INTISARI

Silika termodifikasi asam sulfonat terlapis magnetit telah disintesis, dikarakterisasi, dan dites sebagai katalis untuk reaksi hidrolisis etil asetat. Pelapisan telah dilakukan melalui proses sol-gel dengan mencampurkan magnetit, tetraetilortosilikat dan 2-propanol sebagai solven. Pada modifikasi magnetit terlapis silika, (3-merkaptopropil)trimetoksisilan (MPTMS) digunakan sebagai sumber gugus thiol (-SH) dengan variasi jumlah sulfur. Gugus-gugus thiol dioksidasi dengan asam nitrat pekat untuk menghasilkan gugus-gugus asam sulfonat. Grafting dengan organosilan pada katalis asam sulfonat dilakukan dengan menggunakan prekursor trietoksietilsilane, trietoksifenilsilan dan trietoksioktilsilan. Keasaman katalis dianalisis menggunakan metode pertukaran ion dengan larutan NaCl. Ion-ion natrium dan klorin yang tidak tertukar dianalisis dengan kromatografi ion (IC). Produk-produk dari reaksi katalisis dianalisis dengan kromatografi gas (GC).

Data XRD mengkonfirmasi bahwa pelapisan magnetit dan oksidasi gugus thiol tidak merubah ukuran kristalit magnetit. Hasil karakterisasi XPS menunjukkan bahwa permukaan magnetit terlapis sepenuhnya dengan silika. Rasio Si/Fe tidak berubah pada magnetit dan magnetit terlapis. Kesuksesan pelapisan MPTMS dan grafting organosilan dibuktikan melalui analisis CHN dan S. Diperoleh bahwa densitas sulfur yang tertinggi dan terendah adalah $1,7 \text{ nm}^{-2}$ dan $0,2 \text{ nm}^{-2}$. Analisis IC menunjukkan bahwa jumlah asam tertinggi dan terendah dari sederatan katalis asam sulfonat diperoleh 0,89 dan 0,18 mmol $\text{H}^+ \text{g}^{-1}$. Katalis yang digrafting dengan oktil menghasilkan aktivitas katalitik dua kali lebih tinggi daripada fenil, etil dan tanpa grafting. Peningkatan densitas permukaan dari situs asam menyebabkan peningkatan pada aktivitas katalitik. Jenis organosilan dan jumlah MPTMS yang ditambahkan adalah faktor penting untuk meningkatkan aktivitas katalis dalam reaksi hidrolisis etil asetat. Katalis tergrafting organosilan merupakan katalis asam padat yang toleran terhadap air, dapat digunakan kembali, dan mudah dipisahkan dengan magnet eksternal.

Kata kunci: magnetit, silika, asam sulfonat, katalis asam, etil asetat.