Vanadium oxide supported on mesoporous SBA-15 modified with Al and Ga as catalysts in ODS of DBT.

Lorena Rivoira, M. Laura Martínez, Oscar A. Anunziata and Andrea R. Beltramone.

Centro de Investigación en Nanociencia y Nanotecnología (NANOTEC), Facultad Regional Córdoba, Universidad Tecnológica Nacional, Maestro López y Cruz Roja Argentina, 5016, Córdoba, Argentina.

Abstract

In order to adapt current processes to the strict regulatory requirements, several technologies have been developed for deep desulfurization of diesel fuel. The major portion of sulfur in light cycle oils (LCO) is found in dibenzothiophene (DBT) and alkyl-dibenzothiophenes, which are not easily removable by hydrotreating, because they require high pressure and hydrogen consumption. Vanadium oxides supported on mesoporous SBA-15 catalysts with different vanadium loadings were studied in the oxidative desulfurization (ODS) of dibenzothiophene as a model sulfur compound. The catalytic activity was improved when SBA-15 framework was modified with Al and Ga as heteroatom substituting framework Si. Structural and textural characterization of the catalysts were performed by means of XRD, N2 adsorption, UV–Vis–DRS, XPS, NMR, TEM, Raman, TPR and Py-FTIR. UV–Vis–DRS and Raman demonstrated that highly dispersed vanadium VO4-3 species are responsible for the high activity in the sulfur removal. The Ga modified support with an intermediate V/Si ratio of 1/30 was the most active catalyst for ODS of DBT, using hydrogen peroxide as oxidant and acetonitrile as solvent. 100% of DBT elimination was attained at a short time in mild conditions. Gallium and aluminum incorporation into the support modified successfully the nature of the SBA-15 surface by generating Bronsted and Lewis acidity. The interaction between the acid sites with the active vanadium sites improved the activity of the catalysts. The high dispersion depended on the vanadium loading and on the nature of the support. The more acidic support allowed better dispersion of the vanadium species due to stronger interaction metal-support. The reusability of the catalysts indicates that vanadium oxide supported on mesoporous SBA-15 modified with Ga and Al are potential catalysts for the ODS of dibenzothiophene.

Image

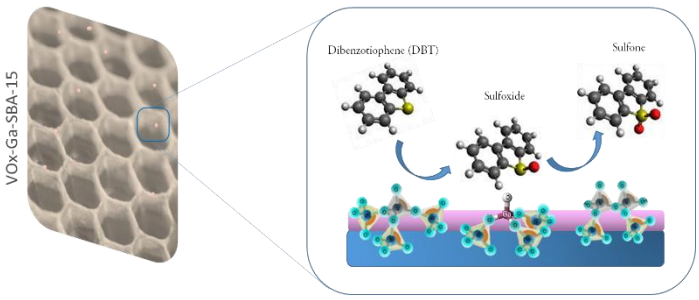

Figure 1: Graphical abstract describing how the oxidation reaction occurs in the active site of the mesoporous catalyst SBA-15 modified with Ga.

Recent Publications

1. Lorena P. Rivoira, Verónica A. Vallés, Brenda C. Ledesma, María V. Ponte, María L. Martínez, Oscar A. Anunziata, Andrea R. Beltramone (2016) Sulfur elimination by oxidative desulfurization with titanium-modified SBA-16. Catalysis Today 271: 102-113.
2. Lorena P. Rivoira; Juárez, Juliana; Horacio Falcón; Marcos B. Gómez Costa; Oscar A. Anunziata; Andrea R. Beltramone (2017) Vanadium and titanium oxide supported on mesoporous CMK-3 as new catalysts for oxidative desulfurization. Catalysis Today. 282, 2: 123–132.
3. Lorena Rivoira; María L. Martínez, Oscar Anunziata and Andrea Beltramone (2017) Vanadium oxide supported on mesoporous SBA-15 modified with Al and Ga as a highly active catalyst in the ODS of DBT. Microporous and Mesoporous Materials. In press.
4. Lorena Rivoira, María L. Martínez, Horacio Falcón, Andrea Beltramone, Pedro Tartaj, José M. Campos-Martín and José L. García Fierro (2017) Probing the Catalytic Activity of Sulfate-Derived Pristine and Post-Treated Porous TiO_2(101) Anatase Mesocrystals by the Oxidative Desulfurization of Dibenzothiophenes. ACS OMEGA. In press.
5. Lorena P Rivoira, Jorgelina Cussa, Maria L Martinez, Andrea R Beltramone (2017) Experimental design optimization of the ODS of DBT using vanadium oxide supported on mesoporous Ga-SBA-15. Applied Catalysis A. In press.

Biography

Lorena Rivoira has her expertise in ODS of sulfur compounds present in diesel fuel. Ultra-low-sulfur diesel (ULSD) must satisfy the upcoming regulation established all over the world in order to avoid global alterations such as greenhouse effect and ozone depletion, resulting in global warming. ODS can be carried out under mild

reaction conditions, liquid phase, low temperature, atmospheric pressure and therefore low operation cost. The research center NANOTEC has years of experience in nanomaterials which are capable to catalyze chemical reactions. These nonporous solid materials are versatile because their structure is easily modified through the addition of metals, oxides, etc. They present very high surface area and it make them adequate for ODS of high molecular weight molecules as benzothiophene (BT), dibenzothiophene (DBT), and substituted DBTs, which are precisely the most refractory compounds in hydrotreating.

Email: lrivoira@frc.utn.edu.ar

Notes/Comments: