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Effect of H_2S on selective hydrogenation of diolefins using NiPdCe(x)/Si-Al-coated structured packing catalyst

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ABSTRACT

The effect of Ce and H_2S on selective hydrogenation of diolefins using NiPdCe(x)/Si-Al-coated structured packing catalyst was studied for the selective hydrogenation of butadiene in the presence of benzene. The structured packing was coated by a silico-aluminate in which Ce, Ni and Pd were incorporated during successive impregnations. The catalyst was activated in the presence of hydrogen containing 10 ppm of hydrogen sulfide and tested in a continuous stirred tank reactor (CSTR) under different operating conditions. The catalysts were characterized by XRD, ²⁷Al- and ²⁹Si-NMR, TPR(H₂), IR, XPS, physical and chemical analysis. The results indicated that Ce and hydrogen sulfide affect the metal dispersion, the electronic configurations of the metals on surface and the acidity of the catalyst. Therefore the activity and selectivity is modified by both Ce and H₂S at constant Ni and Pd contents. The results were interpreted using a previously developed kinetics model.

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1. Introduction

The fast pyrolysis and steam cracking processes of cracked or straight run naphtha and other materials generates a stream of olefins containing a small amount of diolefins and sulfur. To further process the stream, the diolefins need to be selectively eliminated in presence of certain partial pressure of H_2S . The most popular method is liquid hydrogenation. Two inconveniences of this process are the presence of H_2S and the production of coke, which deactivates the catalyst even at a low operating temperature. Several authors [1–7] and our group [8] have studied and discussed different reaction mechanisms for the selective hydrogenation of butadiene. Currently, there is no agreement on how diolefin and olefin adsorption and reaction on Ni-based catalysts proceed.

Metal and coated metal packings were described by Twig and Webster [9]. In particular, the coatings of stainless steel packing were described and characterized by Natali et al. [10] and Truyen et al. [11], among others. We developed a selective and thioresistant catalyst based on PdNiCe deposition on coated stainless steel structured packing that achieved 98% diolefin reduction with a less than 10% loss of 1-butene [8,12]. It was found that the selectivity and stability of butadiene hydrogenation, which is a moderately exothermic process, is negatively affected by an increment in

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reaction temperature. We speculated that these hydrogenation reactions that take place on Ni promoted by Pd sites, while isomerization and dimerization on acid sites occurred at Brönsted acid sites controlled by Ce. A kinetic model was developed in a continuous stirred tank reactor (CSTR) [8,12] that uses Lagmuir-Hinselwood heterogeneous rate expressions for both types of reaction sites. It was also determined that benzene was strongly adsorbed onto both metallic and acidic sites.

Ce incorporated on MCM-41 exhibited high activity for various catalytic reactions, such as acylation of alcohols, vapor-phase dehydrogenation of cyclohexanol to cyclohexane, hydroxylation of 1-naphthol with peroxides and alkylation of naphthalene [13,14]. On PdCe/silicate and aluminosilicate mesoporous molecular sieves, Ce assists the methane oxidation catalyst by changing the reducibility of PdO [15]. PdCeNi/alumina was used for the reforming reaction of CH₄ with CO₂. The effect of the Pd/Ce ratio is considered to be an important factor in controlling Pd particle size, which consequently affects activity and selectivity [16–18]. The effect of Ni on cluster size of PdNi/Ce(Zr) alumina catalysts was discussed by Hungria et al. [19] and Martinez-Arias et al. [20].

The target is to selectively hydrogenate a C_{3-4} cut obtained from steam cracking commercial process that treat cracked naphtha with 100 ppm of sulfur compounds. Part of this sulfur (carbon disulfide and mercaptans) is transferred to the C_{3-4} cut; therefore during the selective hydrogenation of diolefins in liquid phase, H_2S is produced and the typical PdNi type catalysts are exposed to the presence of this compound and deactivated. This paper is focused on studying the effects of incorporating Ce to build a more thioresistant PdNiCe/silico-aluminate-coated 316SS catalytic packing. The effect

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