

Skeletal isomerization of 1-butene to isobutene over acid catalysts obtained by grafting silicon alkoxide on γ -alumina

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Introduction

The skeletal isomerization of 1-butene to isobutene has a strong industrial relevance because isobutene is intermediate in the production of methyl tert-butyl ether (MTBE), actually the most important oxygenated compound used as additive in lead-free gasoline. It is, therefore, important to convert butenes to isobutene, also considering that it is easier to obtain isobutene with the reaction sequence butane-butenes-isobutene than butane-isobutane-isobutenes. Many papers have been devoted to the kinetics and catalytic aspects of this reaction. All these papers agree with the observation that the reaction is catalysed by acid catalysts and occurs through a first step consisting in a double bond shifting, giving 2-butene (*cis* and *trans*), easily reaching the thermodynamic equilibrium. The isomerization to isobutenes, that is, the second reaction step, requires stronger acid sites. However, more acid catalysts promote also dimerization to octenes, cracking reactions with the formation of C₂, C₃, C₅ and C₆ olefins, and the formation of coke. The type of acidity (Lewis and Brønsted) and related strength strongly affect the selectivity. By examining the literature, the best catalysts seem to be those of medium strength, because the selectivity towards isobutene is enhanced and the catalysts deactivation prevented. At this purpose, silicated alumina catalyst seems to be one of the best. In this work, the catalyst has been prepared by grafting silicon alkoxide (TEOS) on γ -alumina in different conditions, i.e., in the presence of a solvent and by using different TEOS concentrations or in the absence of solvents. In this last case, the performances in the isomerization of 1-butene to isobutene were strongly enhanced. We compared the obtained results with those obtained by using other catalysts such as silica and silica-alumina. In particular, we observed that by increasing the amounts of TEOS grafted on alumina there is a progressive decrease of stronger Lewis acid sites and an increase of Brønsted acid sites of medium strength. This fact seems to be responsible of the stability and of the selectivity observed. A particular type of Al-Si site is probably formed at the border line of silica islands grafted on alumina with a uniform character and this justifies the high observed performances.