

Gallium-Promoted Sulphated Zirconia System: Synthesis, Physical-Chemical Characterisation and n-Butane Isomerisation Activity

M. Signoretto¹, F. Pinna¹, F. Somma¹, S. Melada¹, G. Cerrato², C. Morterra², M. Rodriguez Delgado³, C. Otero Arean³, P. Canton⁴

¹Dept. of Chemistry, University of Venice, Venice, I-30123 Italy; ² Dept. of Chemistry IFM, University of Turin, Turin, I-10125 Italy; ³Dept. of Chemistry, University of Balears Islands, Palma de Mallorca, E-07071 Spain, ⁴ Dept. of Physical-Chemistry of Venice, Venice, I-30123 Italy

The isomerization reaction of straight-chain hydrocarbons to branched hydrocarbons is an important process for the production of clean-burning fuels in the petrochemical refining industry. The current technology for n-butane isomerization is based on Pt/chlorided Al₂O₃ catalysts, which operates at elevated temperatures and require constant addition of alkyl chlorides to recover acid functionalities. Owing to the increasingly strict environmental regulations, researchers have paid attention to solid acid catalysts to search for stable and environmentally friendly catalysts. Among solid acids, sulphated zirconia (SZ) systems have attracted considerable attention because they are almost environmentally benign, more active and selective for the transformation of hydrocarbons. In this study, n-butane isomerization has been investigated over sulphated Ga-promoted zirconias and compared with sulphated zirconia, in order to investigate the influence of this promoter on the catalytic performances.

Samples were prepared by a co-precipitation method. ZrOCl₂·8H₂O and the required amount of Ga(NO₃)₃·n H₂O corresponding to 1; 3; 5; 9; 15% mol Ga₂O₃ (*n*GaSZ) were dissolved in distilled water and added dropwise under vigorous stirring to an ammonia solution. During the precipitation the pH value was kept constant at 8 by simultaneous addition of aqueous ammonia. The precipitate was washed free of chlorides, dried at 110°C for 20 h and sulphated by incipient wetness impregnation with an aqueous (NH₄)₂SO₄ solution. Sulphated samples were then dried at 110°C and calcined at 650°C for 3 h.

Isotherms obtained by N₂ adsorption at -196°C relative to calcined samples all belong to type IV IUPAC classification, and are characteristic of well-developed mesoporous systems, whilst the shape of the hysteresis loop is type H2-H3. Specific surface area (SSA) increases with Ga amount (up to *n*=5), and then decreases for higher amounts of Ga. All samples exhibit a unimodal pore size distribution with a maximum at D_p= 30-35Å. Ga-promoted calcined samples retain more sulphur than unpromoted one, following almost the same behaviour of SSA values. This points out that there is an increase in the sulphate retention after calcination paralleled by the surface area increase. If the sulphate content is normalised per surface area, the sulphates spreading is almost the same for all samples, ranging in the half-monolayer sulphates coverage.

The effect of Ga content on the catalytic activity of a sulphated zirconia system was studied in the n-butane isomerization at 250°C by feeding n-butane and H₂ with a ratio 1:4. Prior to the reaction, all catalysts were pre-activated in dry air at 450°C. The profile of conversion vs. time on stream is shown in figure 1. For all catalysts, after a steep initial decrease of activity, the conversion stabilises and no deactivation is then observed after 20 h. Steady state activity is greatly dependent on the Ga amount: a promoting effect is evident in the case of 1-9% GaSZ catalysts (3-5% GaSZ show the best conversion), whereas for 15% GaSZ activity is completely lost.

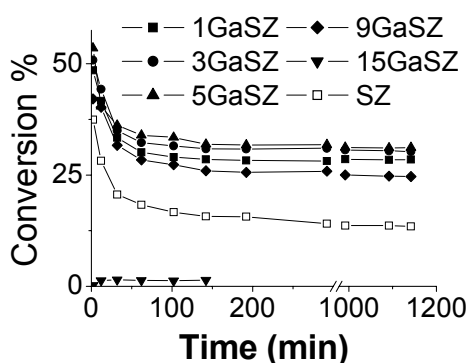


Figure 1. n-C₄H₁₀ isomerization at 250°C in H₂ (Conversion vs. TOS)

The shape of the particles seems to be partly influenced by the Ga loading: both sharp edges and roundish contours are evident for $n < 3$. For higher Ga loading, only roundish contours are observed, and the presence of a thin amorphous overlayer is evidenced in some particles. FTIR spectroscopy of the GaSZ systems indicates that both OH groups and sulphate species are present at the surface of the catalysts, and are similar to those typical of all active SZ-based catalysts. If the catalysts are brought to a medium-high dehydration degree, when $n < 9$, OH groups show a typical two-bands pattern, and surface sulphates exhibit the typical features of isolated polydentate covalent sulphates. For higher Ga loadings, these spectral features become deeply modified, as strong spectral components due to polynuclear sulphate species are observed. FTIR spectroscopy of basic probe molecules adsorbed to test surface acidity of Ga-promoted systems indicates that: (i) Brønsted acidity (2,6-dimethylpyridine ads/des in mild conditions), is always present if the surface is brought to a medium-high dehydration degree, and shows no peculiarity if compared with bare SZ-based systems. (ii) Lewis acidity (CO adsorption at RT as well as at 77K) is also always present (only CO-Zr⁴⁺ adducts are formed). Adsorption microcalorimetry of CO at 303K confirms the indications coming from FTIR spectroscopy: Ga-promoted SZ catalysts exhibit the same type of adsorbing sites (*i.e.*, Zr^{4+} cations) even in the presence of a high Ga loading, but the surface population of these sites turns out to be an inverse function of the loading.

As far as bulk structure is concerned, all GaSZ samples calcined at 650°C exhibit crystalline form belonging to the tetragonal ZrO₂ modification, except for the 15GaSZ specimen, for which crystallinity is almost totally lost. A similar indication comes from Raman spectroscopy: all samples show the spectral pattern typical of tetragonal (sulphated) zirconia, but for high gallia loadings ($n \geq 9$) these features start fading away leaving an almost structureless spectrum. TEM indicates that all catalysts exhibit high crystallinity and individual particles (5-8 nm average size).