



On catalyst activation and reaction mechanisms in propane aromatization on Ga/HZSM5 catalysts

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ARTICLE INFO

Article history:

Received 13 March 2012

Received in revised form 22 May 2012

Accepted 25 May 2012

Available online 4 June 2012

Keywords:

Gallium

HZSM5

Alkane aromatization

In situ DRIFTS

Catalyst activation

Reaction mechanism

ABSTRACT

Ga/HZSM5 catalysts prepared by incipient wetness impregnation of HZSM5 with gallium nitrate solutions and submitted to reductive and oxidative pre-treatments were studied by adsorbed pyridine FTIR, *in situ* DRIFTS and had their catalytic activity tested in propane aromatization reactions at 703 K with different initial hydrogen partial pressures. It is shown that dihydridogallium ions formed under hydrogen at aromatization temperatures, slowly decompose under inert gas flow and rapidly decompose when hydrogen is replaced by propane. During reduction under propane, no dihydridogallium species are observed, only alkylgallium species. Dehydrogenation reactions were inhibited and hydrogenolysis activities went through a maximum with increasing hydrogen partial pressure. The results showed that dihydridogallium ions cannot be the active sites for alkane activation and that, while taking part in hydrogenolysis reactions, hydrogen competes with propane for the active sites. A possible reaction scheme for catalyst activation and the first steps in the aromatization reaction is proposed.

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1. Introduction

Aromatization of light alkanes (methane to butane) has been extensively studied, because of its economic and strategic importance in terms of the exploitation of natural gas resources and valorization of light hydrocarbons obtained in petroleum refining. Commercially, this process using mainly gallium-modified zeolite catalysts of MFI type is named “Cyclar”, and was developed jointly by UOP and British Petroleum (BP) [1]. Most of these studies date from the 90s (for a review see Ref. [4]), but recently interest in studying these catalysts was renewed [2–25], due to the worldwide growing importance of GTL technologies.

Although several papers in the literature suggest that the active gallium species under reductive conditions is a dihydridogallium cation, GaH_2^+ , little experimental evidence really corroborate this hypothesis [4,10,22–25] and only a few papers actually demonstrate that these species are formed under real aromatization conditions.

Rane et al. [5] and Hensen et al. [13], in their FTIR and XANES study of the grafting and reduction of trimethylgallium, observed that zeolite Brønsted acid sites are replaced by dimethylgallium species and the removal of the methyl ligands generates Ga^+ and GaH_2^+ ions, the first process being favored at higher temperatures. Also kinetic data obtained by these authors suggest that

propane was converted only on Ga^+ sites, producing exclusively propene.

According to several papers [5,13,24,30,31] the oxidized gallium species observed in model catalysts, the gallyl ion ($\text{Ga}=\text{O}^+$), is more active than the reduced gallium species formed during the reaction. However, gallyl ions have been found not to be regenerated *in situ* in the absence of an oxidizing agent like water [30,32].

It can be seen that determining the role of gallium and reactant activation mechanisms has proven difficult, due to the multiplicity of gallium species that have been proposed to exist in these catalysts under reaction conditions and the lack of consensus on which is the active one.

This work is part of a project which aims to contribute to the solution of some standing questions involving alkane aromatization on Ga/HZSM5 catalysts. Previously [6], our group studied by EXAFS the nature of the gallium species obtained by impregnation of different amounts of gallium (2–10 wt.%) in a HZSM5 zeolite and their effects on 1-butene aromatization activity. It was observed that the increase in gallium content leads to the preferential formation of a segregated $\beta\text{-Ga}_2\text{O}_3$ phase at the external surface of the zeolite and favors the formation of agglomerated species inside the zeolites channels with low aromatization activity. The gallium species with better dispersion formed at lower gallium loadings showed higher activity.

In another work [19], we established quantitative correlations between the dispersion, acidity, reducibility and catalytic activity for propane aromatization of Ga/HZSM5 catalysts in the oxidized form, with varying composition (zeolite silica-to-alumina ratio and

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