Available online at www.sciencedirect.com

Journal of Molecular Catalysis A: Chemical 242 (2005) 233–240

www.elsevier.com/locate/molcata

Theoretical study of the Ga/SAPO-11 catalyst
Extra-framework gallium species and *n*-butane transformation

Anibal Sierraalta[a,*], Yajaira Guillen[b], Carmen M. Lopéz[b], Ramon Martinez[a], Fernando Ruette[a], Francisco Machado[b], Marcos Rosa-Brussin[b], Humberto Soscún[c]

[a] *Laboratorio de Química Computacional, Centro de Química, Instituto Venezolano de Investigaciones Científicas, Apartado 21827, Caracas 1020-A, Venezuela*
[b] *Centro de Catálisis, Petróleo y Petroquímica, Facultad de Ciencias, Universidad Central de Venezuela, Caracas, Venezuela*
[c] *Laboratorio de Química Inorgánica Teórica, Departamento de Química, Facultada de Ciencias, Universidad del Zulia, Maracaibo, Venezuela*

Received 2 June 2005; received in revised form 3 August 2005; accepted 3 August 2005
Available online 13 September 2005

Abstract

Calculations to study the interaction of Ga^+, $[GaO]^+$ and Ga_2O with a Brönsted acid site of a SAPO-11 silicoaluminophospates were carried out using the semiempirical MSINDO approach. The SAPO-11 structure was modeled by a ring of 10 tetrahedrons and 3 rings of 10 tetrahedrons system. The calculations show that the formation of $[HGaOH]^+$ and $[GaH_2]^+$ species by reduction with H_2 are thermodynamically favored. The transformation of $[HGaOH]^+$ into Ga^+ and water is highly endothermic. The Ga_2O react with the Brönsted acid site to produce anchored species, which can be reduced by molecular hydrogen to give $[Ga(GaH)(OH)]$ and $[GaOGaH_2]$. The Ga^+ and Ga_2O reactions with *n*-butane to produces butenes are all endothermic.

Keywords: MSINDO; Ga; SAPO-11; Calculations; Gallium hydrides; Ga_2O; GaH_2

1. Introduction

Silicoaluminophospates (SAPO) molecular sieves are used in the heterogeneous catalysis research for different reaction types. For example, Pt/SAPO-5, Pt/SAPO-11, Pt/SAPO-31 [1–3] and SAPO based bimetallic bifunctional catalysts such as Ni–Pt/SAPO-5 and Ni–Pt/SAPO-11 [4], has been employed in the hydroisomerization and/or hydrocracking of *n*-heptane and *n*-hexane. Pt/SAPO-31 has shown to be a very efficient catalyst with high activity for Heck reactions of aryl chlorides [5] and SAPO-5 and ceria-modified SAPO-5 exhibited high selectivity in the isopropylation of biphenyl with high conversion (89%) [6]. Different factors have been claimed to be the responsible of the catalytic activity. Parlitz et al. [7] found that the catalytic behavior of these catalysts, not only is a function of the number and acidic strength of their active sites, but also of the pores size and the location of hydroxyl groups. Meriaudeau et al. [8] accounted the differences in isomerization products in terms of diffusional restriction and steric constraints of the SAPOs.

Recently, Ga/SAPO-11 catalyst has been used in the direct transformation of *n*-butane to *iso*-butane [9]. This catalyst, prepared by incipient wetness impregnation, has shown excellent activity, selectivity, and a high activity towards the production of isobutene using *n*-butane and H_2 as the reactants and shows a better activity than the gallium substituted silicoaluminophospates (GaAPSO-11) [10]. These promising results seem to point out the potentiality of the Ga/SAPO-11 system in the direct dehydroisomerization of light paraffins. Before the Ga/SAPO-11 can be used as a catalyst, it is reduced at high temperature in presence of H_2.

---

[*] Corresponding author. Tel.: +58 212 5041774; fax: +58 212 5041350.
E-mail address: asierral@ivic.ve (A. Sierraalta).

1381-1169/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2005.08.011

During this process the gallium oxide, located into the internal cavities of the SAPO-11, is partially reduced forming the active sites for the catalysis. The H_2-TPR profiles show, depending on the Ga content, two peaks, one at around 673 K related to highly dispersed Ga_2O_3 and other at around 973 K, which has been assigned of cationic $[GaO]^+$ species. This cationic extra-framework gallium species has been proposed as the responsible of the catalysis [9]. Others Ga species have been proposed in the literature too. Chao et al. [11] proposed that the Ga species exist as isolated GaO_4 units and after reduction these species are transformed into some kind of gallium hydride oligomers with bridging H atom. Others authors suggest that the gallium species exit like a dihydridegallium ion [12]. Magusin and colleagues [13] by means of chemical vapour deposition technique and using trimethylgallium (TMG) and ZSM-5 zeolite showed that this procedure leads to a homogeneous distribution of the Ga species with a Ga/Al ratio close to unity, indicating that the Ga atoms replace the Brønsted sites. Moreover, the theoretical calculations reported in the Magusin work [13] showed that it is thermodynamically more favored the reaction between the TMG with Brønsted acid site of the zeolite than with the silanol groups. According to Magusin et al. [13], after oxidative and reductive treatments, the most probably species, $[GaO]^+$ react with water

$$[GaO]^+ + H_2O \rightarrow GaO(OH) + H^+$$

with a subsequent decomposition to form gallium oxide clusters

$$2GaO(OH) \rightarrow Ga_2O_3 + H_2O$$

These reactions explain the ^{71}Ga NMR signals which had been attributed to β-Ga_2O_3, where the gallium has an octahedral oxygen coordination. Signal at 140 ppm was attributed to tetrahedral coordinate Ga^{3+} species such as $Ga(OH)_2{}^+$ coordinating to the Brønsted site. Védrine and colleagues [14] using various experimental techniques showed the presence of small GaO(OH) particles in Ga/H-ZSM-2 zeolites prepared by ion-exchange. The fact that repeated H_2-reduction and O_2-oxidation cycles increase the dispersion of gallium into the zeolite was explained considering that, in presence of H_2 at 873 K, the Ga_2O_3 can be reduced to Ga_2O that has a high vapour pressure. Therefore this species migrates into the zeolite channels and can be anchored to the zeolite. A subsequent treatment with O_2 produces GaO^+, Ga^+ or $Ga(OH)_2{}^+$ species in the ion-exchange positions.

On the other hand, Hensen et al. [15] have shown that the species of gallium in Ga/ZSM-5 can adsorb molecular hydrogen at 773 K. Analyzing the DRIFTS spectras they concluded that the following species Ga^+, $HGaOH^+$, and $(GaH_2)^+$ can be presents. The gallium hydride species are quite stable and their formation processes, by adsorption of hydrogen, is reversible at 773 K. Todorova and Su [16] by means of FTIR spectroscopy and analyzing H-ZSM-5, Ga-ZSM-5, GaPt-ZSM-5 found an IR band at 3699 cm^{-1} which was attributed to OH groups attached to Ga species as $Ga_2(OH)_xO_{3-x}$. The types of hydroxyl groups in the Ga-ZSM-5, GaPt-ZSM-5 catalysts are very sensitive to the pre-treatment.

In spite of all experimental works done, the manner in which Ga^+, $[GaO]^+$ or Ga_2O species bind to the surface of the SAPOs or are reduced by H_2 are not totally known. As a consequence, it is not clear which could be the active site of these catalysts or its structure. Therefore, theoretical studies of the interaction of these species with the Silicoaluminophospates molecular sieves are of particular interest for the understanding the reactivity and the chemistry of these systems and, the nature of the active sites of these catalysts. The present work was undertaken in order to understand the chemistry, the structure and the energy changes associated with the interaction of some Ga species with SAPO-11s. It presents the analysis of the geometries, charges and energies interaction of Ga^+, Ga_2O and GaO^+, with different T-ring models and with one H_2 molecule, using semiempirical self-consistent-field (SCF) calculations. To the best of our knowledge no theoretical studies have been done in this field and only few theoretical works on Ga-exchange ZSM-5 system have been published [17–21].

2. Computational details and molecular models

All calculations and geometry optimizations were performed using the MSINDO program [22–25] at UHF-SCF level. In order to simulate the structure of SAPO-11, two molecular models were employed. The incorporation of the Si atoms into the models was done by means of the well-known SM2 + SM3 [26,27] mechanism which avoids the formation of unstable bridges Si–O–P. The first model (S model), corresponds to a ring composed by 10 tetrahedrons (T10-ring) with 3 Si-atom, as shown in Fig. 1. The second model (L model), was constructed with three T10-rings as shown in Fig. 2. In this case, the SM2 + SM3 mechanism produces one Si island [27,28] composed by four Si atoms. Since the T10-rings are not symmetric, the position of the Si island in the S as well in the L model was varied along the structure to obtain the most stable positions. These are the structures shown in Figs. 1 and 2.

3. Results and discussion

3.1. Small model

To determine the position of the Brönsted acid site into the T10-ring, the H^+ was placed close to one oxygen atom of the ring and then, the whole structure was optimized. The results of this procedure show that the lower energy structure corresponds to the H^+ attached to the O1 atom (see Table 1 and Fig. 1), i.e., the H^+ bonded to the bridged O atom between Si and Al, followed by that at the O2 atom. The lower energy position of the H^+ into the T10-ring cannot be explained by electrostatic effects since the charges values show that the O1