Effect of the supported Pt on the migration of structural Ga toward the surface of catalysts of the Pt/H[Ga]ZSM5 type

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The aim of this work is to find out how platinum supported over a gallosilicate of the MFI type influences the removal of Ga from the framework and affects the properties of the Pt/H[Ga]ZSM5 catalysts. In this regard, a gallosilicate and an aluminosilicate of MFI structure, with a Si/M ratio ≈15 (M = Ga, Al) were synthesized and characterized by XRD, nitrogen physical adsorption at −196 °C and chemical analysis by ICP-AES. Afterwards, they were used to prepare the following bifunctional catalysts: xPt/H[Ga]ZSM5 ($x = 0.10$, 0.50 and 1.00 wt.% Pt) and 1.00%Pt/H[Al]ZSM5, which were characterized by ICP-AES, TEM, XPS, and the model reaction of toluene hydrogenation. The results found show dispersions within 50–80% for the supported platinum; the XPS analysis indicated a decrease in the Si/Ga ratio as a response to the increase of Pt content, suggesting a substantial influence of platinum on the migration of structural Ga toward the surface of the catalysts. This nonframework gallium remains oxidic and appears to strongly interact with Pt, which considerably affects the hydrogenating ability of these catalysts.

KEY WORDS: bifunctional catalyst; Pt/H[Ga]ZSM5; Pt-Ga interaction; XPS, TEM characterization.

1. Introduction

Monometallic and bimetallic bifunctional catalysts supported over zeolitic solids are increasingly used not only in bulk chemicals processing (refining and petrochemical industries) [1–5], but also in fine chemistry [6,7], since the catalysts obtained are more stable and have higher selectivity in reactions such as hydro-dehydrogenation, isomerization [3, 8, 9], etc. Therefore, it is of great interest studying how these solids behave when the nature of the supported phase (e.g., Pt, Pd) [6,7] and the strength of the acidic sites in the zeolitic supports (H[Al]ZSM5 versus H[Ga]ZSM5) is changed, or when promoting agents or a second supported phase, such as tin [10,11], or copper [12], are added. However, the presence of a second supported metal does not guarantee that a catalyst with the properties desired for a given process is obtained. This would depend on many factors, among which the following can be mentioned: the type of support, nature and concentration of the supported metals, activation conditions [13,14], etc. As a consequence, preparation and characterization of this type of catalyst have to be carried out very carefully. In the processes of paraffin oligomerization and aromatization, for instance, catalysts of the gallium-doped zeolite type are frequently used. These solids have proved to be very effective in propane and butane aromatization, resulting in a number of studies on the characterization of these solids to determine active species for this kind of reaction [15–17].

Although it is not accurately known how these catalysts work, significant progress has been made regarding their characterization; it has been found, for instance, that species such as Ga_2O_3 are generated on the surface of these solids, which are then apparently reduced to Ga^+ ions [18]. It has also been found that in physical mixtures of Ga_2O_3 and H-zeolite, as well as in zeolites exchanged with Ga^{3+} ions, gallium migrates from the surface toward the bulk to occupy tetrahedral positions [19]. In addition, in solids with framework Ga, a migration of Ga^{3+} toward the surface was observed, with formation of Ga_2O_3 which would then be transformed into other species such as Ga_2O, Ga^+, Ga [15,20]. Nowak *et al.* [21] identified in the surface of Ga/HZSM5 zeolites, freshly prepared by the exchange method, small GaO(OH) particles, as well as Ga_2O_3 particles with diameters around 5 μm. They found that calcination and reduction at 550 °C improved Ga migration within the zeolitic framework and increased the dispersion of the remaining Ga_2O_3. Therefore, catalysts of the Pt/H[Ga]ZSM5 type, such as those used in this work, could be expected to develop platinum and gallium species on their surface, which could interact with each other and result in the passivation of the hydro-dehydrogenating centers of these catalysts.

2. Experimental

Gallosilicates and aluminosilicates of the MFI type were hydrothermally synthesized, washed, dried and

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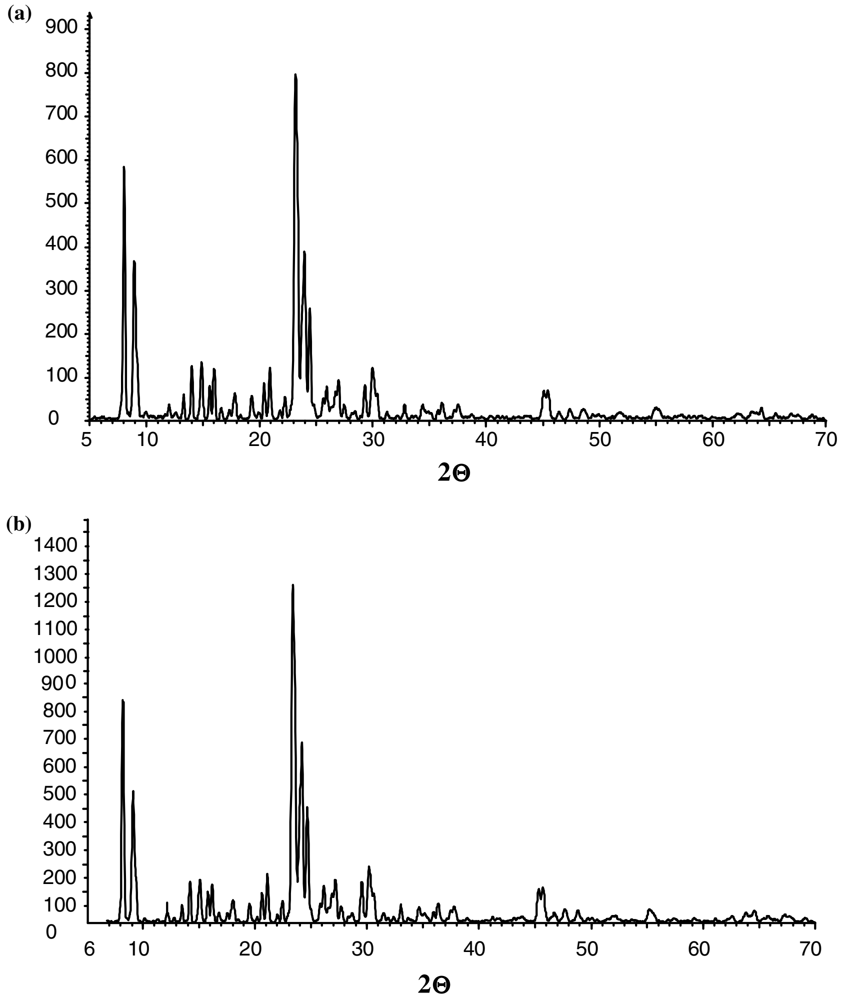

Figure 1. X-ray diffractograms: (a) H[Ga]ZSM5; (b) H[Al]ZSM5.

calcined in dry air at 550 °C. The resulting solids were exchanged with a 2 M $NH_4C_2H_3O_2$ solution and then calcined at 550 °C under dry air flow producing the proton forms (H[Ga]ZSM5 and H[Al]ZSM5), which were characterized by means of X-ray Diffraction (XRD), nitrogen physical adsorption at −196 °C and chemical analysis by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES); this last technique was used to determine the bulk Si/M ratio for both zeolites. These solids were used as supports in the preparation of the following catalysts: xPt/H[Ga]ZSM5 ($x = 0.10$, 0.50, 1.00 wt.% Pt) and 1.00 wt.% Pt/H[Al]ZSM5, using the impregnation exchange method, with $Pt(NH_3)_4Cl_2$ as a precursor salt. The catalysts were dried, calcined under dry air flow at 300 °C for 6 h, and finally reduced "*in situ*" under hydrogen atmosphere for 6 h.

The bifunctional catalysts (Pt/H[Ga]ZSM5 and Pt/H[Al]ZSM5) were evaluated by ICP-AES and Transmission Electronic Microscopy (TEM); these techniques were used to determine the actual content of supported platinum and its dispersion over the surface of both supports, respectively. The specific surface area (SSA) of the catalysts was assessed by N_2 physisorption at −196 °C; in this way, the deposition of the platinum metallic phase was found to produce no blocking in the microporosity. Each of the catalysts was analyzed by X-ray Photoelectron Spectroscopy (XPS), using an ESCALAB 220i-XL spectrometer (VG Scientific) equipped with a hemispherical electron analyzer and a double anode Mg–Al non-monochromatic X-ray source. The pressure in the analysis chamber was kept below 10^{-9} Torr. The samples were reduced by heating at 500 °C for 2 h under hydrogen flow. The reduced samples were protected from exposition to the atmosphere by immersion into a hydrocarbon solvent (purified hexane) while transferring from the reactor to the preparation chamber of the spectrometer. Complex spectra were fitted ("deconvoluted") employing the XPSPEAK 4.1 software, provided by VG. After removal of the S-shaped background, nonlinear least-squares fit of the experimental spectrum by several peaks of variable Lorentzian/Gaussian contributions was carried out. In the case of Pt, the FWHM's of the two components of each

Table 1
Physicochemical characteristics of the catalysts

Catalyst	Si/M	Pt $(\%)_{exp}$	SSA (m^2/g)	D $(\%)_{TEM}$
H[Al]ZSM5	15	–	373	–
H[Ga]ZSM5	16	–	380	–
0.10%Pt/H[Ga]ZSM5	16	0.10	378	83
0.50%Pt/H[Ga]ZSM5	16	0.48	379	–
1.00%Pt/H[Ga]ZSM5	16	0.98	375	83
1.00%Pt/H[Al]ZSM5	15	1.02	370	54

doublet were assumed to be equal, the ratio of areas was kept at 4:3 ($4f_{7/2}$: $4f_{5/2}$), and peak separation was 3.36 eV. The surface Si/Ga ratio was estimated from area ratio of the Si 2p and Ga 3d signals, using the sensitivity factors of the equipment employed. Finally, the activities of the catalysts with the highest platinum content were measured by means of the toluene hydrogenation reaction at 110 °C, 1 atm total pressure, H_2/Toluene molar ratio equal to 4 and WHSV = 21.5 h^{-1}. These measurements were carried out in a fixed bed reactor under dynamic flow of toluene-saturated hydrogen. The gas saturator employed included a coiled tube condenser which guarantees that toluene reaches the catalyst in the vapor state. In this probe reaction, the only observed product is methylcyclohexane, resulting from the complete hydrogenation of the toluene aromatic ring on the metallic centers of the catalyst.

3. Results and discussion

The synthesized zeolites were assessed by means of XRD. This technique allowed us to establish that they are of the MFI type and exhibit high purity and crystallinity, as can be seen in figures 1(a) and (b).

The SSA of both, the supports (H[Ga]ZSM5 and H[Al]ZSM5) as well as the bifunctional catalysts prepared, range within 370–380 m^2/g (table 1), meaning that no part of the solids channel structure would be blocked to nitrogen access by the deposited metal.

Table 1 also shows a Si/M ratio ≈15 (M = Ga, Al) for the supports, suggesting that both solids exhibit a very similar density of their acidic sites. The ICP-AES technique was also employed to determine the content of platinum supported over the bifunctional catalysts. According to table 1, the values obtained are very close to the nominal ones, meaning that the exchange-impregnation method can be used to introduce the desired content of metallic phase.

3.1. Transmission electronic microscopy analysis

If we consider that the hydrogenation reaction depends on the number of metal sites accessible to the reagent, it is important to evaluate the population of metallic centers deposited over the catalysts. This evaluation was carried out for three of the prepared solids (table 1). The results let us infer that the average diameters of the platinum particle are within 1.2–2.0 nm, meaning that the dispersions obtained range between 50 and 80% for the 1.00 wt.% Pt/H[Al]ZSM5 and 1.00 wt.% Pt/H[Ga]ZSM5 catalysts, respectively. This is shown for the 1.00 wt.% Pt/H[Ga]ZSM5 catalyst in the TEM micrograph reported in figure 2(a) and in the distribution histogram of the platinum metallic particles in figure 2(b), which show that the average diameter of the metallic particles for this catalyst is of the order of 1.2 nm.

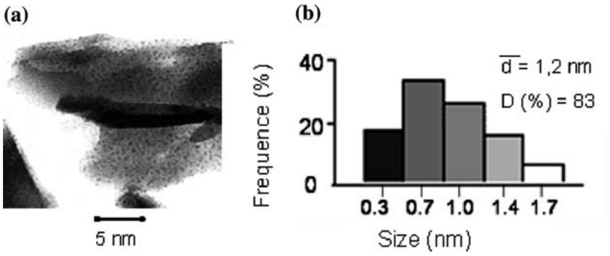

Figure 2. (a) TEM micrograph for the 1.00%Pt/H[Ga]ZSM5 catalyst and (b) distribution histogram of the particle size of the platinum supported over this solid.

Thus, according to the results obtained by TEM, it should be expected that the galosilicate supported 1 wt% Pt catalyst exhibits a higher capacity for toluene hydrogenation than the corresponding aluminosilicate supported one.

3.2. X-ray photoelectron spectroscopy analysis (XPS)

With the aim to determine the chemical species present on the surfaces of the catalysts, the solids were evaluated by means of XPS. This analysis was carried out in the O1s; C 1s; Si 2p; Pt 4f; Ga 3d y O 2s regions. Spectral signals were referred to C 1s (284.6 eV). Figure 3 shows the XPS spectra in the Ga 3d region for the following solids: Ga_2O_3 (reference sample), H[Ga]ZSM5, 0.10 wt.% Pt/H[Ga]ZSM5, 0.50 wt.% Pt/H[Ga]ZSM5 and 1.00 wt.% Pt/H[Ga]ZSM5, after calcination and reduction (c,r).

Figure 3(a) shows the XPS spectrum for Ga_2O_3 (c,r), with an intense signal at 21.5 eV, attributable to Ga (III) in octahedral coordination environment. On the other hand, in the spectrum of H[Ga]ZSM5 (c,r), a signal at 20.5 eV can be seen, which was assigned to Ga (III) with tetrahedral coordination.

Interestingly, in the spectra of the xPt/H[Ga]ZSM5 samples (figure 3(c)–(e)), two signals appear in the Ga 3d region; the first one at a binding energy (B.E.) equal to 20.5 eV that has been assigned to Ga (III) with tetrahedral coordination environment, and the second one at a B.E. between 21.5 and 21.9 eV, which was assigned to extra-framework Ga (III). The intensity of the last signal increases with the content of platinum, as can be seen in figure 3(c)–(e).

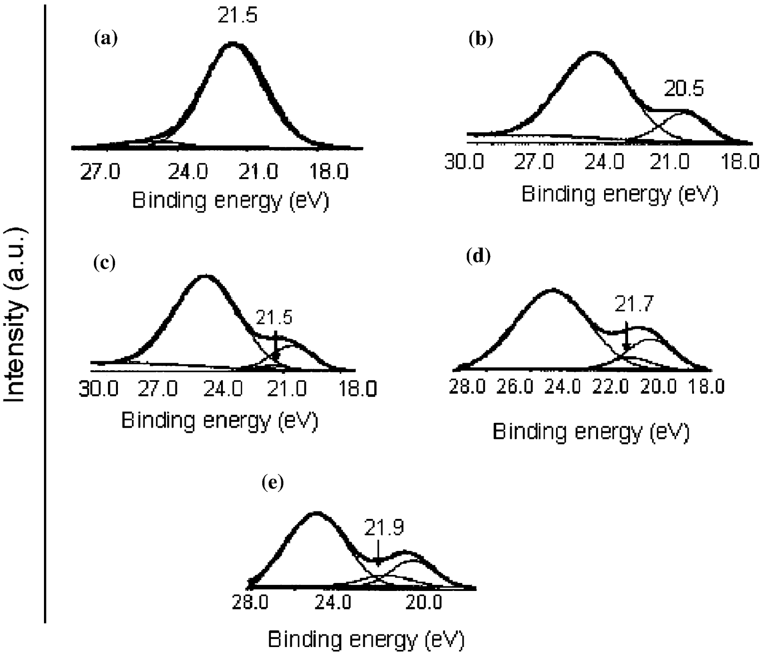

Figure 3. XPS spectra in the Ga 3d region for: (a) Ga_2O_3 (c,r); (b) H[Ga]ZSM5 (c,r); (c) 0.10%Pt/ H[Ga]ZSM5 (c,r); (d) 0.50%Pt/ H[Ga]ZSM5; (e) 1.00%Pt/ H[Ga]ZSM5(c,r).

Thus, these results suggest that supported platinum promotes framework gallium migration toward the surface of the catalysts, which should favor interactions between platinum particles and the extra-framework gallium species; again, this could result in the passivation of platinum metallic centers toward hydrogenation reactions.

The surface Si/Ga ratio in the series of the xPt/ H[Ga]ZSM5 catalysts was determined from the area ratio of Si 2p and Ga 3d signals, allowing us to find out how structural Ga evolves toward the formation of extra-structural Ga species as the content of supported platinum in the catalyst increases. These results are reported in figure 4, as $(Si/Ga)_{surface}$ as a function of the platinum content present in the catalysts.

We can certainly observe that as the content of supported Pt increases, so does extra-framework Ga concentration, which could result from the fact that thermal effects favor migration of framework Ga toward the surface, where it is retained apparently due to the effects of the platinum deposited there. This metal could be forming some kind of interaction species with Ga_2O_3, which could be either a mixed oxide or metallic Pt encapsulated in the Ga oxide. Thus, to evaluate the platinum species on the surface of the catalyst, we have analyzed the Pt 4f region of the XPS spectrum of the 1.00 wt.% Pt/H[Ga]ZSM5 (c,r) and 1.00 wt.% Pt/ H[Al]ZSM5 (c,r) catalysts. In the first case, three doublets, identified in figure 5(a) as A, B and C, can be observed. The binding energies of the corresponding Pt $4f_{5/2}$ peaks are: (A) 72.8 eV; (B) 71.6 eV; (C) 70.8 eV. Signal (A) can be associated to oxidized species of Pt(II) [22] and/or Pt(II) interacting with gallium oxide on the surface, and probably forming mixed platinum–gallium oxides. Doublet (B) could correspond to platinum in the metallic state but interacting with oxygen atoms in the support and forming the known complexes of the Pt-O_{ads} type[22]. Finally, signal (C) is characteristic of Pt^0

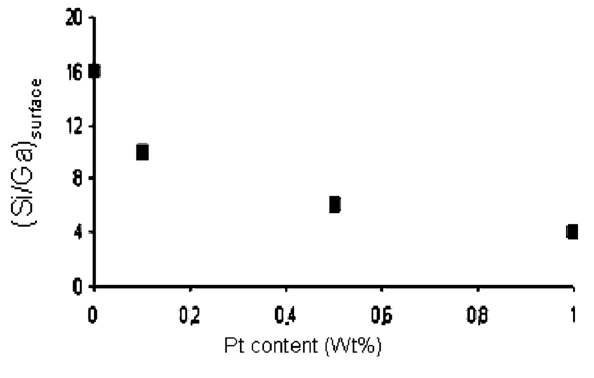

Figure 4. Si/Ga surface atomic ratio as a function of platinum content for the support and the xPt/H[Ga]ZSM5 bifunctional catalysts prepared.

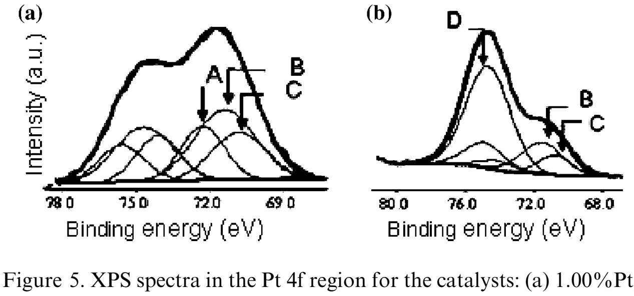

Figure 5. XPS spectra in the Pt 4f region for the catalysts: (a) 1.00%Pt/ H[Ga]ZSM5 (c, r); (b) 1.00%Pt/H[Al]ZSM5 (c, r).

Table 2
Initial hydrogenating activity for he catalysts: 1.00%Pt/H[Ga]ZSM5 and 1.00%Pt/H[Al]ZSM5

Catalyst	Aho (mmol/h gPt)
1.00%Pt/H[Ga]ZSM5	520
1.00%Pt/H[Al]ZSM5	6400

[22,23]. Now, analyzing the spectrum of the 1.00 wt.% Pt/H[Al]ZSM5 catalyst in the Pt 4f region, we can observe in figure 5(b) only doublets B and C. This supports the assumption that doublet A can be assigned to Pt(II) interacting with oxidized gallium species, most probably Ga_2O_3. Signal (D), which appears in the spectrum in figure 5(b), corresponds to Al 2p of the zeolitic support.

3.3. Catalytic evaluation

To determine the hydrogenation capacity of these solids, we have made a comparative evaluation of the initial activity in toluene hydrogenation (AHo) over the bifunctional catalysts with higher Pt content (1.00 wt.% Pt/H[Ga]ZSM5 and 1.00 wt.% Pt/H[Al]ZSM5). The results are reported in table 2, where AHo for the 1.00 wt.% Pt/H[Al]ZSM5 catalyst is about 12 times higher than that of 1.00 wt.% Pt/H[Ga]ZSM5 solid, even though dispersion of the platinum supported over this last catalyst is approximately 1.6 times higher than that obtained in 1.00 wt.% Pt/H[Al]ZSM5 (table 1).

These activity results clearly show that the metallic centers of platinum dispersed over gallosilicate are much less active for hydrogenation processes; this seems to confirm that the interaction proposed between platinum and gallium species brings about passivation of the metallic funtion.

4. Conclusions

Platinum supported over H[Ga]ZSM5 induces migration of Ga from the framework toward the surface, probably forming Ga_2O_3 species.

Platinum hydrogenating capacity is substantially decreased by the presence of Ga, which implies that bifunctional catalysts of the Pt/H[Ga]ZSM5 type would be of little interest for hydrogenation reactions, at least under the operation conditions used in this work.

The results obtained from the physicochemical characterization and the catalytic study point to the presence of a Pt–Ga interaction over the bifunctional Pt/H[Ga]ZSM5 catalysts, which could be of the electronic and/or geometrical type.

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