

Characterization of bifunctional Pt/H[Ga]ZSM5 and Pt/H[Al]ZSM5 catalysts II. Evidences of a Pt–Ga interaction

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Received 6 March 2004; received in revised form 25 September 2004; accepted 27 September 2004

Available online 11 November 2004

Abstract

The purpose of this work is to elucidate how platinum supported on a gallosilicate of the MFI type interacts with extra-framework and/or framework gallium, thus affecting the properties of bifunctional catalysts of the Pt/H[Ga]MFI type. To this end, a gallosilicate and an aluminosilicate of the MFI type, with a Si/M atomic ratio $\cong 15$ (M = Ga, Al) were synthesized and characterized by X-ray diffraction (XRD), nitrogen physical adsorption at -196°C , and chemical analysis by ICP-AES. These zeolites were used as supports in the preparation of a series of bifunctional catalysts with varying Pt content: 0.10 wt.% Pt/H[Ga]ZSM5, 0.50 wt.% Pt/H[Ga]ZSM5, 1.00 wt.% Pt/H[Ga]ZSM5 and 1.00 wt.% Pt/H[Al]ZSM5, which were assessed by transmission electronic microscopy (TEM); dispersion of the supported phase was found to range within 50 and 80%. The supports (gallosilicate and aluminosilicate) as well as the bifunctional catalysts were characterized by X-ray photoelectron spectroscopy (XPS) to determine the chemical species on their surfaces. The presence of extra-structural gallium was observed in Pt/H[Ga]ZSM5, which could be found most probably as Ga_2O_3 ; the presence of Pt^0 , Pt-O_{ads} , and PtO in Pt/H[Ga]ZSM5 and Pt/H[Al]ZSM5 was also observed. It was also evidenced an increase in surface gallium concentration as the content of platinum increases in the Pt/H[Ga]ZSM5 solids. The bifunctional catalysts were catalytically tested under standard conditions by the acetone transformation reaction. The results of the catalytic test confirms that the 1.00 wt.% Pt/H[Al]MFI catalyst shows an initial global activity four times higher than the 1.00 wt.% Pt/H[Ga]MFI one, and additionally a selectivity to the desired product (methyl isobutyl ketone, MIBK), three times higher. The activity and selectivity results observed for the Pt/H[Ga]MFI solids are remarkably similar to those found for the pure H[Ga]ZSM5 support. These results clearly show that the platinum metallic centers on the Pt/H[Ga]ZSM5 catalysts are not active for the hydrogenation reactions of the olefinic and/or carbonylic double bonds, probably due to passivation caused by the gallium species on the surface of the bifunctional catalysts.

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Keywords: Pt/H[Ga]MFI; Pt–Ga interaction; XPS; TEM; Catalyst characterization; Acetone transformation

1. Introduction

Monometallic and bimetallic bifunctional catalysts supported on zeolites are increasingly being used in processes such as refining as well as in the petrochemical industry [1–5] and fine chemical synthesis [6,7], since these catalysts are

stable and have high selectivity in reactions such as hydrodehydrogenation and isomerization [3,8,9]. In this regard, it is of great interest studying how these solids behave when the nature of the supported phase and the strength of the acidic sites in the zeolitic supports are changed, and also when promoting agents or a second supported metal, such as tin [10,11], copper [12], etc., are added. However, it must be considered that the presence of a second supported metal does not guarantee that a catalyst with the desired properties for a given process is obtained. This would depend on several

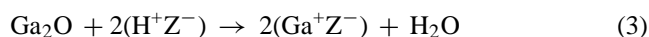
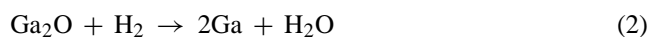
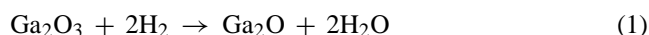
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factors, among which the following can be mentioned: type of support (e.g., H[Al]ZSM5, H[Ga]ZSM5, H[B]ZSM5), nature (e.g., Pt, Pd) [6,7] and concentration of the supported metals, activation conditions [13,14], etc. As a consequence, preparation and 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, as they have proved to be very effective in propane and butane aromatization, a reaction that has been object of a number of studies on the characterization of the catalysts, to determine the active species for this kind of reaction [15–17].

It is not accurately known how these catalysts work, but significant progress has been made regarding their characterization; for instance, it has been found that species such as Ga₂O₃ are generated on the surface of these solids, which are afterwards apparently reduced to Ga⁺ ions [18]. It has also been found that in systems consisting of physical blends of Ga₂O₃ and protonic zeolites, as well as in zeolites exchanged with aqueous solutions of Ga³⁺ precursor salts, gallium migrates from the surface into the framework of the zeolite structure, to occupy tetrahedral positions; this phenomenon has been attributed to the mobility of gallium when it is subjected to thermal treatments [19]. If gallium can migrate from the surface into the crystalline zeolitic structure, the reverse process could also take place; in this regard, Ga³⁺ has been found to migrate from framework sites toward the solid surface in Ga-loaded zeolites. This leads initially to the formation of Ga₂O₃ which could later react producing other species as can be seen below [15,20]:



When bifunctional catalysts of the Pt/H[Ga]ZSM5 type are used, such as those studied in the present work, platinum and gallium could potentially interact at their surfaces [15,21]. This interaction would certainly influence the behavior of these catalysts in the hydrogenation reactions of the unsaturated olefinic and/or carbonylic bonds that take part in acetone transformation. This phenomenon has been object of little study and seems to be both of great scientific and industrial interest. A series of catalyst of the xPt/H[Ga]ZSM5 type were prepared in this work. The catalysts were characterized by means of different techniques (ICP-AES, TEM and XPS), which showed that both platinum and gallium chemical species are present at their surfaces, as well as possible interactions between these elements. The results obtained with the catalysts in the acetone transformation were compared with those found for a Pt/H[Al]ZSM5 catalyst, and considerable differences were found that could be attributed to possible interactions of platinum with gallium species. The acetone transformation to methyl isobutyl ketone (MIBK) was chosen because this reaction requires both acidic as well as metallic

sites in the catalyst to be carried out [21]. Thus, it is ideal to examine the possible interaction between Pt, responsible for the metallic function, with Ga that takes part of the Brønsted acid sites of the zeolitic structure. If there exist interactions between these elements, it is conceivable that one or both of the functionalities required for the acetone transformation would be impaired.

2. Experimental

A gallosilicate and an aluminosilicate of the MFI type were synthesized using the method proposed by Guth and Caultet [22]. After washing and drying, the solids were calcined in dry air at 550 °C for 6 h. These solids, obtained as the sodium form (Na-[M]ZSM5; M = Ga, Al), were exchanged with a 2 M NH₄C₂H₃O₂ solution, dried at 105 °C, heated at 1 °C/min to 550 °C, and kept at this temperature for 6 h in dry air. This procedure resulted in the proton form of the solids (H[Ga]ZSM5 and H[Al]ZSM5), which were then 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); the latter technique was used to determine the Si/M ratio for both solids. The zeolites obtained were used as supports in the synthesis 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. The preparation of catalysts was carried out using the impregnation-exchange method, with Pt(NH₃)₄Cl₂ as a precursor salt. The solids obtained were dried and then calcined under dry air flow at 300 °C for 6 h and finally reduced “in situ” under hydrogen atmosphere at 500 °C for 6 h; in both cases the temperature was increased at a rate of 1 °C/min. The resulting solids were examined by scanning electron microscopy, which show them to consist of spherical particles with about 6 μm of mean diameter.

The bifunctional catalysts (Pt/H[Ga]ZSM5 and Pt/H[Al]ZSM5) were evaluated by means of ICP-AES and transmission electronic microscopy (TEM), as described in previous works [11,21]. These techniques were used to determine the actual content of supported platinum and its dispersion over the surface of both supports. The TEM analysis was carried out on several micrographs, such as that shown in Fig. 2. Typically, more than 500 metallic particles appeared in the sampled zones; these were considered to be spherical, in order to simplify calculations. The frequency of appearance of the different metal particle sizes [d_i (nm)] was determined, as can be seen from the histogram (Fig. 2b). The discrimination of particle size allows to estimate their average diameter [d (nm)] by means of the expression: $d = \sum n_i d_i^3 / \sum n_i d_i^2$ [23]. Thus, (n_i) is the number of particles with diameter [d_i (nm)] in the analyzed sample. Once the average particle diameter [d (nm)] is obtained, the dispersion of the metallic phase was estimated from the equation proposed by Boudart [24], $D \cong 1/d$ (nm). This is a good approximation for transition metals such as platinum.

The specific surface area (SSA) was assessed by the BET method using a Micromeritics 2010 instrument. These results showed that deposition of the platinum metallic phase did not block the microporosity.

X-ray photoelectron spectroscopy (XPS) was employed to determine the nature of the chemical species on the surface of the catalysts. This was carried out by means of 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 reduction treatment was carried out “in situ”, by heating the fresh samples under hydrogen flow at 500 °C for 2 h. 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, non-linear 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 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 the peak areas of the Ga3d and Si2p signals, using the sensitivity factors of the equipment. Several measurements were taken and averaged, the reproducibility of these measurements being very good.

The catalysts were evaluated by means of the acetone transformation reaction in the presence of hydrogen, which was carried out in a dynamic fixed-bed reactor at 160 °C, 1 atm. total pressure, an acetone/hydrogen molar ratio = 3 and variable WHSV. The reactor effluents were analyzed with a HP-6890 Gas Chromatograph, equipped with a FID detector, a CP-SIL 5 CB column (30 m length, 0.25 mm diameter and a composition of 5% phenyl methyl siloxane).

3. Results and discussion

The synthesized solids were assessed by XRD, which showed (Fig. 1a and b) the peaks characteristic of the MFI structure [25]. They seem to have high purity and crystallinity, as no extra-framework Ga or Al were detected (absence of Ga₂O₃ or Al₂O₃ signals). These results do not agree with those reported by Nowak et al. [26], who found segregated Ga₂O₃ after calcination at 550 °C of similar gallosilicate solids. The absence of the signals corresponding to this oxide, however, could not disprove the existence of Ga₂O₃ in low contents and very dispersed. Fig. 1c shows the diffractogram of the 1.00 wt.% Pt/H[Ga]MFI bifunctional catalyst. This result is typical of all metal containing samples, both calcined or calcined and reduced, showing that the introduction of platinum and the activation processes do not appreciably modify the structure of the support.

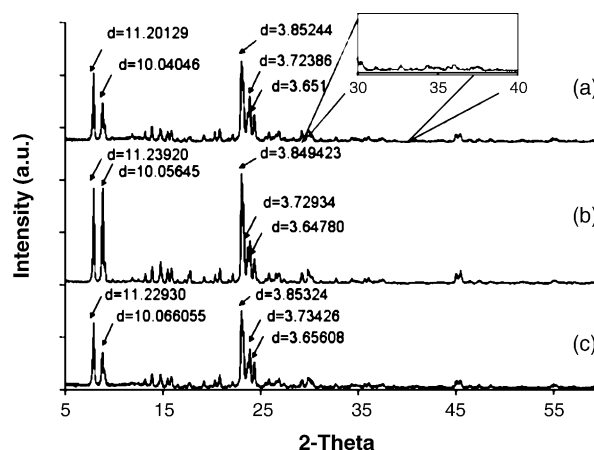


Fig. 1. X-ray diffractogram: (a) H[Ga]MFI; (b) H[Al]MFI; and (c) 1.00Pt/H[Ga]MFI.

SSA of the supports as well as the bifunctional catalysts was evaluated by nitrogen physical adsorption at -196 °C; the results obtained range within 370 and 380 m²/g, (Table 1), indicating that no part of the channel structure of the solids is blocked to nitrogen access by the supported metal. Bulk Si/M (M = Ga, Al) atomic ratios around 15 for both supports can also be seen in the same table. As the solids show high purity and crystallinity (Fig. 1) it can be considered that most Ga and Al atoms are within the framework structure, generating Brønsted acid centers. The coincidence of Si/M ratios (Table 1) means that both catalysts exhibit a very similar density of acidic sites. Previous results suggest that there is a slight difference in the strength of the acid sites, as the gallosilicate and the aluminosilicate desorb ammonia up to 400 and 470 °C, respectively [21,27].

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 theoretical ones, implying that the exchange-impregnation method can be properly used to introduce the content of the desired metallic phase.

3.1. TEM analysis

Since hydrogenation reactions depend on the number of metallic centers accessible to the reagent, the dispersion of the supported platinum in three of the bifunctional catalysts was evaluated by the methodology described previously [21,27].

Table 1
Physicochemical characteristics of the catalysts

Catalysts	Si/M	Pt (%) _{exp.} ^a	SSA (m ² /g)	D (%) _{TEM}
H[Al]MFI	15	–	373	–
H[Ga]MFI	16	–	380	–
0.10%Pt/H[Ga]MFI	16	0.10	378	82
0.50%Pt/H[Ga]MFI	16	0.48	379	–
1.00%Pt/H[Ga]MFI	16	0.98	375	83
1.00%Pt/H[Al]MFI	15	1.02	370	54

^a All samples assessed were anhydrous.

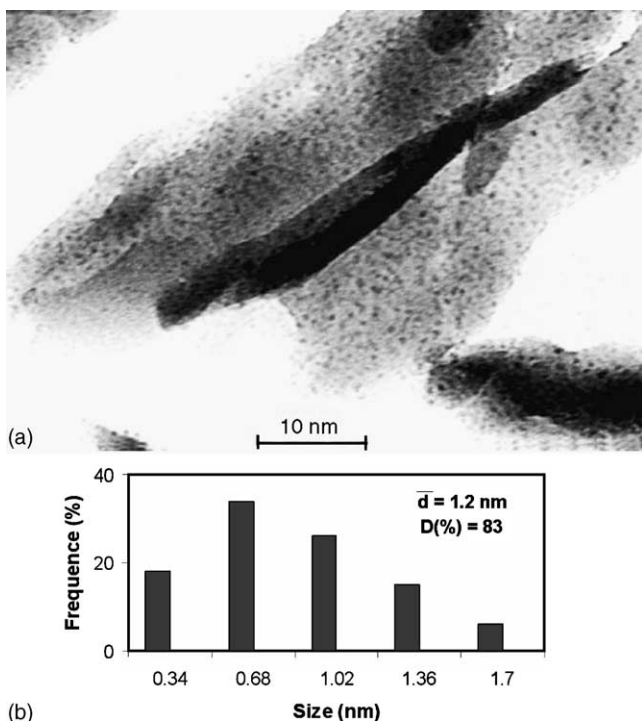


Fig. 2. (a) Micrograph from transmission electronic microscopy for 1.00%Pt/H[Ga]MFI and (b) frequency of appearance of the particles size on the 1.00%Pt/H[Ga]MFI.

The results suggest that the average diameters of the platinum particle range within 2.0 and 1.2 nm (see histogram, Fig. 2b), meaning that the dispersions obtained range within 50 and 80% for the 1.00%Pt/H[Al]ZSM5 and 1.00%Pt/H[Ga]ZSM5 catalysts, respectively. According to the results obtained by TEM, the second catalyst (1.00%Pt/H[Ga]MFI) could be expected to exhibit a higher activity in the hydrogenation of the olefinic and/or carboxylic double bonds. As a consequence, a higher global activity should be obtained with this catalyst in the test reaction (acetone transformation).

3.2. XPS analysis

With the aim to determine the chemical species present on the surface of the catalysts that could take part in the hydrogenation processes mentioned before, the solids were evaluated by means of XPS in the O1s; C1s; Si2p; Pt4f; and the Ga3d–O2s regions. The spectral signals were referred to C1s (284.6 eV) [28], which was used as a standardization parameter.

Fig. 3 shows the XPS spectrum for the supports used in this work, after calcination and reduction (H[Ga]ZSM5 (1) and H[Al]ZSM5 (2)). A signal can be appreciated at a binding energy (B.E.) of 25.0 eV, attributable in both cases to O2s; in the XPS spectra of the H[Ga]ZSM5 solid, a second peak can be observed at B.E. = 20.5 eV, which was attributed to Ga3d.

Once calcined and reduced (c,r), all the x Pt/H[Ga]MFI bifunctional catalysts were evaluated by means of XPS; XPS spectra in the Ga3d region are reported in Fig. 4 for

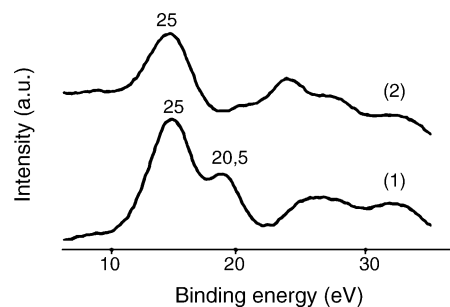


Fig. 3. XPS spectra in the O2s region for the following supports: (1) H[Ga]MFI; and (2) H[Al]MFI.

the following solids: Ga₂O₃ (solid used as a reference), H[Ga]ZSM5, 0.10%Pt/H[Ga]MFI, 0.50%Pt/H[Ga]MFI and 1.00%Pt/H[Ga]MFI (c,r). Fig. 4a shows the XPS spectrum of Ga₂O₃ (c,r) in the region of Ga3d; there, an intense signal is observed at 21.5 eV, which is attributable to Ga(III) with octahedral coordination environment, which suggests that this element is mainly present in this form in the solid. According to Fig. 4b, corresponding to H[Ga]ZSM5 (c,r), a signal at 20.5 eV is observed in the same spectral region. This signal was assigned to Ga(III) with tetrahedral coordination environment.

Fig. 4c–e show that XPS spectra for x Pt/H[Ga]ZSM5 ($x=0.10$; 0.50; and 1.00 wt.% Pt) catalysts present two signals in the Ga3d region; the first one at B.E. = 20.5 eV, as-

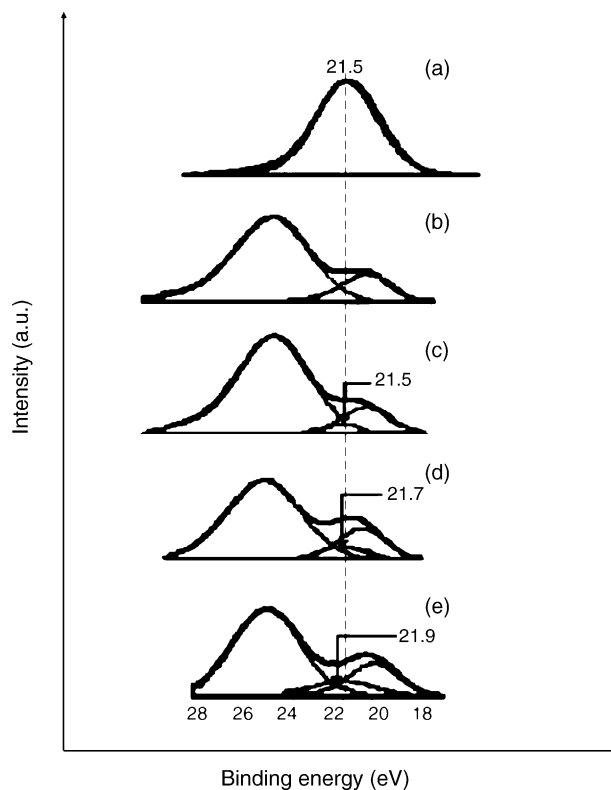


Fig. 4. XPS spectra in the Ga3d region for: (a) Ga₂O₃ (c,r); (b) H[Ga]MFI (c,r); (c) 0.10%Pt/ H[Ga]MFI (c,r); (d) 0.50%Pt/ H[Ga]MFI; (e) 1.00%Pt/ H[Ga]MFI (c,r).

signed to Ga(III) with tetrahedral coordination environment, and the second one at B.E. between 21.5 and 21.9 eV, assigned to extra-framework Ga(III); this signal increases in intensity as the content of platinum supported over H[Ga]ZSM5 increases, as can be seen in Fig. 4c–e. These results suggest that supported platinum may induce segregation of gallium from the zeolite structure, which should favor interactions between platinum particles and the extra-framework gallium species (Ga_2O_3 , Ga_2O , Ga^+) [18]. This could be causing passivation of the platinum metallic centers toward hydrodehydrogenation reactions.

In this regard, the surface Si/Ga ratio in the series of catalysts [$x\text{Pt}/\text{H}[\text{Ga}]\text{ZSM5}$ ($x=0.10$; 0.50 and 1.00 wt.% Pt)] was evaluated by means of XPS, which permitted to determine the evolution of the migration of structural Ga toward the formation of extra-structural Ga species as the content of supported platinum in the catalyst increases. The results are reported in Table 2, according to which the values of the bulk Si/Ga ratio (determined by ICP-AES) and the surface Si/Ga ratio (obtained by XPS) for the H[Ga]ZSM5 support, are 15 and 16, respectively; these results suggest that the processes of calcination and reduction do not increase the structural Ga (III) migration toward the surface of H[Ga]ZSM5. However, as platinum is introduced into the surface of these solids, the activation processes of the Pt/H[Ga]ZSM5 catalyst bring about a strong migration of Ga from the framework to the surface, as can be observed in Table 2, where the surface Si/Ga ratio decreases from 16 to 4 when the supported platinum content increases from 0 to 1%.

These results clearly demonstrate the effect of the supported platinum on the “degalliation” process (equivalent to the dealumination of aluminosilicate zeolites) of these Pt/H[Ga]ZSM5 catalysts, a phenomenon that could be associated to the mobility of gallium in this solids as a consequence of thermal effects, but basically due to the formation of stable chemical species between platinum and gallium, which have been proposed as bimetallic (Pt–Ga) by Chao et al. [19]. Therefore, it was suggested that the non-sintering of the supported metallic phase (dispersion is over 80% in the present solids) and the low hydrogenating activity of the solids are a direct consequence of the formation of these species. Notwithstanding, the XPS analyses of these catalysts do not permit to confirm the presence of species such as Ga_2O , Ga^+ , Ga^0 , Pt–Ga on the surface. Therefore, what could be happening in the present catalysts is that the particles of metallic platinum could be interacting with Ga_2O_3 species, probably forming mixed platinum and gallium oxides and/or

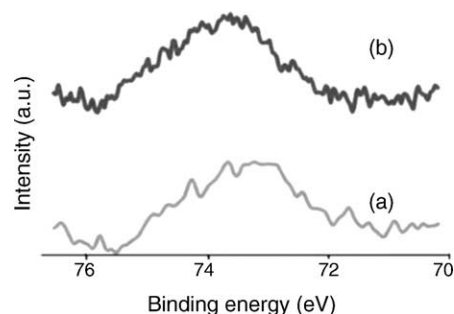


Fig. 5. XPS spectra in the Pt 4f region of: (a) 0.10%Pt/H[Ga]MFI (c,r); (b) 0.50%Pt/H[Ga]MFI (c,r).

producing a geometrical effect by means of which the Pt^0 clusters could be covered by gallium oxide species, which would make metallic platinum insensitive to the hydrogenation reactions or inaccessible for the reactants.

The XPS analysis for the Pt 4f region, Fig. 5, shows ill-defined spectra for samples with 0.10 and 0.50 wt.% Pt. On the other hand, catalysts with 1.00 wt.% Pt showed spectra with higher intensities and better definition of the signals, which could be curve fitted by several doublets, as shown in Fig. 6. In the case of the sample calcined at 300 °C, two sets of doublets, (A) and (B), suffice to fit the experimental signal. The corresponding $\text{Pt}4f_{7/2}$ signals show binding energies (B.E.) of: (A) 72.8; and (B) 71.6 eV. Generally, $\text{Pt}4f_{7/2}$ peaks below 71.8 eV are assigned to Pt in metallic state [28–31]. On the other hand, $\text{Pt}4f_{7/2}$ peaks with a B.E. of 71.8 eV have been previously assigned to a surface Pt– O_{ads} (adsorbed oxygen complex) [28]. Other authors have assigned a signal at the same position to Pt nanoclusters modified with different organic ligands [32]. The $\text{Pt}4f_{7/2}$ signal at 72.8 eV is at a somewhat lower binding energy than PtO (73.3 eV) [28].

Thus, the (A) doublet could be assigned to oxidized Pt(II) species and/or Pt(II) interacting with Ga_2O_3 , probably forming mixed oxides species, while (B) could reflect very dispersed Pt^0 interacting with surface O groups of the zeolite. Upon H_2 reduction at 500 °C there is a strong decrease of the total area of the (A) doublet, an increase of (B) and the appearance of a new doublet (C) with a $\text{Pt}4f_{7/2}$ peak at 70.8 eV. The latter value is characteristic of bulk Pt^0 , as reported elsewhere [28,33]. Again, (B) would correspond to dispersed Pt^0 interacting with surface oxygen groups. In this regard, it must be pointed out that dispersed noble metal particles (palladium) have been said to show binding energies up to 2 eV higher than the bulk metal [34], probably due to a decreased metallic character of such highly dispersed clusters.

Considering that (B) can be assigned to essentially metallic Pt particles anchored to surface O groups, then the decrease of the size of the (A) doublet and the parallel increase of (B) upon reduction, could reflect an increase of the dispersion of Pt on the zeolite surface. It is worth noting that a 1.00% Pt/H[Al]MFI catalyst, calcined and reduced under the same conditions, showed only two doublets, with binding energies corresponding to (B) and (C) in 1.00% Pt/H[Ga]MFI

Table 2

Si/Ga atomic ratios for the series of catalysts ($x\text{Pt}/\text{H}[\text{Ga}]\text{MFI}$ ($x=0.00$, 0.10, 0.50 and 1.00 wt.% Pt))

Sample	Si/Ga _(XPS)
H[Ga]MFI (c,r)	15 (ICP-AES) 16
0.10%Pt/H[Ga]MFI (c,r)	10
0.50%Pt/H[Ga]MFI (c,r)	5
1.00%Pt/H[Ga]MFI (c,r)	4

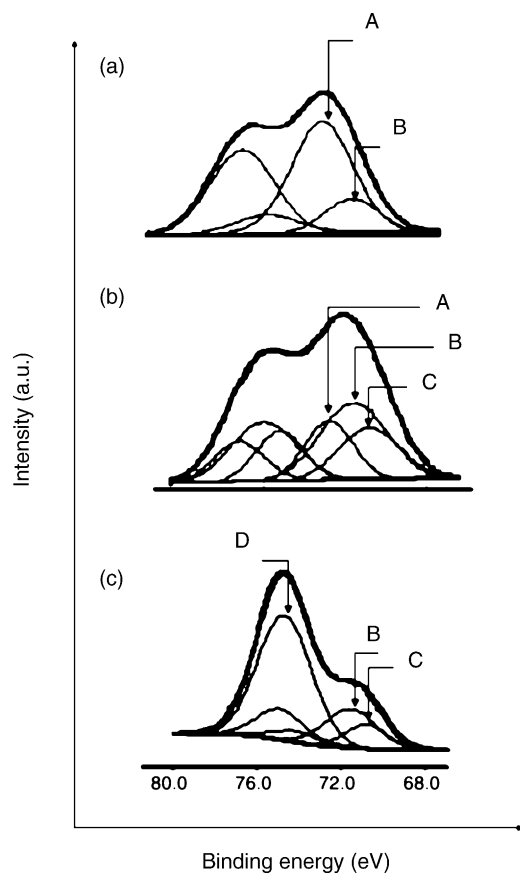


Fig. 6. XPS spectra in the Pt4f region: (a) 1.00%Pt/H[Ga]MFI (c,r); (b) 1.00%Pt/H[Al]MFI (c,r); (c) 1.00%Pt/H[Al]MFI (c,r). A, B, and C correspond to the Pt4f_{7/2} peaks of three different sets of doublets obtained by deconvolution of the Pt4f envelope. D is the Al2p signal of an aluminosilicate-supported sample.

(Fig. 6c). Thus, the (A) doublet in the latter catalyst in the reduced state could be assigned to Pt(II) interacting with a Ga oxidic species which is not present in the Pt/H[Al]ZSM5 catalyst.

3.3. Catalytic test

The acetone transformation reaction was carried out under the conditions already described over each one of the prepared catalyst (x Pt/H[Ga]MFI and Pt/H[Al]MFI), in order to evaluate activity, selectivity and stability over each one of them. Considering that acetone is transformed over these catalysts according to the following reaction scheme [6]:

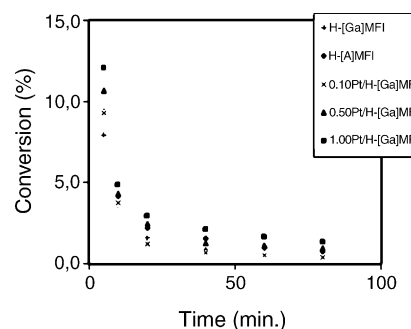
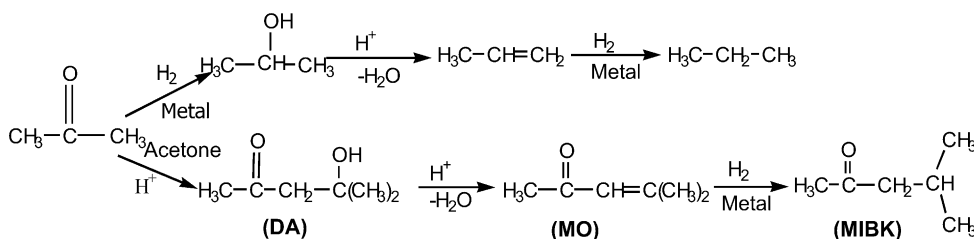


Fig. 7. Evolution of acetone conversion as a function of reaction time for H[Ga]MFI; H[Al]MFI; 0.10%Pt/H[Ga]MFI; 0.50%Pt/H[Ga]MFI; 1.00%Pt/H[Ga]MFI at 160 °C, 1 atm., PAc/PH₂ = 3 and WHSV = 9.4 h⁻¹.

then it should be expected that if both functions in these catalysts are “switched on” (acidic function supplied by the protonic sites in the support and hydro-dehydrogenating function by the metallic centers of the supported platinum), acetone transformation should take place as proposed in the previous reaction scheme [6]. It would account for the formation of products such as methyl isobutyl ketone (MIBK), propane (C₃), 2-methyl-pentane (2MP), mesityl oxide (MO) and heavy products such as diisobutyl ketone (DIBK). However, the higher or lesser degree of formation of a given product will depend on which function (acidic or hydro-dehydrogenating) has the highest number of sites and/or is the most active. For instance, if there were no acidic function or the acidic sites would not have the necessary acid strength to catalyze aldolization of two acetone molecules, then the concentrations of MO, MIBK and DIBK should be relatively low. On the other hand, if there is no metallic function or it is not active and/or selective to hydrogenation of the C=O acetone bond, propane formation would be severely restricted. Thus, this test reaction is considered to be convenient to assess the solids and to correlate the resulting catalytic parameters (activity, selectivity and stability) with the characterization data obtained by means of the different analytical techniques employed.

Fig. 7 shows the evolution of the acetone conversion as a function of the reaction time, over the H[Ga]ZSM5, H[Al]ZSM5 supports and the x Pt/H[Ga]ZSM5 ($x = 0.10$; 0.50 and 1.00 wt.% Pt) bifunctional catalysts, at WHSV = 94 h⁻¹. In this reaction it can be seen that the initial conversion (X_0) of these solids varies little; however, the initial activity increases with the content of supported metallic phase, so that

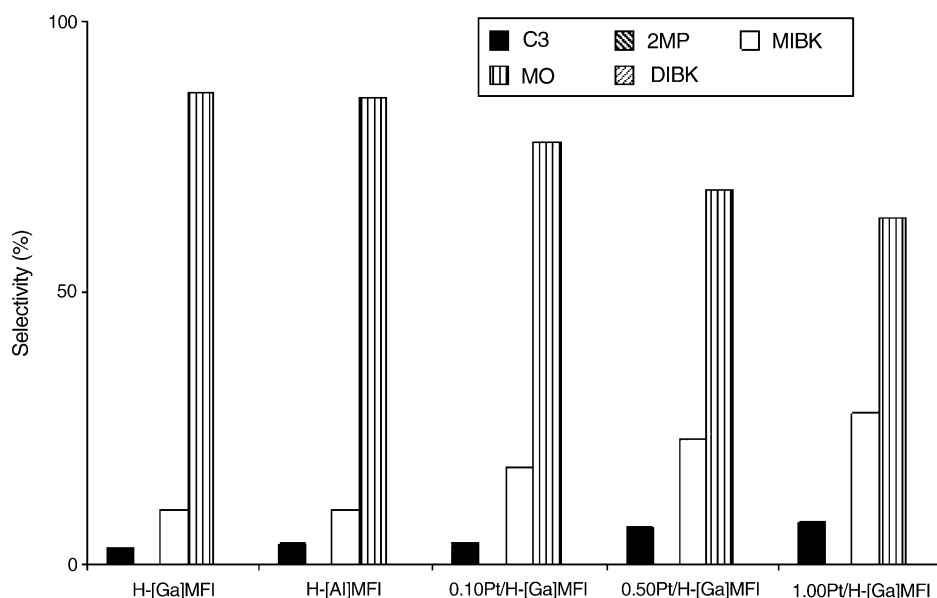


Fig. 8. Distribution of products (selectivity) at 10% conversion for H[Ga]MFI; H[Al]MFI; 0.10Pt/H[Ga]MFI; 0.50Pt/H[Ga]MFI; 1.00Pt/H[Ga]MFI.

the following order can be established: X_0 (1.00 wt.% Pt) > X_0 (0.50 wt.% Pt) > X_0 (0.10 wt.% Pt) > X_0 (0 wt.% Pt). This behavior could be related to the number of active metallic centers initially on their surface, which should be higher as the concentration of supported platinum increases. It can also be observed that deactivation of the bifunctional catalysts is drastic and very similar to that shown by H[Ga]ZSM5; this suggests that the bifunctional catalysts (xPt/H[Ga]MFI) do not have a high number of active metallic centers, even though they showed an excellent dispersion of the supported metallic phase, as measured by TEM (Fig. 2 and Table 1). The ability of these solids to act mostly as acidic catalysts can be explained suggesting that their metallic phase has been passivated by the presence of gallium, as pointed out by the presence of doublet (A) in the Pt 4f XPS spectra of the 1.00 %Pt/H[Ga]MFI catalyst (Fig. 6a and b). Thus, as a consequence of annulling the hydro-dehydrogenating function in these solids, carbonaceous residues formed in these catalysts are of the cyclic ketones type, such as isophorone and isoxylitones [12], substances having large molecular weight and volume, as well as high boiling point. This causes them to be retained inside the inner structure of the support, leading to a rapid deactivation of the catalysts, as can be seen in Fig. 7. The mobility of Ga, as demonstrated by the decreasing XPS Si/Ga ratio (Table 2), is in line with the observed passivation of Pt by either decoration or reaction of the metal particles with extra-framework Ga species, which occurs mostly within the zeolite channels.

The selectivity to the different products generated in this reaction over each catalyst has also been determined; the results are shown in Fig. 8 for 10% conversion. According to this figure, selectivity to the products generated in the acetone transformation over these catalysts (H[Ga]ZSM5, H[Al]ZSM5 and xPt/H[Ga]MFI) is certainly very similar for

all solids; that is to say, low and high selectivity toward MIBK and MO respectively, meaning that the hydrogenation reaction of the olefinic double bond of the unsaturated α - β ketone (mesityl oxide), allowing MIBK formation, is severely restricted simply due to the fact that most of the platinum metallic centers are not active for this reaction; this is a phenomenon attributable to the interaction between platinum and gallium.

Fig. 9 compares the development of acetone conversion as a function of the reaction time over the catalysts with highest Pt loading (1.00%Pt/H[Ga]MFI and 1.00%Pt/H[Al]MFI), which was carried out under the conditions described in the Section 2 and at $WHSV = 9.4 \text{ h}^{-1}$. It can be observed that 1.00%Pt/H[Al]MFI catalyst's initial activity is virtually 4 times the value obtained over the 1.00%Pt/H[Ga]MFI catalyst. This figure also shows how the Pt/H[Ga]MFI catalyst is completely deactivated after 40 min of reaction, which could be associated to an un-

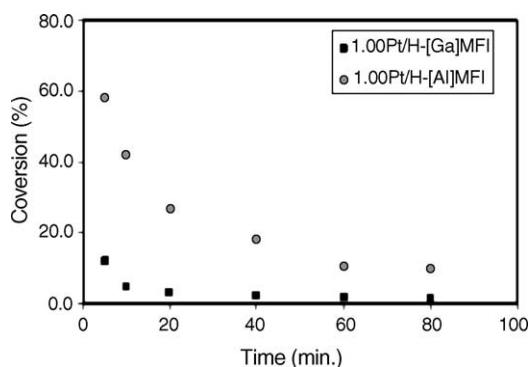


Fig. 9. Evolution of acetone conversion as a function of reaction time for 1.00%Pt/H[Ga]MFI; 1.00%Pt/H[Al]MFI at 160 °C, 1 atm., $P_{Ac}/P_{H_2} = 3$ and $WHSV = 9.4 \text{ h}^{-1}$.

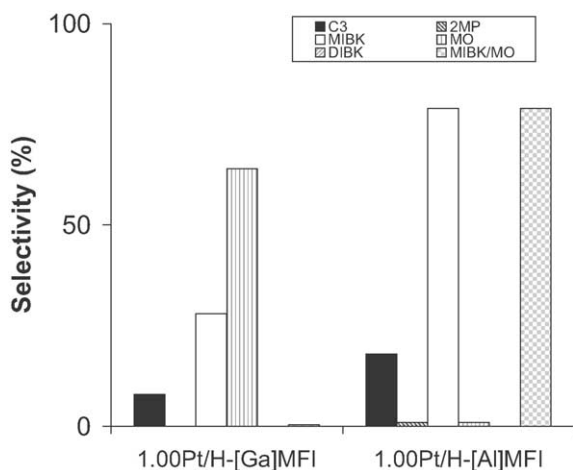


Fig. 10. Distribution of products (selectivity) at 10% conversion for 1.00Pt/H[Ga]MFI; 1.00Pt/H[Al]MFI and MIBK/MO formation rate ratios.

balance between the acidic and the hydro-dehydrogenating functions.

Considering that the method used to prepare the catalysts was the same, that both solids have a very similar density of acidic sites ($\text{Si}/\text{Ga} = 16$ and $\text{Si}/\text{Al} = 15$), and that the Pt/H[Ga]MFI catalyst dispersion of the supported metallic phase is higher, it is odd that (at a 10% conversion) the Pt/H[Al]MFI produces three times more MIBK than the Pt/H[Ga]MFI (Fig. 10); however, the latter solid produces 64 times more MO than the Pt/H[Al]MFI catalyst. At the same time, it can be appreciated in this figure that both solids are able to catalyze acetone aldolization in more than 80% selectivity and the MIBK/MO formation rate ratios obtained are 0.4 and 79 for the 1.00Pt/H[Ga]MFI and 1.00Pt/H[Al]MFI catalysts, respectively. These rate ratios could be explained considering that the platinum metallic centers over the 1.00Pt/H[Ga]MFI catalyst are not active for the hydrogenation of the olefinic double bond of MO. As a result, MO is produced in a higher proportion than MIBK, which would be in accordance with the results obtained by means of the XPS analysis of the 1.00Pt/H[Ga]MFI catalyst. Additionally, experiments carried out at other different WHSV values (not shown), confirm that the selectivities shown in Fig. 10 are independent of the extent of deactivation of the catalysts.

4. Conclusions

Platinum supported over solids of the H[Ga]ZSM5 type has an effect on framework Ga, allowing it to migrate out of the structure to form species of the Ga_2O_3 type, which interact with the supported Pt.

The Pt/H[Ga]MFI bifunctional catalysts behave as unbalanced catalysts, even in the case of the solid with the highest content of supported metallic phase.

Even though the 1.00Pt/H[Ga]MFI and 1.00Pt/H[Al]MFI catalysts have similar physicochemical properties, they exhibit completely different catalytic behaviors; the first one acts as a mere acid catalyst, with a supported metallic phase virtually annulled, as shown by its low activity toward hydrogenation of the double bonds of acetone and the unsaturated α - β ketone; this behavior seems to be due to the interaction of platinum with extra-framework gallium formed over the H[Ga]ZSM5 support, as observed in the XPS analysis.

All the facts confirm that the hydrogenating capacity of platinum is substantially decreased due to the presence of Ga in the zeolite, implying that bifunctional catalysts of the Pt/H[Ga]MFI type would not be attractive to be used in hydrogenation reactions, at least under the operation conditions employed.

The results obtained from the physicochemical characterization and the catalytic study evidence an interaction between platinum and gallium in the bifunctional catalysts of Pt/H[Ga]MFI type, which could be of electronic and/or geometrical type.

Acknowledgements

The authors would like to acknowledge FONACIT (Project QF-10) for financing the acquisition of the XPS spectrometer and Mr. Ricardo Morales (currently a Ph.D. student at the University of California, Riverside) for providing us with the aluminosilicate.

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