

Acetone transformation over Pt/H[Al]ZSM5 and Pt/H[Ga]ZSM5 catalysts Evidences of a Pt–Ga interaction

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Abstract

Acetone transformation into methyl–isobutyl ketone (MIBK) under hydrogen atmosphere, using bifunctional catalysts of the platinum supported over medium-pore zeolites (MFI)-type, was studied. This methodology offers a number of advantages; however, since it implies working at low hydrogen pressure (P_{H_2}) with respect to the acetone pressure (P_{Ac}), a rapid catalyst deactivation is observed. Therefore, to minimize deactivation of bifunctional catalysts, a solid with less strong acidic sites has been considered as a platinum support. In this sense, the use of an MFI-type gallosilicate has been deemed convenient to compare the results with those obtained over a catalyst of the platinum/aluminosilicate MFI-type. The H[Al]ZSM5 and H[Ga]ZSM5 solids were synthesized and evaluated by means of DRX, nitrogen adsorption at -196°C , TPD– NH_3 and chemical analysis, and later used as a support for the metallic phase. Platinum of 0.50 wt.% was introduced by means of the exchange–impregnation method and the $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ salt was used as a platinum precursor. The solids were calcinated under dry air flow at 300°C for 6 h and then reduced under dry hydrogen atmosphere at 500°C also for 6 h. The bifunctional catalysts obtained, 0.50Pt/H[Ga]ZSM5 (Si/Ga = 42) and 0.50Pt/H[Al]ZSM5 (Si/Al = 40), were evaluated by means of chemical analysis, nitrogen adsorption, transmission electronic microscopy (TEM), electronic paramagnetic resonance (EPR), and the model reactions of toluene-hydrogenation and *n*-heptane hydrocracking under the conditions established in previous works. Acetone transformation was run in a dynamic reactor at 160°C , atmospheric pressure, $P_{Ac}/P_{H_2} = 3$ and variable WHSV. The results obtained with the model reactions and the acetone transformation shows that metallic centers in the Pt-gallosilicate catalysts exhibit a much lower hydro-dehydrogenating activity than that of the metallic centers in the Pt-aluminosilicate catalyst; this, together with the EPR results, seems to indicate that a strong interaction between platinum and a species of structural or extra-structural gallium (EFGS) of the support used has occurred over the Pt/H[Ga]ZSM5 catalyst. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Acetone; Methyl-isobutyl ketone; Pt/H[Al]ZSM5; Pt/H[Ga]ZSM5; Bifunctional catalysts

1. Introduction

Recent studies on acetone aldolization show that medium-pore zeolites generate 4-methyl-3-penten-

2-one (usually known as mesityl-oxide (MO)), as a main product [1,2]. Currently, this α – β unsaturated ketone is the closest intermediate in the 4-methyl-2-pentanone synthesis, better known as methyl–isobutyl ketone (MIBK), a substance widely used in the industry in manufacturing of a great

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number of products, such as inks, lacquers, varnishes, etc. [3]. Hence, the interest in studying this chemical transformation over zeolite solids. The compound MIBK has been synthesized by means of a process comprising several stages. The first one is the aldolization of two acetone molecules to form 4-hydroxy-4-methyl-2-pentanone or DA. This stage is normally catalyzed by mineral acids or bases. The second stage consists of DA dehydration, which is normally carried out by acid catalysis using H_3PO_4 or H_2SO_4 to obtain MO. The last stage is the selective hydrogenation of the MO olefinic double bond (C=C) to obtain MIBK, which is normally carried out over a supported metallic phase [4]. However, this complex process has recently been studied in a single apparent stage, under hydrogen atmosphere and using bifunctional catalysts of the metal type (Pt, Pd, Ni, etc.) supported over acid, basic solids and crystalline aluminosilicates [5–7].

Processes in a single apparent stage are undoubtedly very efficient and advantageous, since MIBK synthesis can be completed without using corrosive and polluting substances such as mineral acids or bases, and separation of the catalyst from the reaction products is easier [3]. On the other hand, this new methodology calls for a high partial acetone pressure [1], which favors the aldolization reaction but results in a rapid catalyst deactivation. To overcome this last drawback, the possibility of regenerating the solids has been considered, but this introduces additional problems such as sinterization of the supported phase when regeneration occurs in the presence of air, which of course can cause solids to exhibit unpredictable behaviors [8].

In this sense, and aiming at minimizing deactivation, bifunctional catalysts have been supported over solids with less acidic strength, capable of catalyzing the aldolization reaction and, at the same time, extending the catalysts' useful life. Under this premise, the possibility has been considered of using an MFI-type gallosilicate as a platinum support with the same porous structure, but less strong acidic sites than those in the MFI aluminosilicate.

2. Experimental

The synthesis of two MFI-type solids, aluminosilicate and gallosilicate, was carried out using the method

proposed by Guth and Caullet [9]. The solids were calcinated to discard the orientating agent, and later exchanged with 1 M NH_4NO_3 solution; then they were filtered and stove dried overnight at 105 °C, and finally calcinated under air atmosphere at 500 °C to obtain the MFI protonic solids (H[Al]ZSM5 and H[Ga]ZSM5).

The solids prepared were assessed using DRX, N_2 adsorption at –196 °C, ammonia TPD and chemical analysis to determine the Si/Al and Si/Ga relationships. These solids were used as supports in the preparation of the bifunctional catalysts (Pt/H[Al]ZSM5 and Pt/H[Ga]ZSM5). In this process, 0.50 wt.% of platinum was introduced into each solid by means of the exchange–impregnation method [10], using the $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ complex as a precursor salt. The solids obtained were washed with deionized water, stove dried overnight at 105 °C, and then calcinated at 300 °C for 6 h under dry air flow. Finally, they were reduced under hydrogen atmosphere for 6 h at 500 °C. The bifunctional catalysts obtained, Pt/H[Al]ZSM5 (Si/Al = 40) and Pt/H[Ga]ZSM5 (Si/Ga = 42) were also analyzed by atomic absorption to determine the real content of supported platinum and by N_2 adsorption at –196 °C. Their specific surface area (SSA) was evaluated and they were analyzed using transmission electronic microscopy (TEM) to determine dispersion of the supported platinum. The bifunctional catalysts obtained were assessed by means of the toluene-hydrogenation and *n*-heptane hydrocracking model reactions under the conditions established in previous works [1,6].

These bifunctional catalysts were then analyzed using electronic paramagnetic resonance (EPR). This analysis was carried out at room temperature, using a Varian E-Ling X-band spectrometer operating under TE₁₀₂ mode, to spectroscopically determine the possible cause of the passivation of the platinum supported over gallosilicate.

Finally, acetone transformation was carried out over these solids in a dynamic reactor at 160 °C, atmospheric pressure, acetone/ H_2 molar ratio = 3 and variable WHSV.

The reactor effluents were in-line injected into an HP-6890 chromatograph equipped with a 30 m column of the methyl–phenyl xyloxane type. The products generated and identified were: propane (Hc), 2-methyl-pentane (2-MP), methyl–isobutyl ketone (MIBK), MO and traces of di-isobutyl ketone (DIBK).

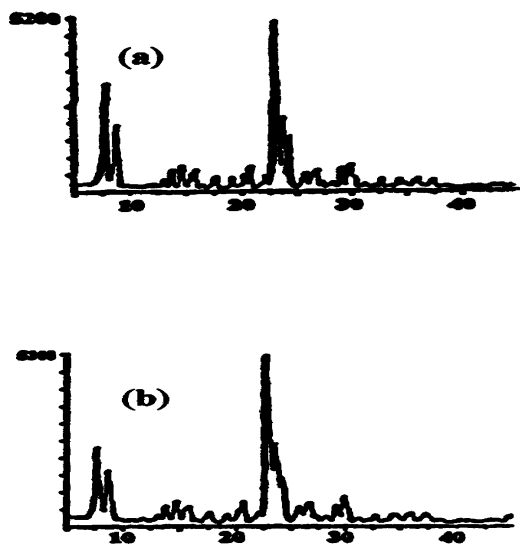


Fig. 1. XRD of synthesized aluminosilicate (a) and gallosilicate (b).

3. Results and discussion

The analyses to which both solids were submitted by means of XRD and nitrogen adsorption at -196°C suggest their high purity and crystallinity (as can be observed in Fig. 1), as well as a specific area of $380\text{ m}^2/\text{g}$, meaning that they are unblocked solids. In addition, both zeolites were submitted to elemental analysis by means of the atomic absorption technique, which showed Si/Al and Si/Ga relationships equal to 40 and 42, respectively. Aluminosilicate and gallosilicate characterization by means of TPD– NH_3 resulted in ammonia desorption, even at 723 and 673 K, respectively. Platinum of 0.50 wt.% was introduced into each solid by means of the exchange–impregnation method so that all of the desired metal was introduced. These solids were washed with deionized water to eliminate chlorides, and then calcinated and reduced following well-established protocols [6]. The

results of the analyses to which the bifunctional catalysts were submitted are shown in Table 1. We can observe that platinum percentage in both catalysts was very close to the theoretical value, which is completely logic given the method used to introduce the supported phase.

We have also assessed the dispersion of the metallic phase supported over both solids. This process was carried out by means of TEM in a JEOL-100 C XII microscope. For this analysis, a suspension of the solid in ethanol was prepared, which then was deposited over a copper grid and covered with a coal film [12]. Samples with 500 and 1000 metallic particles were randomly selected from the micrographs taken, and then under the assumption that all of the particles are spherical, their average diameter (\bar{d}) was determined using the following expression [10]:

$$\bar{d} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$

where (d_i) corresponds to the diameter of each metallic particle and (n_i) is the number of particles present in the selected sample with that diameter. Obtaining the average diameter of the present particles (expressed in nanometers) dispersion of platinum (D , %) supported over both catalysts' surface can be estimated using the following expression [12]:

$$D = \frac{100}{\bar{d}}$$

The dispersion values (D) found are reported in Table 1, showing that both catalysts exhibit similar dispersion. This seems fully reasonable because both solids were prepared and activated using the same methodology.

These solids were further evaluated by means of a toluene-hydrogenation model reaction, which made it possible to determine each catalyst's hydrogenating activity. Since, this is a reaction depending only on the number of active and accessible metallic centers

Table 1
Physicochemical characteristics of the bifunctional catalysts prepared

Catalysts	Pt _{experimental} (%)	SSA (m ² /g)	D _{TEM} (%)	A _H (mmol/h g)
0.50Pt/H[Al]ZSM5 (Si/Al = 40)	0.48	367	35	13
0.50Pt/H[Ga]ZSM5 (Si/Ga = 42)	0.49	371	36	7

[1,6], we could expect both bifunctional catalysts to present a similar hydrogenating activity, but surprisingly initial activity in toluene-hydrogenation of the 0.50Pt/H[Al]ZSM5 catalyst (Si/Al = 40) is practically twice that of the 0.50Pt/H[Ga]ZSM5 catalyst (Si/Ga = 42). These results do not coincide at all with the platinum dispersions obtained by TEM for both catalysts. Therefore, to elucidate a possible effect of SSA reduction on these results, we have determined this parameter for both bifunctional catalysts and found that their areas are alike (Table 1) and within the range of a normal reduction (3–5%) due to the effect of the deposition of a metallic phase such as platinum. These results coincide to those obtained in previous works [1].

As a consequence of these observations, we consider convenient evaluating these catalysts by means of the *n*-heptane hydrocracking model reaction [1,13]. The results found under the conditions established in the literature [1,13] and at WHSV = 14 h⁻¹ are shown in Fig. 2. As can be seen in this figure, total initial activity of the 0.50Pt/H[Al]ZSM5 catalyst (Si/Al = 40) is 10 times higher than that obtained for the 0.50Pt/H[Ga]ZSM5 catalyst (Si/Ga = 42). These results cannot be attributed to differences in the strength of the acidic sites present in both supports, since ammonia desorption at temperatures up to 723 and 673 K, for aluminosilicate and gallosilicate, respectively, means that both solids have acidic sites strong enough to catalyze isomerization and cracking reactions existing in the process.

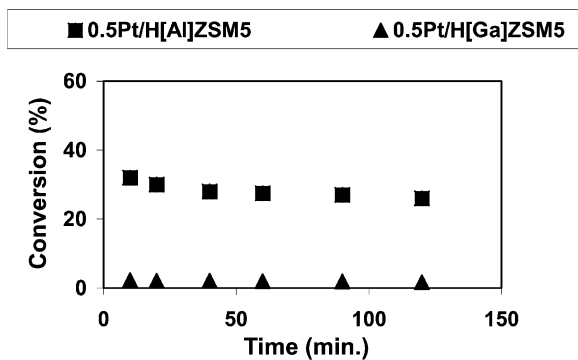
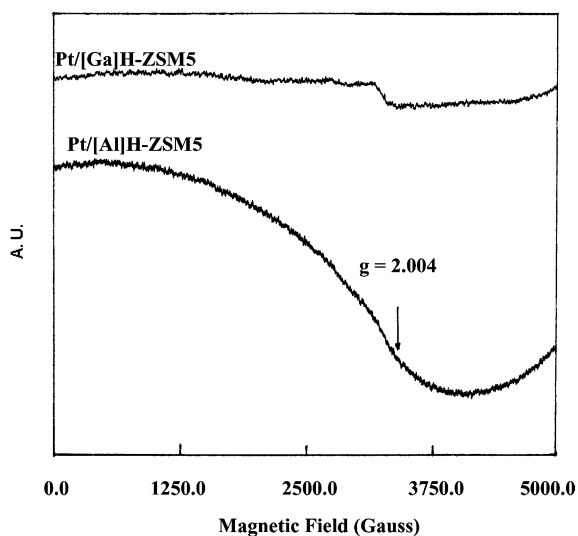


Fig. 2. Evolution of *n*-heptane conversion at 250 °C, $P = 1$ atm, $P_{H_2}/P_{n-C_7} = 9$, and $WHSV = 14$ h⁻¹.

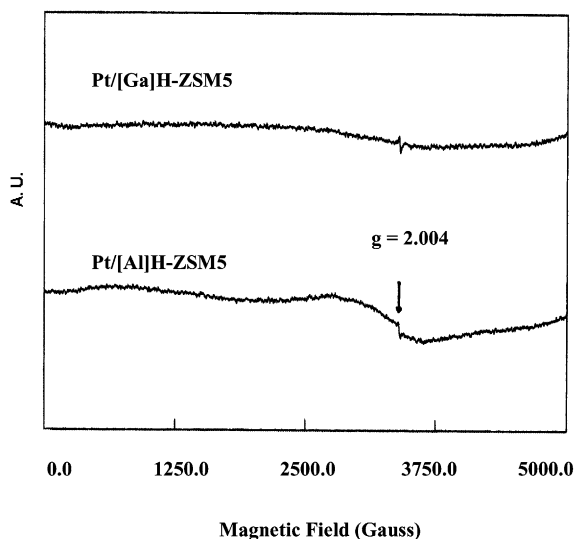
On the other hand, considerable changes are observed in product selectivity for *n*-heptane hydrocracking reaction. In this regard, for the Pt/H[Al]ZSM5 catalyst (Si/Al = 40), the isomerization products/cracking products relationship (I/C) is 1.1 for 10% conversion, and this relationship is similar to the values obtained in previous works [1,13]. However, at the same conversion, the I/C relationship for the Pt/H[Ga]ZSM5 catalyst (Si/Ga = 42) is 10 times lower. This result does not correspond to the dispersion of the platinum supported over gallosilicate, but it does correlate with the hydrogenating activities of the catalysts. This suggests that the metallic centers present in the 0.50Pt/H[Ga]ZSM5 catalyst (Si/Ga = 42) are not totally active to the hydro-dehydrogenation reactions, which could explain why toluene-hydrogenation is limited over these catalysts. The same happens to the *n*-heptane dehydrogenation, a stage necessary to form olefinic intermediates that will feed the catalyst's acidic sites so that it can generate the isomerization products.

Thus, by looking for an explanation for the catalytic behavior of the 0.50Pt/H[Ga]ZSM5 solid (Si/Ga = 42), we have evaluated both catalysts by means of the EPR spectroscopy technique (Fig. 3). This characterization was carried out before and after the reaction, employing calcinated and reduced fresh catalysts (Fig. 3a) and catalysts used for 120 min in the acetone transformation under standard conditions (Fig. 3b).

According to the Fig. 3a, EPR analysis shows that both fresh bifunctional catalysts have different magnetic environments, because the 0.50Pt/H[Ga]ZSM5 catalyst (Si/Ga = 42) does not practically show a paramagnetic signal. The opposite is observed for the 0.50Pt/H[Al]ZSM5 catalyst (Si/Al = 40), which shows wrapping over 5000 G, suggesting the existence of a considerable number of non-paired electrons in this catalyst. As a consequence, these results signify that the metallic phase of the platinum supported over the gallosilicate (Si/Ga = 42) could be passivated by the effect of an interaction with the structural and/or extra-structural gallium (EFGS), represented by species such as Ga₂O and GaO⁺, which have been reported in the literature [15–18]. Based on the analysis of the EPR spectra for both catalysts once they were used in the acetone transformation (Fig. 3b), we can observe that the paramagnetic signal



(a)



(b)

Fig. 3. EPR spectrum of calcinated-reduced fresh 0.5Pt/H[Ga]ZSM5 (Si/Ga = 42) and 0.5Pt/H[Al]ZSM5 (Si/Al = 40) catalysts (a) and used in the acetone transformation; (b) taken under TE₁₀₂ mode at room temperature.

of the 0.50Pt/H[Al]ZSM5 catalyst is much lower than that of the fresh catalyst. This drastic decrease in its paramagnetism once the acetone transformation has been carried out could be attributed to the presence of carbonous residues deposited over the metallic parti-

cles; this would have electronic and geometric effects that could be causing electronic transfer from coke towards platinum particles and also could be limiting the reactant access to the surface of the metallic centers. The magnetic behavior of the 0.50Pt/H[Ga]ZSM5 catalyst, shown in Fig. 3a and b, indicates that this catalyst has an inactive supported metallic phase before and after the reaction.

3.1. Acetone transformation

The acetone transformation reaction over these catalysts was run at 160 °C at a total pressure = 1 atm, an acetone and hydrogen partial pressure ratio of 3 ($P_{Ac}/P_{H_2} = 3$), and variable WHSV. The results obtained under the aforementioned conditions and at WHSV = 9.4 h⁻¹ are reported in Fig. 4.

According to Fig. 4, total initial activity in acetone transformation over the 0.50Pt/H[Al]ZSM5 catalyst (Si/Al = 40) is five times higher to that obtained over the 0.50Pt/H[Ga]ZSM5 catalyst (Si/Ga = 42). Considering that acidic sites present in every support (aluminosilicate and gallosilicate) are strong enough to catalyze the limiting stage in the aldolization process [14], these results could be explained if we understand that acetone under these conditions and over this type of catalyst is transformed by two different ways [4,11]. The first one requires hydrogenation of the acetone carbonyl double bond (C=O), leading to propane formation through the reaction intermediates (isopropanol and propene), which would be a minimized way over the Pt/H[Ga]ZSM5 bifunctional catalyst (Si/Ga = 42); given the drastic decrease in the active metallic centers in the hydrogenation processes, this would perfectly coincide with the results of the catalytic test and the EPR analysis. The other way initially requires a catalysis per site of moderate and/or high acidic strength [14], which would allow aldolization of two acetone molecules to form DA. Since, this substance is a tertiary alcohol, it probably dehydrates over the same acidic sites where it is formed, generating MO, which is an α - β unsaturated ketone acting as one of the main precursors of the coke deactivating these catalysts [6].

Thus, acetone aldolization can be carried out over both catalysts, meaning that a high MO concentration and a low MIBK and propane concentration should be formed over the 0.50Pt/H[Ga]ZSM5

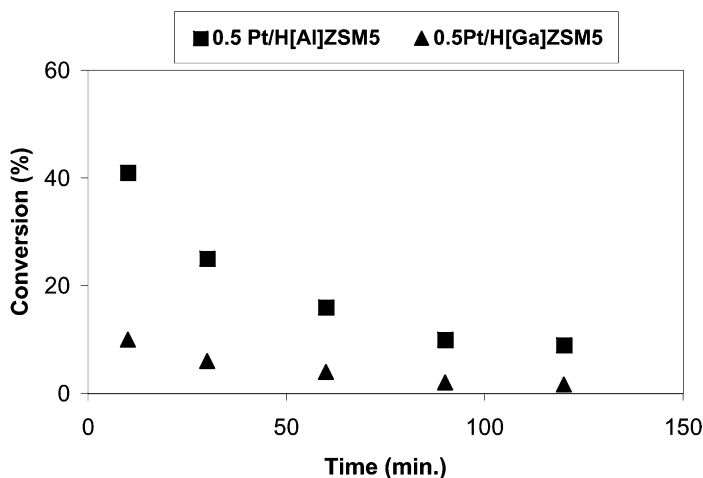


Fig. 4. Evolution of the acetone conversion as a function of the reaction time at 160 °C, $P = 1$ atm, $P_{Ac}/P_{H_2} = 3$, and $WHSV = 9.4 \text{ h}^{-1}$.

catalyst (Si/Ga = 42), given the presence of sites with a high acidic strength and the low density of the active metallic centers. On the contrary, high concentration of MIBK and propane should be observed over the 0.50Pt/H[Al]ZSM5 catalyst (Si/Al = 40) as a consequence of the presence of the active sites (acid and metallic) required to catalyze both reactions. The results obtained over both catalysts are shown in Table 2 and fully coincide with the physicochemical characteristics of the solids.

Table 2 shows that selectivity of the main products obtained in the acetone transformation fully coincides with the analyses carried out by test reactions and with the paramagnetic characteristics exhibited by both catalysts. This definitely suggests that metallic centers of the platinum supported over the MFI-type gallosilicate would be somehow passivated towards hydrogenation reaction of the carbonyl (C=O) and olefinic (C=C) double bonds, due to the fact that particles of

the supported platinum would be interacting with the structural gallium and/or the EFGS.

4. Conclusions

Initial activity in the toluene-hydrogenation over the 0.50Pt/H[Al]ZSM5 catalyst (Si/Al = 40) is twice of that obtained with the 0.50Pt/H[Ga]ZSM5 catalyst (Si/Ga = 42). The I/C relationship for the *n*-heptane hydrocracking reaction at 10% isoconversion is 10 times higher for the Pt/H[Al]ZSM5 catalyst than for the Pt/H[Ga]ZSM5 one.

Total initial activity over the 0.50Pt/H[Al]ZSM5 catalyst (Si/Al = 40) in the acetone transformation is practically five times higher than that obtained over the 0.50Pt/H[Ga]ZSM5 (Si/Ga = 42) catalyst.

The selectivity obtained in the acetone transformation completely corresponds to the paramagnetism exhibited by both catalysts, meaning that hydro-dehydrogenating activity of the metallic centers in the Pt/H[Ga]ZSM5 catalyst is much lower than that of the metallic centers in the Pt/H[Al]ZSM5 catalyst. These results seem to indicate that a strong interaction of platinum with a species of the supporting structural or EFGS has occurred.

According to these results, we can conclude that the 0.50Pt/H[Ga]ZSM5 bifunctional catalyst

Table 2

Selectivity of the main reaction products obtained over the bifunctional catalysts at 10% isoconversion

Catalysts	MIBK	MO	Hc
0.50Pt/H[Al]ZSM5 (Si/Al = 40)	5.7	0.2	4.0
0.50Pt/H[Ga]ZSM5 (Si/Ga = 42)	0.8	8.5	0.3

(Si/Ga = 42) is not recommendable for the MIBK synthesis from acetone.

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