Isomerization of Pinene with Al- and Ga-modified MCM-41 Mesoporous Materials

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Abstract

In recent years the pharmaceutical and cosmetics industries have increased the usage of camphene, an intermediate for the manufacture of, for instance, camphor, anti-swelling drugs and K vitamin. Therefore, recent research efforts have been focused on developing new reaction paths towards a higher selectivity to camphene while avoiding other terpene by-products, such as p- cumene and limonene, which are of little industrial value. The aim of the present work was to study the structure and catalytic performance of Al- and Ga- substituted MCM-41 mesoporous materials for the α -pinene isomerization reaction. Both, Al and Ga, enhance the Brönsted and Lewis acidity of the parental MCM-41 material. At low conversion (± 10%) there was little deactivation, mainly due to the absence of secondary reactions; at higher conversion (± 50%) considerable amount of cyclic products are obtained.

Introduction

Ordered mesoporous materials have had a big impact on heterogeneous catalysis because their controllable pore size and high surface area. One of the most studied materials has been MCM-41 (Mobil Composition of Matter No. 41),



characterized by its unidirectional pore system, by a long- range hexagonal array and by a high surface area, usually between 750 and 1250 m²/g. On the other hand, one major drawback for employing MCM-41 in acid-catalyzed reactions is the weak acidity of the purely siliceous material [1-5].

The incorporation of AI and Ga, both elements of the IIIA Periodic Table Group, should improve the acidity of the material's surface groups. Specific synthesis procedures allow the substitution of silicon oxide tetrahedral units with aluminum and gallium oxide units, also with tetrahedral geometry, within the material framework [6, 7]. Several reports have studied the cycling and aromatization properties of gallium involved in organic compounds reactions [3]. Camphene can be obtained through the isomerization of pinene under acid conditions, as in several industrial processes. Several solid catalysts have been tried in recent years, including TiO₂, ZrO₂, ion exchange resins, clays, zeolites and mesoporous materials, with typical selectivity values to camphene of 40 and 45 % [8, 9]. Therefore, the aim of the present work was to compare the catalytic performance of AI- and Ga- substituted MCM-41 materials in the isomerization of α - pinene reaction.

Experimental

Materials synthesis

The synthesis of the MCM-41 was carried out by co-precipitation [10]. A 0.7 % w/w aqueous solution of cetyltrimethylammonium (CTAB, Aldrich) was prepared and kept under stirring (700 rpm) for the rest of the procedure. 500 ml of NH₄OH (30% w/w) were added and stirred until a homogeneous mixture was formed, then appropriate amounts of gallium (Ga (NO₃)₃ and aluminum salts (AI (NO₃)₃, Aldrich)



were added for attaining Si/AI and Si/Ga molar ratios since 5 until 25. After 0.5 hour tetraethylsilicate (TEOS, Aldrich) was added, drop by drop and kept under stirring for 24 hours at room temperature. The resultant solid was filtered, washed and dried for 12 hours at room temperature. The solid was then calcined at 823 K for 3 hours under dry air flow (10 ml/min).

Catalyst characterization

X-ray diffraction measurements were performed on a Philips X'PERT with automatic slits using CuKα radiation. Adsorption isotherms of N₂ and Ar were obtained on an ASAP 2020 instrument after pretreating the samples under vacuum at 673 K overnight. NH₃ Temperature Programmed Desorption (NH₃-TPD) was carried out with a Belcat-B TPD equipment. The sample was pretreated under a 50 ml/min He flow at 673 K for 5 h. The TPD test was run from 323 to 1073 K. NH₃ was adsorbed at 323 K for 20 min employing a 30% NH₃/He mixture. Prior to taking the measurements, the non-adsorbed NH₃ was removed by applying 20 min of He flow. The distribution of Ga on the samples surface was studied by Transmission Electron Microscopy (TEM), using a Carl Zeiss EM910 instrument operating at a 120 KV voltage and a clear field technique. In addition to looking at the materials structure, diffracted electrons were employed in order to check the presence of gallium or aluminum oxides outside the materials framework.

IR spectra were obtained in a Nicolet 710 FTIR by using a Pyrex vacuum cell (CaF₂ windows) and self-supported wafers of 10 mg cm⁻². For acidity measurements, the samples were previously degassed at 673 K in vacuum (10^{-3} Pa) overnight (background spectrum). Then pyridine (6 x 10^{2} Pa) was admitted at room



temperature and degassed at 423, 523, and 673 K for 1 h. After each treatment spectra were recorded at room temperature and the background was subtracted.

Isomerization Reaction

The α -pinene to camphene isomerization reaction, [11-13] was carried out in liquid phase, employing a 0.8 mol pinene /1 g catalyst ratio and 250 min reaction time. In every test, 373 K was the constant reaction temperature. Samples were taken every 50 min in order to calculate conversion at t = 0 (initial conversion) and the initial yield. Reaction products were analyzed by gas chromatography with a flame ionization detector (FID-GC). Conversion (X), Yield (R), and Selectivity (S) were calculated according to the following formulas[14]:

$$X (\%) = \frac{(\alpha \text{-pinene concentration at } t = 0) - (\alpha \text{-pinene concentration at t time})}{(\alpha \text{-pinene concentration at } t = 0)} \times 100$$

$$R (\%) = \frac{(Product concentration)}{(\alpha \text{-pinene feed concentration})} \ge 100$$

 $S(\%) = \frac{(Product yield)}{(Initial Conversion)} \times 100$

Results and Discussion

Structural properties

Table 1 shows the textural properties of materials prepared, containing AI and Ga. AI- and Ga- modified materials were compared to a purely siliceous MCM-41 sample. Samples were labeled as AI- or Ga-MCM-41-N, where N can take values of 5, 10, 15, 20 or 25, depending on the Si/M³⁺ molar ratio. It has been seen that in the aluminum modified materials, aluminum content results in a reduction of the surface



area and an increase of pore volume. The sample with a molar ratio Si to Al 20 has a largest surface area 1071.40 m²/g and a biggest pore diameter pore volume 0.81 cm³/g. In the series of Ga-MCM-41 samples, the addition of Ga ions linearly increases the surface area until the Si/Ga ratio reaching 20, Ga-MCM-41-20 sample has the largest surface area 1356.02 m²/g and pore volume 1.25 cm³/g.

Sample	Surface Area BET (m²/g)	Pore Volume (em^3/g)	Pore Size (nm)
MCM-41	796.85	0.52	2.64
Al-MCM-41-5	763.40	0.59	3.10
Al-MCM-41-10	669.18	0.57	3.43
Al-MCM-41-15	727.69	0.71	3.92
Al-MCM-41-20	1071.40	0.81	3.04
Al-MCM-41-25	965.25	0.75	3.14
Ga-MCM-41-5	876.48	0.77	3.52
Ga-MCM-41-10	834.63	0.75	3.60
Ga-MCM-41-15	977.25	0.91	3.76
Ga-MCM-41-20	1356.02	1.25	3.69
Ga-MCM-41-25	916.75	0.83	3.65

Table 1. Specific surface area and pore volume of the different samples measured from N_2 adsorption isotherms data.

Figures 1 and 2 show the XRD patterns of the Ga-MCM-41 and Al-MCM-41 calcined samples. All XRD patterns correspond to the typical ordered hexagonal array of MCM-41 materials; the diffractions arising from (100), (110) and (200) planes can be observed. As the M³⁺ content increases, the intensities of diffraction peaks from (110) and (200) planes decrease, in an indication of a less ordered structure; even so, the hexagonal channel system is preserved [1, 15, 16].

The ordered hexagonal porous structure is also visible in the Ga-MCM-41 and



Al-MCM-41 electron micrographs, Figure 3 a) and b). Structural and morphological features, such as porosity, in both images are rather similar. Figure 3 a) and b) insets belong to the Al-MCM-41-5 and 20, and Ga-MCM-41-5 and 20 samples electron diffraction patterns, which do not show point sequences in an indication of an amorphous microstructure. Comparison of Ga-MCM-41-5 and Ga-MCM-41-20 images do not show particular structural or morphological differences. The incorporation of Ga atom within the material framework by substitution of Si atom is expected to increase the catalytic activity.



Figure 1. X-ray diffraction patterns of Ga-MCM-41-n (n =5, 10, 15, 20, 25) samples.





Figure 2. X-ray diffraction patterns of Al-MCM-41-n (n= 5,10,15,20,25) samples.

On the other hand, due to the size difference between Si, Al and Ga atoms, the incorporation of Ga within the material's framework could cause the distortion of the framework (the ionic radius of Si, Al and Ga are 0.41, 0.51 and 0.62 Å, respectively). A very big atom may not fit inside the framework, staying on the surface or, it may distort the framework. SEM electron patterns of crystalline materials can indicate framework distortion, but, since our samples are amorphous, none of such information can be inferred. Even so, a good Ga dispersion on the sample can relate to the incorporation of Ga within the matrix. Furthermore, XRD results did not show the characteristic gallium oxide and gallium nitrate diffraction peaks at 20 diffraction angles between 20 and 80°, in an indication that Ga atoms are incorporated within the matrix. Changes in the interatomic distance resulting



from Si substitution by Ga could be measured by radial distribution studies (FDR),

which are not included in this contribution.





Figure 3a. Clear field transmission electron microscopy images of two representative Al-MCM-41 samples. Inset: electron diffraction patterns.





Figure 3b. Clear field transmission electron microscopy images of two representative Ga-MCM-41 samples. Inset: electron diffraction patterns.



Sample	a ₀ (nm)	$d_p(nm)$	t (nm)
MCM-41	5.47	2.64	2.82
Ga-MCM-41-5	5.60	3.52	2.06
Ga-MCM-41-25	5.58	3.65	1.92
Al-MCM-41-5	5.59	3.10	2.48
Al-MCM-41-25	5.59	3.14	2.45

Table 2. Structural lattice parameters.

Structural features such as cell parameter (interplanar spacing), pore diameter and wall thickness, calculated from XRD results, are given in Table 2. There is relatively little difference of the interplanar spacing and the pore diameter of the samples with different AI and Ga content, in agreement with previous results by R. Luque *et al* [1]. However, we obtained a small difference of the wall thickness at different Ga contents that may be due to the relatively big size of the Ga atom, as previously mentioned. Results of surface area, pore size and pore volume in Table 1, obtained by N₂ adsorption/desorption isotherms, show a relatively small variation of the pore size at different M³⁺ contents, however, the smallest pore volumes obtained belonged to samples with high M³⁺ content (AI-MCM-41-5 and Ga-MCM-41-5); these samples also exhibited less-ordering from XRD patterns.

Figure 4 shows representative N₂ adsorption/desorption isotherms, type IV, according to the BET classification and typical of mesoporous materials [1, 10] The characteristic inflection of the curve has been associated to capillary condensation inside the mesopores, in this case, taking place in the ordered hexagonal tubes.

Calculated with: $a_0 = d_p + t$ Structural features such as cell parameter (interplanar spacing), pore



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Figure 4. Nitrogen adsorption/desorption isotherms of the studied samples (Ga-MCM-45-25 and Al-MCM-41-25)

NH₃TPD and Pyridine adsorption/desorption FTIR



In order to determine the surface acidity of the samples, NH₃-TPD profiles were measured, as shown in Figure 5a and b. Since no peaks are observed in the pure silica MCM-41, peaks observed on the NH₃-TPD lines in the Ga and Al modified samples are caused by the Al and Ga in the structure. The sample with the highest peak and highest total acidity is Al-MCM-41-10, whereas the acidity decreases for the sample with the highest Al content, Al-MCM-41-5. It may be due that in the case of large aluminum contents, some of the Al ions may form extra-framework species, such as aluminum oxide [17, 18, 19].

Figure 5b shows the NH₃-TPD profiles of the Ga-containing samples. As with Al samples there is a wide variation of the total acidity. For this series, the highest acidity was obtained in the Ga-MCM-41-20 sample. The presence of NH₃-TPD peaks at temperatures above 673 K indicates strong acid sites, present in both type of materials and slightly higher in Ga samples.

All the Ga and Al modified samples exhibit two sets of peaks in the NH₃-TPD profiles. The low temperature peaks locate around 393.15K and high temperature peaks at around 823.15 K. These results indicate that all the Ga or Al containing samples have two kinds of acid sites, these corresponding to NH₃ desorption at low temperature are sites with weak acidity strength, while, these corresponding to NH₃ desorption at high temperature are strong acid sites.

In order to determine the acidity type, pyridine adsorption/desorption FTIR spectroscopic analysis was applied, the results are shown in Figures 6 and 7. We can observe for samples with AI, that as the AI content increases, the number of Brönsted and Lewis acid sites also increases. The larger increase of Brönsted acid



sites corresponds to weak acid sites (373 K), whereas the number of strong acid sites (673 K) is relatively constant and smaller.



Figure 5a. NH₃-TPD profiles for AI-MCM-41 samples





Al has a more evident effect on the Brönsted acidity than Ga. The larger number of Brönsted acid sites of Ga-containing samples belong to the Ga-MCM-41-15 material and a further increase of the gallium content does not enhance the Brönsted acidity. On the other hand, Ga enhances Lewis acidity more than Al, in agreement with literature reports [1,7, 17, 18] Most Lewis sites are strong, about twice in number than weak sites. Previous reports state that Lewis acid sites play an important role in isomerization reactions [1, 17, 18]



Figure 6. Brönsted acid sites as function of the Metal content (M⁺³)



Figure 7. Lewis acid sites as function of the Metal content (M⁺³)



Catalytic activity

During the isomerization reaction of α -pinene to camphene experiments, for all the different catalysts, there was a very low decrease of activity with time, probably due to the formation of coke on the catalysts surface, or because the strong adsorption transition reactive complexes.

In order to compare the catalytic activity of the samples in absence of deactivation, the α -pinene conversion at zero time reaction was estimated from the values of conversion obtained at different times [14]. All samples exhibited catalytic activity but not the purely siliceous MCM-41 that exhibited no catalytic activity.

Figure 8 contains experimental data relating the conversion of α-pinene versus the reaction time, employing the AI-MCM-41-5 and Ga-MCM- 5 catalysts at 373 K. We may observe that samples with AI show very little deactivation; the activity stays almost constant with time, when the reactive/catalyst ratio is 1.25. Under the same reaction conditions, Ga catalysts are slightly more active, due to a relatively higher acidity and show a slightly higher deactivation.





Figure 8 . α -pinene conversion with Al-MCM-41-5 and Ga-MCM-41-5 samples as a function of reaction time.

Catalytic selectivity

Figure 9 shows the camphene yield depending on the catalyst/feed ratio (feed = α -pinene). When the catalyst/feed ratio increases, the camphene yield also increases, up to a ~3.75 maximum but then slightly decreases at bigger catalyst/feed ratios. The limonene yield also likewise increases; the maximum limonene yield is about 15 at 38 % conversion. This behavior indicates that the α -pinene isomerization reaction paths towards camphene and limonene are parallel and competitive [1, 20-23]

Correlating the selectivity to camphene to the aluminum or gallium content,



this selectivity decreases as the gallium content increases, whereas the selectivity to limonene increases (Table 3). This behavior has also been reported by Chimal-Valencia et al. [5], and Luque et al. [1] have suggested that it is due to a larger number of Brönsted acid sites.



Figure 9. Camphene and limonene yield at different catalyst/feed ratios, for the Ga-MCM-41-5 catalyst.

Table 3 shows that the selectivity to camphene is very similar within one series of catalysts. Only the catalysts with a high Ga content exhibit a noticeable decrease of the selectivity to camphene and limonene. In general terms, for Gacontaining catalysts, the selectivity to camphene decreases as the Ga content increases. On the other hand, as the Ga content increases, the selectivity to limonene increases. Aluminum-containing catalyst exhibit a similar trend, but this even more evident in the case of the selectivity to camphene.

The selectivity to camphene, plotted against the number of Brönsted and Lewis acid sites (as adsorbed pyridine μ moles) at 373 K is shown in Figure 10. At high Al and Ga content, the acid density increases. The selectivity to camphene



decreases as the acid surface increases [1-5] This is more evident for Brönsted sites in Ga materials.

Catalyst	Selectivity % (mol)			
	Camphene	limonene	others	
Ga-MCM-41-5	38.00	36.36	25.64	
Ga-MCM-41-10	39.88	35.80	24.32	
Ga-MCM-41-15	41.26	36.23	22.50	
Ga-MCM-41-20	42.24	35.00	24.23	
Ga-MCM-41-25	45.94	32.83	16.94	
Al-MCM-41 05	40.21	37.12	22.35	
Al-MCM-41-10	41.30	34.87	23.80	
Al-MCM-41-15	42.04	35.01	22.02	
Al-MCM-41-20	44.95	35.94	19.11	
Al-MCM-41-25	46.96	28.42	24.62	

Table 3. Selectivity to main products with the different catalysts at conversion 10 %.



Figure 10. Selectivity to camphene as a function of Brönsted and Lewis acid sites.



Conclusions

All catalysts under evaluation showed good catalytic activity in the α -pinene isomerization reaction, being the main reaction products camphene and limonene. Aluminum and gallium ionic radius are not so different to produce considerable morphological, textural or framework differences, and both certainly increase the acidity of the MCM-41 mesoporous material. The introduction of gallium results in the right acid properties that make feasible to employ Ga-MCM-41 as a substitute of zeolite materials such as ZSM-5 and beta zeolite. The selectivity towards camphene or limonene can be varied depending on the gallium and aluminum content. At low conversion (\pm 10 %) there was little deactivation, mainly due to the absence of secondary reactions; at higher conversion (\pm 50 %) considerable amount of cyclic products are obtained. This work has shown that the incorporation of Al and Ga within the MCM-41 structure makes possible the conversion of \Box pinene into camphene and limonene.

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