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Gas- versus liquid-phase α-pinene transformation over faujasite-like zeolites and an amorphous silicoaluminate

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The transformation of α-pinene was studied in both gas and liquid phase over a series of faujasite-like zeolites having different framework composition. A comparison with an amorphous silicoaluminate having 13 wt% of Al_2O_3 (SA) was made. Camphene + limonene were the major products observed in liquid phase at 393 K at conversion levels lower than 90%. At 473 K, where the reaction in gas phase took place, limonene suffered an ulterior transformation mainly into terpinenes and terpinolenes and a faster deactivation of the zeolite catalysts as compared to the one in liquid phase was observed. This behaviour contrasts with the high stability shown by SA in gas phase. Over the wider pore system of SA undesired heavy products were formed in liquid phase at the expenses of the terpene isomers. However, in gas phase this ulterior transformation of monoterpenes was minimised. A maximum activity for the zeolite catalysts was observed when the number of Al^{IV} per unit cell reached about 17, a value where the population of Si(0Al) sites has been shown to reach the maximum.

Keywords: α-pinene conversion, dealuminated faujasite, gas- versus liquid-phase activity, acidity

1. Introduction

The well known acid and shape-selective properties of zeolite molecular sieves, in addition to the growing concern for the environmental protection, have stimulated the exploration of these innocuous materials as heterogeneous catalysts in the acid-catalysed synthesis of fine chemicals, in substitution of mineral acids [1–3].

Monoterpenes are widely used in the pharmaceutical, cosmetic and food industries as active components of drugs and ingredients of artificial flavours and fragrances. α-pinene is a very reactive substrate, being abundant in natural essential oils such as pine and eucalyptus resins. Protonation of the α-pinene double bond generates a tertiary carbocation that rearranges to a variety of isomers such as bornylene, tricyclene, camphene, α-fenchene, limonene, terpinolene and other terpenes [4].

It has been shown that faujasite-like zeolites isomerise α-pinene through two parallel routes: one leading, by ring rearrangements, to bi- and tri-cyclic products (bornylene, tricyclene, camphene) and the other to monocyclic products (limonene, terpinolenes, terpinenes and p-cymene) [5,6]. In a previous work [7], we have studied the liquid-phase transformation of α-pinene over a series of mordenite and Y-zeolites with different composition. Camphene + limonene were the main products observed in this study. Over dealuminated mordenites the combined yield camphene + limonene was higher than 68% with a camphene/(camphene + limonene) ratio higher than 0.54.

The main purpose of the present work is to make a comparison between the liquid- and gas-phase transformation of α-pinene over a series of faujasite-like zeolites of different composition. An amorphous silicoaluminate having 13% of Al_2O_3 (SA), is also included to assess the influence of pore accessibility on the catalyst selectivity and stability.

2. Experimental

2.1. Sample preparation and characterisation

Dealuminated faujasites were obtained by self-steaming under different conditions the ammonium form of the commercial zeolite designated LZY-52 from Union Carbide. The zeolite was first ion-exchanged with 20 ml of 1.5 M ammonium acetate per gram of zeolite at 60 °C for 2 h. Then, the zeolite was partially dried to about 40% humidity and statically calcined either at 600 or 800 °C for 3 h in a deep bed to produce dealuminated products designated YDA(600) and YDA(800), respectively. To dealuminate further a portion of the sample YDA(600) was again ion-exchanged with the ammonium acetate solution at comparable conditions. The product was dried as before and calcined at 800 °C to yield a dealuminated product designated YDB(800). The protonic form of the starting material, HY, was prepared by first drying at 100 °C for 12 h the ammonium-exchanged LZY-52 and then calcining the thus dried zeolite at 550 °C for 3 h. Such a treatment, however, caused about 14% dealumination.

For comparison purposes, a home-made sample of an amorphous silicoaluminate (13% alumina), prepared as di-

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rected by Magee and Blazek [8], was also tested. This sample was designated SA.

Zeolite crystallinity was determined using a Philips diffractometer PW 1730 using Co Kα radiation (λ = 1.790255 Å) operated at 30 kV, 20 mA and scanning speed of 2° 2θ/min. Diffraction lines between 18 and 40° 2θ were taken as reference for this calculation. The starting material LZY-52 (Union Carbide) was taken as 100% crystalline. Unit cell parameters were determined using a computing package PDP (powder diffraction package) [9] to speed up the calculation.

Bulk chemical analyses of the solids were carried out by atomic absorption spectrometry using a Varian Techtron AA6 spectrometer.

The N_2 surface area (m^2/g) of the zeolites was obtained with the aid of a Micromeritics Flow Sorb II 2300 equipment, using 30% N_2 diluted in He as adsorbate at the liquid-nitrogen temperature. The pore size distribution for the amorphous silicoaluminate was evaluated using a Digisorb 2600 analyser.

^{27}Al and ^{29}Si MAS NMR spectra of the zeolites were taken in a Bruker AM 300 spectrometer using a resonance frequency of 78.21 MHz for ^{27}Al and 59.52 MHz for ^{29}Si with a MAS frequency of 3900 in both cases and scanning numbers between 500 and 2000. External references were $Al(H_2O)^{3+}$ and TMS.

2.2. Catalytic test

Liquid-phase conversion of α-pinene (Aldrich) at 393 K was effected using a 10 ml stirred batch reactor into which 2 ml of α-pinene and 0.1 g of catalyst were charged. Gas-phase transformation of α-pinene was carried out in a continuous-flow tubular reactor made in glass, charged with about 0.1 g of catalyst and feeding α-pinene at a flow rate of 6 ml/h using dry nitrogen as carrier gas with a molar ratio N_2/α-pinene of 4. The reaction temperature was 473 K. Products were collected over an ice-tramp after 10 and 30 min on-stream for the chromatographic analysis. Products from both liquid- and gas-phase experiments were analysed in a HP 6980 gas chromatograph with a 30 m fused-silica non-polar (methyl silicone) DB-1 capillary column. Nineteen different chromatographically pure monoterpene standards were used. Retention times (RT), measured after injecting a mixture of the above 19 monoterpene standards to the chromatographic column, as well as their respective Kováts' retention indices (I_k) as given by Davies [10] for methyl silicone phase were collected. The data were fit with the following logarithmic correlation between RT and I_k with a regression coefficient (R^2) of 0.989:

$$\log(\mathrm{RT}) = 0.002 I_\mathrm{k} - 0.699. \tag{1}$$

Products with retention times lower than α-pinene were designated LRTP (low retention time products), those with higher retention times than terpinolene as HRTP (high retention time products) and unidentified products in the range between α-pinene and terpinolene as UP. Product identification was confirmed using ^{13}C NMR in an Eclipse 270 Jeol spectrometer with an automated identification system developed in our NMR laboratory.

The following catalytic parameters were determined:

(a) Percentage of components in the final mixture (%i),

$$\%i = \frac{A_i}{\sum A_i} \times 100, \tag{2}$$

where i stands for a particular component i in the final mixture, including the reactant α-pinene.

(b) α-pinene conversion (X_α),

$$X_\alpha = \left(1 - \frac{A_{\alpha\text{-pinene}}}{\sum A_i}\right) \times 100. \tag{3}$$

3. Results and discussion

3.1. Characterisation

Some characteristics of the catalysts studied are given in table 1. The percentage dealumination ranged from 14 to 76 with a concomitant decrease of the unit cell parameter (a_0) from 24.72 to 24.29 Å. From these values the number of Al^{IV} atoms per unit cell (Al/UC) could be obtained. For that, we have used the following correlation obtained from the data reported by Kerr et al. [11] for dealuminated faujasites:

$$\mathrm{Al/UC} = 87.27(a_0 - 24.15). \tag{4}$$

In a previous paper [7] we have observed a good agreement between the framework composition calculated from the cell parameter and from ^{29}Si MAS NMR. Subtracting the structural Al^{IV} atoms calculated from the cell parameter from the total Al content determined from bulk chemical analysis (51 Al atoms per unit cell) the amount of extra-framework Al species (EFAl) could be obtained, as presented in table 1.

^{29}Si MAS NMR and ^{27}Al MAS NMR spectra of the dealuminated faujasites were presented in figures 1 and 2 of [7]. For the sake of completion a summary of the most important features is given: The starting material LZY-52 showed four ^{29}Si MAS NMR signals at -90.5, -96.0, -100.8 and -108.3 ppm, corresponding to the chemical environments Si(3Al), Si(2Al), Si(1Al) and Si(0Al), respectively, with Si(2Al) and Si(1Al) predominating. The calculated Si/Al ratio from their respective intensities was 2.84. This value agrees well with the one obtained from bulk chemical analysis (2.77). As dealumination proceeds signals associated to the Si(1Al) for YDA(600) and Si(0Al) for YDB(800) became predominant giving Si/Al ratios of 4.0 and 12.0 for both zeolites, respectively, in good agreement with the ratios calculated from the cell parameters. However, a correction for the most dealuminated sample YDB(800) had to be made [7]. Generation of extra-framework aluminium species (EFAL) by the hydrothermal

Table 1
Some characteristics of the solids studied.

Sample	Cell parameter (Å)	Crystallinity (%)	Specific surface area (m^2/g)	Al per unit cell[a]	Dealumination[b] (%)	EFAl[c]
LZY-52	24.72	100	695	50	0	0
HY	24.65	90	609	44	14	7
YDA(600)	24.60	98	604	39	22	12
YDA(800)	24.35	90	574	17	67	34
YDB(800)	24.29	55	522	12	76	39

[a] Al/UC = 87.27(a_0 − 24.15) [11].

[b] Based on bulk chemical analysis of LZY-52 (51 Al atoms per unit cell).

[c] EFAL = extra-framework aluminium.

Table 2
Composition (%) of the reaction mixture, after 1 h of reaction, for the liquid-phase transformation of α-pinene.

Compound	Blank	HY	YDA(600)	YDA(800)	YDB(800)	SA
LRTP	0.4	2.5	9.0	4.4	2.2	10.1
α-pinene	98.0	51.0	2.2	15.1	70.6	1.1
Camphene	0.8	19.9	31.7	41.9	8.9	17.7
Limonene	0.0	14.6	4.6	22.9	6.4	0.5
Terpinenes	0.0	2.5	25.9	5.1	0.6	8.6
Terpinolenes	0.0	3.7	14.2	8.0	1.4	1.5
p-cymene	0.0	0.5	2.3	0.51	0.2	0.0
UP	0.7	3.5	6.6	1.6	7.7	11.7
HRTP	0.1	1.6	5.4	0.4	1.9	43.4
X_α (%)	2.0	49.0	98.0	85.0	29.4	99.0

treatment was evidenced from the ^{27}Al MAS NMR spectra. In fact, the starting material LZY-52 showed only one signal at around 59 ppm associated to framework Al^{IV}. After dealumination a second signal at around 0 ppm related to EFAL (Al^{VI}) species was developed, its intensity being directly proportional to the degree of dealumination.

Dealumination caused a reduction of the sorption capacity probably associated with a partial loss of microporosity to generate mesopores, as has been largely established for hydrothermally dealuminated faujasites [12,13]. Additionally, the most dealuminated samples YDA(800) and YDB(800), should contain a high proportion of neutral boehmite-like EFAL which have been shown to block the access to the faujasite cages [14]. The sample YDB(800) submitted to the most severe dealumination treatment showed the highest loss of both sorption capacity and X-ray crystallinity.

Pore size distribution of the amorphous silicoaluminate (SA) showed two maxima at around 50 and 170 Å, the latter being the absolute one. The calculated specific surface area and total pore volume were 120 m^2/g and 0.48 cm^3/g, respectively. From the calculated micropore volume of 0.043 cm^3/g the percentage of microporosity was determined as to be about 10. These figures contrast with those for zeolites ranging from 70% for YDB(800) to 100% (LZY-52). Previous characterisation has shown that the average mesopore diameters of hydrothermally dealuminated faujasites are in the order of 30–40 Å [12,13].

3.2. Catalytic test

3.2.1. Liquid-phase transformation

Composition of the reaction mixture after 1 h of reaction is presented in table 2. A blank experiment (no catalyst) has been included. As seen, the absence of catalyst led to a negligible conversion discarding any thermal effect. The main products observed over zeolites at conversion levels lower than 90% were camphene and limonene, ranging between 53 and 76% of the products with a constant ratio camphene/(camphene + limonene) of 0.6. At conversion levels higher than about 95% this ratio approaches the unity with a camphene yield above 30%. The latter observation indicates that limonene is more reactive than camphene and, therefore, suffers further transformation to other monoterpenes such as terpinenes and terpinolenes, according to the reaction pathway previously reported [7]. Over the amorphous silicoaluminate, SA, the conversion of α-pinene after 1 h of reaction was almost 100%, indicating that this catalyst contains the highest proportion of sites with the required acid strength. Again, the major isomerisation product was camphene (18%) confirming the high stability of this compound. Limonene was almost completely transformed. However, contrarily to zeolites non-monoterpenes heavy products (HRTP) were mainly formed over SA (43%) at the expense of limonene. The larger average pore size of SA (90% mesoporosity of 50–500 Å diameter) as compared with zeolites (at most 30% mesoporosity of 30–40 Å diameter) would facilitate both the formation of bulky transition states required for forming polymeric products and the dif-

Table 3
Product distribution (%) after 10 min on-stream for the gas-phase transformation of α-pinene.

Compound	Blank	HY	YDA(600)	YDA(800)	YDB(800)	SA
LRTP	0.3	3.0	7.3	2.5	1.0	8.3
α-pinene	96.0	58.8	17.0	62.0	84.2	23.2
Camphene	0.5	11.5	22.9	13.1	4.7	20.5
Limonene	0.1	4.4	6.4	6.9	2.3	5.5
Terpinenes	0.1	7.4	16.9	5.0	1.3	12.9
Terpinolenes	0.6	3.8	6.5	3.6	1.5	6.2
p-cymene	0.0	3.3	8.8	1.8	0.6	5.6
UP	0.2	5.4	8.7	3.3	1.0	11.1
HRTP	2.3	2.5	5.7	1.7	3.4	6.7
X_α (%)	4	41	83	38	16	77

fusion of the heavy products formed out of the catalyst pore system.

3.2.2. Gas-phase transformation

Under the continuous-flow condition used the space time, proportional to the contact time, was about 1.4 min which is much smaller than the reaction time of 60 min used for the liquid-phase transformation in the batch system. This shorter contact time is compensated by increasing the reaction temperature to 473 K instead of 393 K used for the liquid-phase mode. At 473 K, however, the thermal effect was more pronounced (4% conversion during the blank experiment). Product distribution measured at 10 min on-stream is presented in table 3. Main isomerisation products are, again, camphene and limonene. However, a significant increase in other monoterpenes (terpinenes, terpinolenes and p-cymene) in comparison with liquid-phase transformation can be observed. This increment in these monoterpenes seems to occur at the expense of both camphene and limonene. This observation can be explained in terms of the higher reaction temperature used in gas phase that increases the ulterior rate of camphene and limonene transformation. With the exception of the catalyst YDB(800) the selectivity towards HRTP for the zeolite-based catalysts was lower than 7%, as should be expected for restricted pore systems. The surprisingly high HRTP selectivity shown by the most dealuminated YDB(800) sample can be explained in terms of its high mesoporosity (30%) and low crystallinity (55%), allowing more space for the HRTP formation and diffusion out of the solid.

Catalyst deactivation can be empirically evaluated by comparing the conversion at 30 min on-stream to the one at 10 min on-stream. Thus, a deactivation index (DI) can be defined as the ratio of the conversion at 30 min on-stream to the conversion at 10 min on-stream. The higher the value of DI the lower the deactivation. Zeolite-based catalysts showed high deactivation with DI ranging from 0.21 for YDA(600) to 0.5 for YDB(800). Contrarily to what was observed during the liquid-phase test, SA showed the lowest deactivation with DI of 0.92. Moreover, a dramatic decrease of the HRTP yield (9% in gas phase versus 43% in liquid phase) was also observed for SA. A possible explanation to this performance can be attempted in terms of the reaction space time. In fact, the shorter contact time used in the gas-phase test minimises further transformation of terpinenes, terpinolenes and p-cymene, first formed mainly from limonene (and to a lesser extent from camphene) into heavier HRTP products.

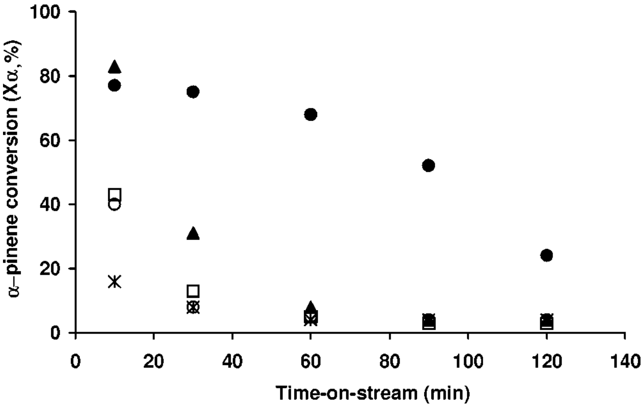

Figure 1. Deactivation curves during gas-phase transformation of α-pinene: (□) HY, (▲) YDA(600), (○) YDA(800), (∗) YDB(800), and (●) SA.

Deactivation curves during gas-phase transformation are presented in figure 1. As seen, amorphous silicoaluminate, SA, showed the highest stability of all. The higher reaction temperature used in gas phase promotes polymerisation and coke formation leading to a blockage of the zeolite micropore system. In contrast, the wider pore size distribution of SA minimises site deactivation by pore plugging.

3.2.3. Gas- versus liquid-phase catalytic performance

Selectivity values at isoconversion are given in table 4 for zeolite-based catalysts and for the amorphous silicoaluminate. Selectivity data in table 4 are not referred to any particular Y-zeolite sample, instead they represent average values taken at similar conversion levels from different Y-zeolites. In general, the selectivity to camphene + limonene was higher for the liquid-phase experiment. As the severity of the reaction increases (increasing conversion) limonene selectivity (S_L) seems to be more affected than that of camphene (S_C) with a simultaneous increment in the selectivity to other monoterpenes (S_OM) grouping terpinenes, terpinolenes and p-cymene. This is particularly true for the experiment in gas phase where the summation of $S_\mathrm{L} + S_\mathrm{OM}$ remains fairly constant. This observation strongly suggests that limonene is more easily

Table 4
Gas-phase (GP) versus liquid-phase (LP) selectivity as a function of conversion for the transformation of α-pinene over Y-zeolites and amorphous silicoaluminate.[a]

Catalyst type	X_α	S_C (%)		S_L (%)		S_OM (%)		S_HRTP (%)	
	(%)	LP	GP	LP	GP	LP	GP	LP	GP
Y-zeolite	30	31	35	23	18	8	29	6	8
Y-zeolite	45	41	28	29	11	14	35	3	6
Y-zeolite	84	49	28	27	7	16	39	1	7
Y-zeolite	98	32	–	5	–	43	–	5	–
SA	77	–	27	–	7	–	32	–	9
SA	98	18	–	0	–	10	–	43	–

[a] S_C, S_L, S_OM and S_HRTP stand by selectivity to camphene, limonene, other monoterpenes (terpinenes, terpinolenes and p-cymene) and high retention time products, respectively.

transformed than camphene. A reaction scheme for the transformation of limonene over silica gel shows that this compound can be isomerised, through a carbocation intermediate, to terpinenes and terpinolenes. The latter compounds can, in turn, be subsequently disproportionated into p-cymene [15]. Over amorphous silicoaluminate the production of undesired HRTP was very high in liquid phase at nearly total conversion. In such a case not limonene was observed and the yield to other monoterpenes was low. This further confirms the successive transformation of limonene into terpinenes and terpinolenes and of the latter into HRTP. In gas phase, due to the short space-time used, this ulterior transformation to HRTP was minimised.

The rate of α-pinene transformation, expressed as moles of α-pinene transformed per hour per gram of catalyst, can be used to compare the catalytic activity of the catalysts under study. This parameter was obtained from the following expressions:

$$(-r_\alpha) = \frac{N_{\alpha 0} X_\alpha}{t_\mathrm{r} W}$$

for the batch liquid-phase system, (5)

$$(-r_\alpha) = \frac{Q_\alpha \rho_\alpha X_\alpha}{W M_\alpha}$$

for the continuous-flow gas-phase system, (6)

where $N_{\alpha 0}$ represents the initial amount of α-pinene (0.0126 g mol) and t_r the reaction time (h). For the continuous-flow system, Q_α, ρ_α and M_α represent the volumetric flow of α-pinene fed (cm^3/h), density (g/cm^3) and the α-pinene molecular weight, respectively. X_α and W are the α-pinene conversion and the weight of catalyst, respectively. The calculated values of $(-r_\alpha)$ for both the liquid-phase and the gas-phase tests are plotted as a function of the Al$^\mathrm{IV}$ density (Al$^\mathrm{IV}$ per 1000 Å^3 unit cell) in figure 2. As seen, a typical volcano-like curve was obtained as a result of the opposite effect of acid site density and strength. In fact, as dealumination proceeds, site density decreases, whereas acid strength increases. Reaction rates are higher for the gas-phase transformation suggesting that the reaction temperature exercises a greater influence on this parameter than contact time. A unique maximum for both systems was observed at about 2.64 Al$^\mathrm{IV}$ per 1000 Å^3 unit cell, which corresponds to about 39 Al$^\mathrm{IV}$ atoms per unit cell. At about this value occurs the maximum summation of sites N1 and N0 in faujasites [16], strongly suggesting the participation of both types of sites in this transformation.

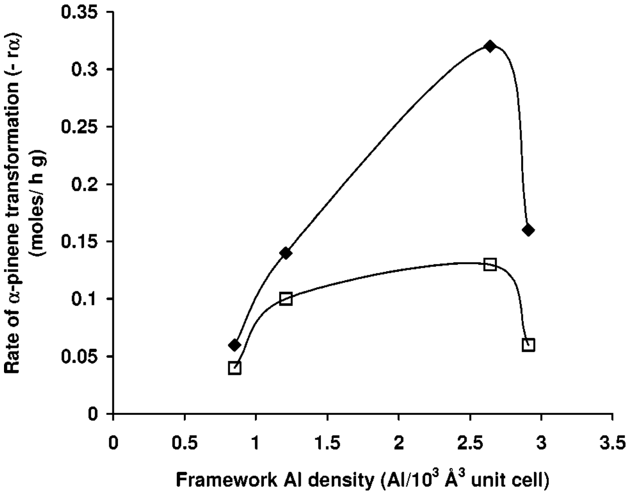

Figure 2. Average rate of α-pinene transformation as a function the Al$^\mathrm{IV}$ density for (☐) liquid-phase and (◆) gas-phase experiments.

The specific rate of α-pinene transformation, $(-r_\alpha)^*$, expressed as molecules of α-pinene transformed per hour per Al$^\mathrm{IV}$, can be used to evaluate the site strength of the catalysts under study. This parameter was calculated from $(-r_\alpha)$ using the following expression:

$$(-r_\alpha)^* = \frac{(-r_\alpha) M_\mathrm{Z}}{F_\mathrm{c} \mathrm{Al}^\mathrm{IV}}, \qquad (7)$$

where M_Z represents the formula weight of the anhydrous unit cell (g zeolite/mol unit cell) and F_c stands for the crystalline fraction (g zeolite/g catalyst). Results have been plotted against Al$^\mathrm{IV}$ density in figure 3. As expected, $(-r_\alpha)^*$ progressively increases with dealumination to reach a maximum at about 1.21 Al$^\mathrm{IV}$ per unit cell (about 17.5 Al$^\mathrm{IV}$ per unit cell), where sites N0 are close to its maximum value for faujasite. Again, the effect of temperature on site activity is clear.

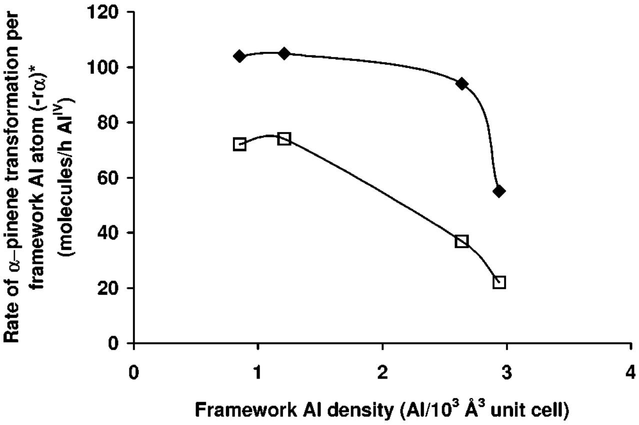

Figure 3. Specific transformation rate of α-pinene as a function of the Al^{IV} density for (□) liquid-phase and (◆) gas-phase experiments.

4. Conclusions

Zeolite-based catalysts were highly selective towards the desired product (camphene) in liquid phase, particularly at high conversion levels. In fact, at conversion of about 85% the selectivity to camphene was 49%. Polymeric heavy products, HRTP, were less favoured over zeolites as compared to amorphous SA, in liquid phase.

In gas phase the performance of amorphous silicoaluminate was very interesting. Thus, its selectivity towards camphene and other monoterpenes (terpinenes and terpinolenes) was comparable to that of zeolites at a similar conversion level, with a much higher stability (DI $=$ 0.92) as compared with the strong deactivation showed by zeolites ($0.2 < \mathrm{DI} \leqslant 0.5$). Similarly, HRTP production was drastically reduced in gas phase to about 7%, comparable to zeolites.

The average transformation rate (mol/h g) as a function of the Al^{IV} density passes through a maximum at 2.64 Al^{IV} atoms per 1000 Å^3 of zeolite crystal (about 39 Al^{IV} atoms per unit cell) for both liquid- and gas-phase transformations. At this Al^{IV} loading sites N0 $+$ N1 reach their maximum value. On the other hand, the specific transformation rate (mol/h Al^{IV}) progressively increases with decreasing the Al density to reach a constant value at 1.21 Al^{IV} per 1000 Å^3 corresponding to about 18 Al atoms per unit cell where the prevailing chemical environment is Si(0Al) (sites N0).

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