Article

# Flash Vacuum Pyrolysis over Solid Catalysts. 2. Pyrazoles over Hydrotalcites

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Flash vacuum pyrolysis (fvp) reactions of NH-pyrazole (1) and 3,5-diphenylpyrazole (2) were investigated in the presence of anionic clays having hydrotalcite structure (HT). Solid catalysts with Mg:Al ratio equal to 2:1 containing carbonate (HT-1), nitrate (HT-2), and silicate (HT-3) as interlayer anions were employed. Between 400 and 600 °C, compound 1 remained almost unchanged and only unidentified volatile products were detected in small amounts. In contrast, 2 afforded benzonitrile (3) and phenylacetonitrile (4) by a ring fragmentation reaction at 450 °C. At a higher temperature (660 °C), the same products obtained in homogeneous fvp reactions, i.e., 2-phenylindene (5) and 3-phenylindene (6), were obtained showing no catalysis by HT under these conditions. Results showed that the yield is strongly dependent on the nature of the interlayer anion in the hydrotalcite structure. In comparison with reactions of 2 over zeolites, HTs exhibit selectivity for ring fragmentation reaction.

#### Introduction

Flash vacuum pyrolysis (fvp) reactions of pyrazoles have proved to be an interesting tool to study the reaction mechanisms of their own thermal reactions. These heterocycles lead to different reactions depending on N1 substitution. Thus, in the case of NH-pyrazoles, the main reaction is nitrogen extrusion, affording a vinylcarbene intermediate<sup>1,2</sup> that is formed in a stepwise process where the elimination of nitrogen is the rate-determining step (Scheme 1).<sup>1</sup>

The team's previous studies showed that substituents in the vinylcarbene induced different reactions. Therefore, it is possible to find hydrogen or alkyl migration, insertion into aryl C–H bonds, addition to a carbonyl bond,<sup>2</sup> and others. These studies provides interesting results concerning vinylcarbene's reactivity, and in some cases, they appeared to be an alternative synthetic methodology for some interesting compounds but, due to their large activation energies (182–298 Kj/mol), it is necessary to use high temperatures (580–800 °C).<sup>2</sup>

Since it may be a problem in organic synthesis to use these reactions, to smooth reaction conditions a heterogeneous system has recently been developed using zeo-

#### **SCHEME 1**



lites as solid catalysts.<sup>3</sup> At that time, fvp reactions of **1**, 2, and 3,5-dimethylpyrazole were studied. In the case of 1, as in the homogeneous system, the same reaction was found, which is nitrogen extrusion. On the other hand, 2 afforded ring fragmentation to nitriles and isomerization, while 3,5-dimethylpyrazole afforded ring fragmentation as well as nitrogen extrusion, all of these reactions at lower temperatures than in the homogeneous system, thus showing an effective catalysis. These results showed that the nitrogen extrusion reaction is catalyzed by zeolites, provided the transition state is formed inside the zeolites' cavity. It is interesting to note that these nitriles, arising from fragmentation reactions, have been obtained in thermal reactions of other five-membered rings but never in fvp of NH-pyrazoles.<sup>4</sup> The same isomerization reaction of 2 had already been described

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 <sup>(1) (</sup>a) Pérez, J. D.; Yranzo, G. I.; Phagouapé, L. M. Bull. Soc. Chim. Fr. 1987, 129. (b) Pérez, J. D.; Yranzo, G. I.; Ferraris, M. A.; Claramunt, R. M.; López, C.; Elguero, J. Tetrahedron 1988, 44, (20), 6429. (c) Pérez, J. D.; Yranzo, G. I. J. Anal. Appl. Pyrol. 1989, 16, 165. (d) Ferraris, M. A.; Yranzo, G. I.; Pérez, J. D.; Cabildo, P.; Sanz, D.; Claramunt, R. M.; Elguero, J. Anales Quim.-Int. Ed. 1996, 92, 3. (e) Pérez, J. D.; Yranzo, G. I. Bull. Soc. Chim. Fr. 1986, 473-476.

<sup>(2) (</sup>a) Moyano, E. L.; Yranzo, G. I.; Elguero, J. J. Org. Chem. **1998**, 63, 8188 and references therein. (b) Yranzo, G. I.; Moyano, E. L.; Rozas, I.; Dardonville, C.; Elguero, J. J. Chem. Soc., Perkin Trans. 2 **1999**, 211.

<sup>(3)</sup> Moyano, E.; Yranzo, G. J. Org. Chem. 2001, 66, 2943–2947.
(4) (a) Lifshitz, A.; Wohlfeiler, D. J. Phys. Chem. 1992, 96, 11, 4505.
(b) Mitchell, W. R.; Paton, R. M. J. Chem. Res. (S) 1984, 58.

for *N*-aryl-substituted pyrazoles,<sup>1</sup> but this case with zeolites was the first one described in fvp of an unsubstituted pyrazole. On the other hand, it was observed that pyrazole isomerization was present only in protonic zeolites with strong acid sites (Brönsted sites), while extrusion and fragmentation reactions were catalyzed on materials having Brönsted and Lewis sites or Lewis sites only.<sup>3</sup>

As an extension of these studies on fvp reactions over solid catalysts, anionic clays such as hydrotalcites were chosen as catalytic materials. It is known that hydrotalcites or calcined hydrotalcites have been used extensively as catalysts in many organic processes due to their basic properties and mainly for their ability to exchange anions.<sup>5</sup> Thus, it is possible to find these materials as efficient basic catalysts for the epoxidation of various olefins<sup>6</sup> and also for aldol condensation reactions.<sup>7</sup>

It is important to point that the name anionic clay is applied to natural or synthetic layered hydroxides containing anionic species in the interlayer space. The general formula describing the chemical composition of anionic clays is  $[M^{II}_{1-X}M^{III}x(OH)_2](A^{n-})_{x/n} \cdot mH_2O$ . When  $M^{II}$  is Mg,  $M^{III}$  is Al, and the interlaminar anion (A) is carbonate, the compound is usually known as hydrotalcite  $[Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O]$ . The structure consists of brucite layers, which are positively charged because of partial substitution by trivalent cations, with the interlayer space filled with anions (to balance the positive charge of the layers) and water molecules.

As can be seen, these solids show an ion-exchange properties  $^{5,8}$  and, depending on the nature of the cations and the calcination temperature, the recovery of the structure is possible.<sup>9</sup>

Anionic clays may be synthesized by different methods such as precipitation, hydrothermal synthesis, anion exchange, and others. However, they are usually prepared by coprecipitacion of metal hydroxides of divalent and trivalent cations in a basic aqueous solution in the presence of the anions that will be located in the interlayer. Physicochemical and structural properties of the resulting solids depend on the precipitation pH, temperature, aging, washing, drying, and crystallization conditions. When the clays are calcined at moderate temperatures, new materials are formed, and a mixture of the oxides of the starting cations is developed. These new materials are used as catalysts in different relevant processes.<sup>5,10</sup> Previous studies on these materials showed that these systems are usually more effective as catalyst after calcinations where the layered structure is lost starting from 350 °C and large specific areas are developed, the largest being with silicate.<sup>11</sup>

**TABLE 1.** Flash Vacuum Pyrolysis Reactions of 1

			5		
<i>T</i> (°C)	catalyst	% <b>1</b>	<i>T</i> (°C)	catalyst	% <b>1</b>
400	none	100 <sup>a</sup>	500	HT-2	90
	HT-1	95		HT-3	88
	HT-2	88	600	none	100 <sup>a</sup>
	HT-3	70		HT-1	89
500	none	100 <sup>a</sup>		HT-2	87
	HT-1	91		HT-3	83
<sup>a</sup> Fron	n ref 2a.				

The aim of this study is to research the effect of the basic sites as well as the hydrotalcite structure on thermal reactions of NH-pyrazoles and product selectivity in the process. This study may be a significant contribution in the development of heterogeneous fvp systems, since the existing literature does not provide any comparative studies between zeolites and hydrotalcites with the same substrates.

Therefore, some hydrotalcites having different structures and interlayer spaces were chosen with carbonate (HT-1), nitrate (HT-2), and silicate (HT-3). The substrates employed are NH-pyrazole (1) and 3,5-diphenylpyrazole (2), which afford nitrogen extrusion in the homogeneous systems.<sup>1e,2a</sup>

#### **Results and Discussion**

**Flash Vacuum Pyrolysis of NH-Pyrazole (1).** The fvp experiments were carried out between 400 and 600 °C using hydrotalcites HT-1, HT-2, and HT-3 as solid catalysts. The results here obtained, as well as the ones previously reported in the homogeneous system, <sup>1,2</sup> are shown in Table 1. It can be seen that **1** has very low reactivity under the experimental conditions, and high amounts of unreacted material were recovered. Some unidentified volatile products were formed, probably arising from ring fragmentation or coke reactions, and also starting material was adsorbed on the catalyst surface. No propyne, was detected—the expected product from a nitrogen extrusion reaction. This is an important difference when comparing these reactions with the ones over zeolites.<sup>3</sup>

In reactions where HT-2 was used, loss of the interlayer anion as gaseous  $NO_2$  was observed. This elimination is accompanied by an increase of the surface area, which results in the collapse of the layered structure and, after the thermolysis, the material became useless for other experiments. It is worthwhile to mention here that this loss was also detected when HT-2 was submitted to experimental conditions without substrates, showing the instability of this material.

It was also seen that the decomposition of **1** was greater when HT-3 was used. In this case, a small amount (20%) of substrate was adsorbed by the catalyst. This adsorption was low at 500 °C, due probably to a partial saturation of the material. Since the catalysts underwent continuous deactivation during the reaction, it was impossible to recover the total amount of the catalytic material employed as a result of a carbonaceous deposit (coke), which restricted their lifetime.

<sup>(5)</sup> Roy, A.; Forano, C.; El Malki, K.; Besse, J. *Expanded Clays and Other Microporous Solids*, Occelli, M. L., and Robson, V. N. R., Eds.; New York, 1992; p 108.

<sup>(6)</sup> Ueno, S.; Yamaguchi, K.; Yoshida, K.; Ebitani, K.; Kaneda, K. Chem. Commun. **1998**, *3*, 295.

<sup>(7)</sup> Rao, K. K.; Gravelle, M.; Valente, J. S.; Figueras, F. *J. Catal.* **1998**, *173*, 1, 115.

<sup>(8) (</sup>a) Bennani, M. N.; Tichit, D.; Figueras, F.; Abouarnadasse, S. *J. Chim. Phys. Phys. Chim. Biol.* **1999**, *96*, 1498. (b) Cavani, F.; Trifiro, F.; Vaccari, A. *Catal. Today* **1991**, *11*, 1.

<sup>(9) (</sup>a) Chibwe, K.; Jones, W. *Chem. Mater.* **1989**, *1*, 489. (b) Del Arco, M.; Malet, P.; Trujillano, R.; Rives, V. *J. Mater. Chem.* **1999**, *9*, 1499.

<sup>(10) (</sup>a) Uzunova, E.; Klissurski, D.; Kassabov, J. J. Mater. Chem. **1994**, 4, 153. (b) Uzunova, E.; Klissurski, D.; Mitov, I.; Stefanov, P. Chem. Mater. **1993**, 5, 576.

<sup>(11)</sup> Del Arco, M.; Gutierrez, S.; Martin, C.; Rives, V. Phys. Chem. Chem. Phys. **2001**, *3* (1), 119.





 TABLE 2.
 Flash Vacuum Pyrolysis Reactions of 2

T(°C)	catalyst	% 2	<i>T</i> (°C)	catalyst	% 2
450	none	100 <sup>a</sup>	560	HT-2	0
	HT-1	73		HT-3	39
	HT-2	5	660	none	$47^{a}$
	HT-3	45		HT-1	34
560	none	100 <sup>a</sup>		HT-2	0
	HT-1	60		HT-3	20
<sup>a</sup> From	ı ref 2a.				

**Flash Vacuum Pyrolysis of 3,5-Diphenylpyrazole** (2). This pyrazole was subjected to fvp between 450 and 660 °C using HT-1, HT-2, and HT-3 as catalytic materials. In this case, two different reactions were present: (a) ring fragmentation, starting from 450 °C, and (b) nitrogen extrusion at the same temperatures of reactions in the homogeneous systems (660 °C). The results of these experiments, as well as the ones reported earlier for the homogeneous system,<sup>2</sup> are shown in Scheme 2 and Table 2.

When fvp reactions of **2** were studied over zeolites, it was found that **2** afforded two different reactions, i.e. fragmentation to benzonitrile (**3**) and phenylacetonitrile (**4**) and isomerization to 2,5-diphenylpyrazole,<sup>3</sup> however, in reactions over hydrotalcites, the only catalyzed reaction was fragmentation, affording nitriles **3** and **4**. In both cases (zeolites and hydrotalcites), **2** afforded phenylindenes **7** and **8** at the same temperatures of the homogeneous reactions, showing that at low temperatures the catalysis is not effective. Fragmentation reactions correspond to N–N and C3–C4 bond fissions that were previously reported in shock tube reactions of isoxazole<sup>12</sup> SCHEME 3



and fvp of 3,6-diphenyl-1,2,4,5-dioxodiazine.<sup>13</sup> It is proposed that this fragmentation reaction go through a mechanism that involves a three-membered ring intermediate, as shown in Scheme 3.

In this case both nitriles may be formed by H and Ph migrations. It is interesting to remark that this reaction is catalyzed over acid (zeolites) as well as over basic solids (hydrotalcites). While in the former fragmentation is a competitive reaction, in the latter this is the exclusive reaction, thus making this catalytic process more selective; in other words, fragmentations seem to need only active sites while isomerizations need Brönsted acid ones.

Some polycyclic aromatic hydrocarbons such as phenanthrene (5) and anthracene (6) were also formed at high temperatures from benzonitrile and phenylacetonitrile. These transformations were also observed in fvp on zeolites and proceeded through radical intermediates, since dibenzyl was identified as reaction product when toluene was used as carrier gas. The use of toluene as carrier gas is a normal test reaction to detect radicals.

On the other hand, in reactions at higher temperatures, phenylindenes 7 and 8 were also found in the reaction products. These compounds arise from the expected nitrogen extrusion through the intermediacy of vinylcarbene 2a (Scheme 2). However, it should be emphasized that this reaction is not catalyzed by hydrotalcites at low temperatures.

A very significant conversion of substrate was observed over HT-2. This behavior could be related to a high surface area developed in the catalyst in the fvp system. The values of specific surface areas are enhanced about 4 times when the material is calcined at 600 °C<sup>11</sup> (at normal pressures), this enlargement may be increased under fvp conditions, even when the material was already calcined. Thus, the formation of mixed oxides with high catalytic properties can be accelerated and the fragmentation process catalyzed.

Besides, HT-1 and HT-3 showed lower activity than HT-2. Under fvp conditions these HTs are more stable and it may be that the increase of the surface area by calcination is slower than for HT-2 under the experimental conditions. In the case of HT-3, a portion of substrate was adsorbed by the catalyst, causing an earlier poisoning of the material. A possible explanation can be the higher interlayer space (11.4 Å) in silicate hydrotalcite,

<sup>(12)</sup> Aldous, G. L.; Bowie, J. H.; Thompson, M. J. J. Chem. Soc., Perkin Trans I 1976, 1.

<sup>(13)</sup> Mitchell, W. R.; Paton, R. M. J. Chem. Res. (S) 1984, 58.

which favors the trapping of molecules inside the hydrotalcite structure when the interlaminar anion is eliminated, thus inactivating the catalyst.

## Conclusions

NH-pyrazole did not react when HT-1, HT-2, and HT-3 were used as catalysts. Under the same conditions, **2** afforded nitriles by a fragmentation reaction at 450 °C. In both cases (pyrazoles **1** or **2**) no nitrogen extrusion reaction was observed, unlike thermolysis in the presence of zeolites. This fact may be an indication that the nitrogen extrusion reaction needs acid catalysis.

The results here reported indicate that hydrotalcites show low activity but selectivity in fvp reactions of NHpyrazoles, in comparison with zeolites, provided that the pyrazole is ring-substituted. Among the different materials used in this study, HT-2 containing nitrate as interlayer anion showed better performance toward fragmentation reaction.

### **Experimental Section**

General. Flash vacuum pyrolysis was carried out in a Vycor glass reactor using a GAYNOR PRDH temperature controller and a Thermolyne 21100 tube furnace. Oxygen-free dry nitrogen or a mixture of nitrogen/toluene was used as carrier gas. Samples to be pyrolyzed were 50-80 mg. Contact times were around 10<sup>-2</sup> s and pressures of 0.02 to 0.01 Torr were used. In a typical run, 0.75-1.50 g of fractured catalyst was placed along the reactor (30 cm length, 1 cm diameter) using ceramic wool fiber as inert support. Products were trapped at the liquid air temperature, extracted with solvent, and submitted to different analyses or separation techniques. Gas chromatography/mass spectrometry (GC/MS) analyses were performed with an SE-30 column, using helium as eluent at a flow rate of 1 mL/min and a heating rate of 40 °C for 5 min and 400 to 280 °C for 40 min. Chemical shifts are reported in parts per million (ppm) downfield from TMS. Column and thinlayer chromatography were performed on silica gel. Conversion values in reactions of 1 and 3 were determined by quantifying substrate by <sup>1</sup>H NMR using nitromethane as internal standard.

**Catalysts.** Catalyst HT-1 was prepared following the methodology described by Reichle,<sup>14</sup> and the sample having nitrate (HT-2) was obtained by coprecipitation from Mg and

Al nitrates in NaOH-NaNO3 aqueous solution by the method previously described.<sup>15</sup> The silicate catalyst is obtained by anionic exchange of the nitrate precursor (HT-2) using the SiO<sub>2-</sub>NaOH-H<sub>2</sub>O system<sup>15</sup> In all cases, the ratio of cations Mg:Al was 2:1. Powder X-ray diffraction diagrams were recorded for the three samples, the signals corresponded to a hydrotalcite structure. Diffraction values were 7.4, 8.8, and 11.4 Å, very close to those reported for hydrotalcite-like materials containing carbonate, nitrate, and silicate, respectively.<sup>15</sup> The specific surface areas, calculated following the BET method,<sup>11</sup> for the uncalcined and calcined HTs at 600 °C were the following (m  $^2$  g  $^{-1}$ ): 86 and 120 (HT-1), 25 and 85 (HT-2), 72 and 75 (HT-3). The catalysts were pressed, fractured, sieved to the desired particle size fraction of 12-20 mesh, and stored under ambient atmosphere. The materials were calcined at 300 °C under nitrogen flow for 3 h when they were prepared.

**Flash Vacuum Pyrolysis of 1.** Pyrazole 1 was commercially available from SIGMA and purified by sublimation in vacuo. The amount of unreacted starting material was measured by <sup>1</sup>H NMR using nitromethane as internal standard. After the fvp reactions, both starting material and a mixture of unknown volatile products were obtained. A portion of substrate was adsorbed on the catalyst's surface. This was detected by checking the mass of catalyst before and after each reaction.

**Flash Vacuum Pyrolysis of 2.** This compound was synthesized from dibenzoylmethane as described in the literature.<sup>16</sup>After the reaction was finished, the products were separated by column chromatography using benzene:ethyl acetate (95:5). Compounds **3, 5,** and **6** were unidentified by comparison with authentic samples. Nitrile **4** was identified by its NMR spectrum, and results of CG/MS analysis agreed with previously reported ones.<sup>17</sup>

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<sup>(14)</sup> Reichle, W. T. J. Catal. 1980, 63, 295.

<sup>(15)</sup> Del Arco, M.; Gutierrez, S.; Martin, C.; Rives, V.; Rocha, J. J. Solid State Chem. **2000**, 151, 272.

<sup>(16)</sup> Elguero, J.; Jacquier, R. Bull. Soc. Chim. Fr. 1996, 90.

<sup>(17)</sup> Organic Syntheses; Wiley: New York, 1990; Collect. Vol. VII, p 27.