

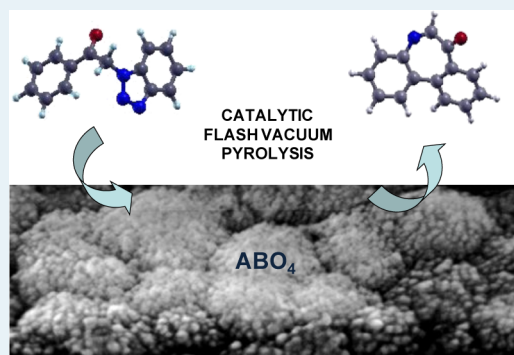
Mixed Oxides as Highly Selective Catalysts for the Flash Pyrolysis of Phenacyl Benzotriazole: One-Pot Synthesis of Dibenzazepin-7-one

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Supporting Information

ABSTRACT: The one-pot synthesis of dibenzo[*b,d*]azepin-7-one (**3**) was selectively achieved from 1-phenacyl-1,2,3-benzotriazole (**1**) using the catalytic flash vacuum pyrolysis (cfvp) methodology. Catalysts with the scheelite structure ABO_4 ($A = Ca^{2+}, Sr^{2+}, Ba^{2+}$ and $B = Mo^{6+}, W^{6+}$) and fergusonite $BiVO_4$ were explored in this new catalytic reaction. These oxides promoted high conversion of starting material at lower temperatures than those observed for noncatalytic reactions. The chemical nature of A and B cations in the scheelite structure showed a strong influence on the formation toward the desired azepinone. In addition, the catalyst's morphology had a significant influence on the course of the cfvp reaction.



KEYWORDS: catalytic pyrolysis, catalysis, mixed oxides, dibenzazepinone, phenacyl benzotriazole

1. INTRODUCTION

The chemistry of heterocycles has been widely explored because of the known interest in organic, inorganic, and medicinal chemistry. In this context, nitrogen-containing heterocycles have received much attention essentially as a result of a detailed history as significant medicinal pharmacophores.¹ In particular, the dibenzazepinone nucleus exhibits a wide range of biological activities. Thus, for example, some dibenzo[*b,d*]azepin-6-one derivatives have displayed a potent inhibition of γ -secretase, which appears as an important target for drug discovery in the treatment of Alzheimer's disease.² Even though dibenzo[*b,d*]azepin-7-one compounds have shown interesting pharmacological properties, conventional organic syntheses have not been adequately developed, and the known protocols involve many steps and, hence, low yields.^{3–6}

Taking into account these difficulties in obtaining this fused ring by conventional synthesis, we applied flash vacuum pyrolysis (fvp) methodology to afford the dibenzazepinone ring from a simple benzotriazole precursor. This gas phase synthesis consists of a nitrogen extrusion reaction of the starting benzotriazole, followed by rearrangement of the carbene intermediate to get the desired azepinone.^{7,8} In the fvp procedure, the substrate molecules are subjected to high temperatures (200–600 °C) and low pressures ($\sim 10^{-3}$ Torr) over a short period of time ($\sim 10^{-2}$ s) to promote their reaction in a pyrolysis tube. In addition, solid and thermostable catalysts can be used in the pyrolysis reactor; the methodology is called catalytic flash vacuum pyrolysis (cfvp). This technique is an extension of the conventional homogeneous fvp and keeps important features and advantages: the possibility to isolate kinetic as well as unstable products; absence of solvents and

oxygen; and the promotion of intramolecular reactions, which do not take place under other conventional thermal conditions. Cfvp reactions represent a good technique to study catalytic gas–solid interaction in dynamic conditions. Some experiments have been developed using alumina, amorphous silicates, and zeolites.⁹

In our group, we have studied the cfvp reactions of many nitrogen heterocycles using acid and basic catalysts (zeolites, hydrotalcites, and mesoporous materials).¹⁰ In general, the application of cfvp has decreased the reaction temperature with respect to the noncatalyzed homogeneous process.⁸ Moreover, in the zeolite and mesoporous-catalyzed experiments, the presence of Lewis acid sites were extremely important in the selectivity of the thermal process.^{9,10} With the aim to develop new catalytic gas phase pyrolysis, we decided to study the behavior of different mixed oxides in these heterogeneous systems. Thus, catalysts containing scheelite-type compounds ABO_4 ($A = Ca^{2+}, Sr^{2+},$ or Ba^{2+} and $B = Mo^{6+}$ or W^{6+}) and the fergusonite-type $BiVO_4$ were investigated.

Scheelites possess interesting physical properties that make them useful in several technological applications.^{11–13} These materials can be synthesized by several methods, with the possibility to incorporate a large number of different A or B cations.¹⁴ The flexibility in their preparation as well as the accessible precursors makes this family of oxides a model system for different catalytic reactions. Some scheelites have been reported to be efficient in the catalytic oxidation of

Received: December 20, 2012

Revised: March 8, 2013

Published: April 3, 2013

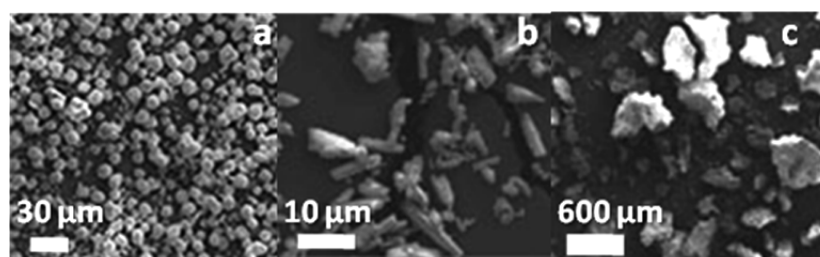


Figure 1. SEM images of SrMoO₄ synthesized by different methods: (a) dp, (b) cm, (c) sg.

hydrocarbons;¹² however, the performance of these materials in more complex catalytic processes have not been explored.

The crystallographic phase of these oxides shows that the A cations are coordinated by eight O²⁻, forming a distorted cube, and the B cations are coordinated by four O²⁻, giving a slightly asymmetric tetrahedron. If the A cation has a nonbonding electron, such as Bi³⁺, the structure is distorted to monoclinic fergusonite phase (SG = I 2₁/b, #15). Typical oxides that present a transition from scheelite to fergusonite structures are Pb(Mo,W)O₄ and BiVO₄.^{15,16} The latter has been investigated because of its photocatalytic properties,^{17,18} solar-driven hydrogen production,¹⁹ and catalytic use in ammoxidation of alkanes.²⁰ BiVO₄ can be synthesized by different preparation routes.^{21–24} In this work, we used ultrasound and microwave irradiation as two alternative approaches to obtain the desired monoclinic phase of this oxide in short reaction times.

We report herein the application of different mixed oxides with scheelite and fergusonite type structures in the catalyzed gas phase pyrolysis of 1-phenacyl-1,2,3-benzotriazole (1) toward the formation of 7H-dibenzo[*b,d*]azepin-7-one (3).

2. EXPERIMENTAL SECTION

2.1. Preparation of Catalysts. Scheelite ABO₄ Catalysts. Synthesis of ABO₄ oxides by a dissolution–precipitation (dp) method: Materials were prepared by dissolution of (NH₄)₆Mo₇O₂₄·4H₂O or (NH₄)₂WO₄ in water at room temperature. The pH of these solutions was increased to 10 by addition of NH₃ solution, of A(NO₃)₂ (A = Ca²⁺, Sr²⁺, or Ba²⁺) was added dropwise. The white precipitate was filtered and dried at 100 °C. Some samples were also heat treated at 600 °C for 12 h for comparison with the other preparation methods.

Synthesis of ABO₄ supported on inert ceramic fiber (method dp–fc): Oxides were prepared following the dp method. The ceramic fiber was added in the solution before the precipitation process. Thus, the oxide was uniformly deposited on the ceramic fiber. After the deposition, the material was dried at 200 °C.

Synthesis of SrMoO₄ by a ceramic (cm) method: This oxide was prepared from SrCO₃ and MoO₃ solids thoroughly mixed with acetone in an agate mortar. Then this mixture was heated at 600 °C under air for 12 h.

Synthesis of SrMoO₄ by a sol gel (sg) method: This oxide was prepared by dissolution of (NH₄)₆Mo₇O₂₄·4H₂O and Sr(NO₃)₂ in a saturated solution of citric acid. Then the water was evaporated at 80 °C until gel formation. After grinding, this amorphous precursor was calcined at 600 °C for 12 h in flowing air.

All catalytic materials were characterized by powder X-ray diffraction (PXRD) carried out with a Panalytical X'Pert Pro Diffractometer (40 mV, 40 mA), Cu K α (λ = 1.5418 Å).

The surface area was determined by a six-point nitrogen adsorption isotherm according to the Brunauer–Emmett–Teller (BET) method. Micrometrics Series 680, Mod. Accusorb 2100E-210-00001-01. In these experiments, the samples were dried and degassed at 110 °C.

2.2. Fergusonite BiVO₄ Catalyst. *a). Ultrasound Synthetic Method.* The experiment was performed using an Ultrasonic Cleaner Testlab (80 W, 40 kHz). Stoichiometric amounts of Bi(NO₃)₃·5(H₂O) and NH₄VO₃ were dissolved in 30 mL of 1 M HNO₃. Then an excess of urea was added, and the mixture was subjected to ultrasound irradiation at 60 °C for 4 h. The yellow-orange precipitate was filtered, washed, and dried at 80 °C for 12 h. The PXRD–Rietveld analysis indicated the presence of tetragonal zircon structure (space group *I4/m*) and a fergusonite monoclinic structure (space group *I2₁/b*) in a 50/50 relationship. The pure desired monoclinic fergusonite crystallographic phase was achieved after heat treatment at 450 °C for 10 h.

b). Microwave Synthetic Method. Stoichiometric amounts of Bi(NO₃)₃·5(H₂O) and NH₄VO₃ were dissolved in 30 mL of 1 M HNO₃, then an excess of urea was added. The mixture was irradiated at 100 °C for 4 min in a 50 mL reactor using an open vessel CEM-Discovery monomode microwave apparatus working at 100 W as power supply. The yellow precipitate was separated, washed, and dried at 80 °C for 12 h. The PXRD–Rietveld analysis indicated a high purity of monoclinic fergusonite phase, over 97%. The pure 100% monoclinic phase was achieved after a thermal treatment at 250 °C for 12 h.

2.3. Fvp and cfvp Experiments. The apparatus for fvp experiments consists of three main parts: (1) the injection region; (2) the pyrolysis region; and (3) trapped the condensation region, where products are condensates in a glass U-tube immersed in cryogenic liquids. The system is evacuated to 1×10^{-3} mmHg by a high-capacity vacuum pump. A flow of carrier gas (dry N₂) is regulated as 1 mL per 10 s. Under these experimental conditions, substrate molecules spend about 1×10^{-2} s in the hot region. Sample amounts were 18–20 mg with catalyst/substrate ratios equal to 25 (experimental approach I) and 1 (experimental approach II), respectively.

In these experiments, the mass balance percentage is calculated as the ratio between the mass of inputs and the mass of outputs multiplied by 100. The mass of outputs is the total mass trapped in the condensation zone of the system.

Catalysts were placed in the middle region of the reactor, perpendicular to the trajectory of the carrier gas, using ceramic fiber as an inert support. All catalysts were reused approximately six times. Products were analyzed by GC/MS and ¹H and ¹³C NMR spectroscopy.

3. RESULTS AND DISCUSSION

3.1. Synthesis of ABO_4 Scheelite Oxides ($A = Ca^{2+}$, Sr^{2+} , and Ba^{2+} ; $B = Mo^{6+}$ and W^{6+}) and Fergusonite $BiVO_4$. $SrMoO_4$ was the initial oxide evaluated in the cfvp study of phenacyl benzotriazole **1**. To compare the effect of the morphology of the particles in the catalyst performance, this scheelite was synthesized by four different methods: (a) dp, (b) dp–fc, (c) cm, and (d) sg. PXRD analysis indicated that all catalysts were pure and crystallized with scheelite-type tetragonal structure (space group $I4_1/a$, #88). PXRD showed intense and well-defined peaks, suggesting a good degree of crystallization or long-range structural ordering. The experimental lattice parameters and atomic positions were refined using the Rietveld method²⁵ with the FULLPROF program. SEM micrographs were of fundamental importance to study the morphology and microstructures of scheelite crystals, depending on the synthetic methods (Figure 1). Thus, the application of the dp method produces quasispherical particles with 10 μm diameter composed of a large number of nanocrystallites. In all cases, our findings by SEM were coincident with the average size of crystallite obtained by the Scherer's equation (about 15 nm).²⁶ Samples synthesized by the dp method, but with a heat treatment at 600 °C for 12 h, showed the same particle size (see Supporting Information Figure S2), but the PXRD data showed an increase in the crystallite size to ~ 40 nm. On the other hand, the cm method led to stick-shaped crystals with a length of 10 μm composed of nanostructured crystallites. Using the sg method, the assemblies of particles were randomly organized with the formation of irregular and porous crystals with a large size (about 600 μm).

According to the results of cfvp reactions (see Table 1), the oxide $SrMoO_4$ synthesized by the dp method displayed the

Table 1. Fvp (homogeneous) and Cfvp Reactions of **1 over Scheelites ABO_4 ; Experimental Approach I**

catalyst ^a	method of synthesis	S_{BET} (m^2/g^{-1})	T (°C)	% 1 ^b	% 3 ^b	% 4 ^b
none			400	78	0	0
none			500	35	30	0
none			550	0	10	0
$SrMoO_4$	sg	3.3	400	55	20	4
$SrMoO_4$	cm	1.4	400	20	20	20
$SrMoO_4$	dp	2.6	400	0	20	4
$CaMoO_4$	dp	6.5	400	0	30	6
$BaMoO_4$ ^c	dp	1.1	400	0	0	0
$SrWO_4$	dp	2.3	400	0	5	5
$CaWO_4$	dp	8.7	400	0	20	20
$BaWO_4$ ^c	dp	0.5	400	0	0	0

^aCatalyst/substrate ratio was 25. ^bValues determined by ¹H NMR. At temperatures below 400 °C, the conversion was not significant. ^cMain products formed by fragmentation of **1**: benzotriazole, benzonitrile, benzaldehyde, acetophenone, and aniline.

better catalytic performance. For this reason, the rest of the ABO_4 ($A = Ca^{2+}$, Sr^{2+} , Ba^{2+} ; $B = Mo^{6+}$, W^{6+}) catalysts were synthesized by the same synthetic method.

Regarding the synthesis of fergusonite $BiVO_4$, it was determined that direct coprecipitation followed by heat treatment at 450 °C allowed obtaining of the monoclinic fergusonite phase (I 2₁/b).²¹ By the ultrasound-assisted method, synthesis of the monoclinic $BiVO_4$ was also achieved at 60 °C over 2 h.²⁴ Using microwave irradiation, the same

vanadate was conveniently prepared during 3 h of irradiation at 180 °C.²³

In this work, fergusonite $BiVO_4$ was synthesized by two approaches: (a) ultrasound assisted synthesis ($BiVO_4$ -US) and (b) microwave-assisted synthesis ($BiVO_4$ -MW) (see the Experimental Section). The morphologies of particles prepared by these two methods are shown in Figure 2. Ultrasound

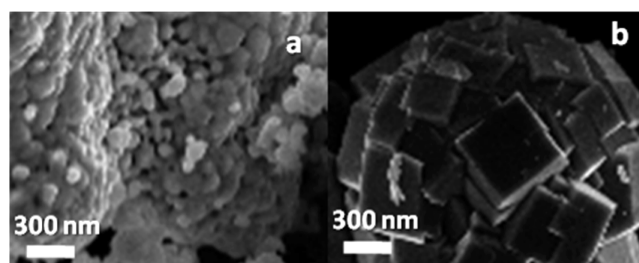


Figure 2. SEM images of $BiVO_4$: (a) synthesized by the ultrasound method and (b) synthesized by the microwave method.

precipitation produced irregular spherical particles between 50 and 100 nm in size, giving place to agglomerates of around 1 μm . Using microwave precipitation, irregular cubic particles of 500 nm in size were formed alongside spherical agglomerates of around 2 μm .

For cfvp experiments, the catalyst $BiVO_4$ was supported on inert ceramic fiber. An aqueous suspension of the fergusonite $BiVO_4$ was mixed with the ceramic fiber, and after the deposition of the oxide was completed, the impregnated fiber was dried at 200 °C. Figure 3 shows the SEM image of the $BiVO_4$ -supported fiber, where it can be seen that the distribution of the oxide particles is uniform.

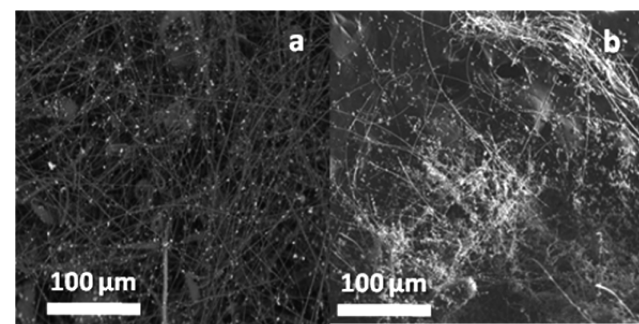


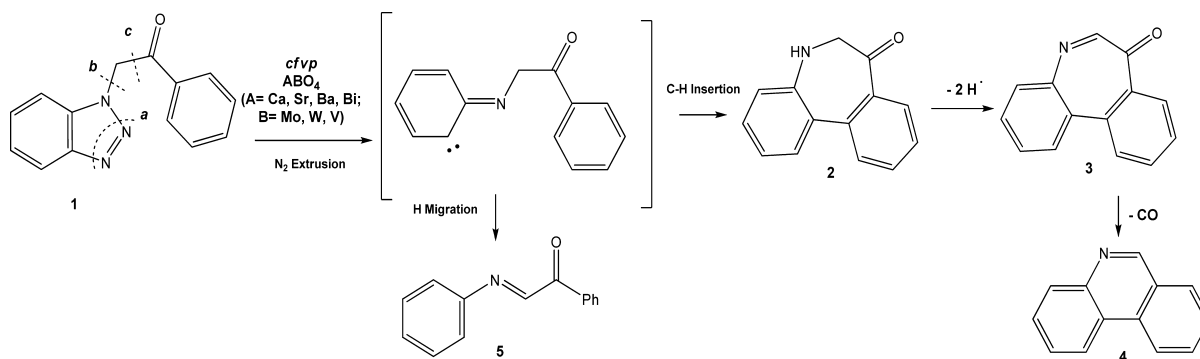
Figure 3. SEM images of oxides deposited on ceramic fiber: (a) $BiVO_4$ synthesized by MW and (b) $BaWO_4$ synthesized by dp method.

It should be noted that after the cfvp experiments, all catalysts were characterized by PXRD, and the results indicated that the crystal structure remained unchanged during the thermal reaction.

3.2. Catalytic Flash Vacuum Pyrolysis of **1.** In the development of the scheelite–heterogeneous catalytic pyrolysis, two experimental approaches (I and II) were evaluated. In approach I, the bulk solid catalyst was packed inside the middle section of the reactor tube, covering all the transversal area, and the inert support (ceramic fiber) was placed in the outer region of the catalyst section to avoid the emission of solid particles. In this case, the amount of catalyst was minimized to get an efficient covered cross section of the reactor.

In procedure II, the catalyst was supported on the ceramic fiber, which was then placed inside the middle region of the

Scheme 1. Formation of Products in the CfvP Reactions of 1



reactor tube. This arrangement enabled a significant decrease in the amount of catalysts exposed to the reaction, increasing their surface area. To confirm the deposition of the oxides on the ceramic fiber, SEM images and PXRD of these fiber-supported catalysts were performed (see Figure 3 for BiVO_4 and BaWO_4).

To verify that ceramic fiber could be used as an inert support, this fiber was used alone in the gas phase pyrolysis reactions of phenacyl benzotriazole **1**. Under these conditions, no catalysis was achieved and formation of products was comparable to the homogeneous system.

3.2.1. Catalytic Reactions Using a Packed Catalyst (Experimental Approach I). CfvP reactions of **1** in the presence of scheelites ABO_4 ($A = \text{Ca}^{2+}$, Sr^{2+} , or Ba^{2+} and $B = \text{Mo}^{6+}$ or W^{6+}) were carried out in the temperature range 270–450 °C (Scheme 1). The ratio between catalyst and substrate was 25. In general, high conversion of **1** (>80%) was achieved at 400 °C, exceptions being the reactions performed with SrMoO_4 synthesized by the cm and sg methods. These results as well as the obtained ones in noncatalytic fvp systems are depicted in Table 1. The analysis of the pyrolysate indicated the presence of products coming from nitrogen extrusion and other fragmentations of the starting phenacyl benzotriazole **1**. Thus, the formation of the desired 7H-dibenzo[*b,d*]azepin-7-one (**3**) can be rationalized by nitrogen elimination of **1** to give the iminocarbene intermediate, which rearranges to 5,6-dihydro-7H-dibenzo[*b,d*]azepin-7-one (**2**), followed by dehydrogenation (Scheme 1, fragmentation *a*). Although azepinone **2** was not isolated, this product was detected in the reaction mixture, providing evidence of the proposed mechanism. Dehydrogenation reactions have been obtained in this kind of pyrolysis system, and many of transformations involve radicals as intermediates.²⁷

Product **3** was also formed in homogeneous fvp reactions in which the greatest yield (30%) was obtained at 500 °C. In that case, total conversion of **1** was achieved at 550 °C, giving **3** and 1-phenyl-2-(phenylimino)ethanone (**5**) as the main products. This imine is proposed to be formed by the same iminocarbene precursor as **2** after rearrangement involving hydrogen migration. On the other hand, heterogeneous mesoporous-catalyzed fvp of **1** led to the synthesis of **3** in very good yields.¹⁰

Using SrMoO_4 synthesized by the dp method, total conversion of **1** was achieved at 400 °C. This catalytic system exhibited a reduction of 150 °C in the reaction temperature with respect to the noncatalyzed pyrolysis. The same results were obtained with catalysts that, after being precipitated, were heat-treated at 600 °C for 12 h, which is reasonable, since particle size and shape are similar to those not heat-treated (see Supporting Information Figure S2). In the same way, the

material prepared by the cm method exhibited an acceptable conversion of **1** (80%). In contrast, the oxide SrMoO_4 synthesized by the sg method displayed a low conversion of **1**. These results indicated that the surface morphology of the catalyst prepared by the dp method was more reactive than the others, even though the sample is heat treated at 600 °C. On the basis of the results, the regular and small size distribution of catalyst particles increased the conversion of **1**, although the selectivity of **3** has remained low.

Thus, the catalytic activity of SrMoO_4 was strongly dependent on the preparation method of the catalyst. This could be attributed to the influence of the preparation method on the formation of the active sites on the catalyst surface, promoting different gas–solid interactions, and also to differences in particle size, with the smaller particles having the highest conversion.

CfvP in the presence of CaMoO_4 and BaMoO_4 also displayed total conversion of **1** at 400 °C. The yield of the desired **3** was 30% for reactions carried out over CaMoO_4 , the best result in the catalytic pyrolysis using this experimental approach. In the BaMoO_4 -cfvp systems, other reactions instead of the expected N_2 extrusion of **1** were promoted.

Regarding the tungstate scheelite-catalyzed reactions, total conversion of **1** was also obtained at 400 °C, but the formation of azepinone **3** was detected only when CaWO_4 was used (Table 1).

A secondary and competitive reaction was the decarbonylation of **3** to give phenanthridine (**4**) in a typical aromatization process. CO elimination usually requires more than 600 °C in a typical gas phase thermolysis;²⁸ however, this elimination is commonly favored in cfvp systems.^{9,10} According to the results, decarbonylation was mainly promoted in the reactions using SrMoO_4 (prepared by the cm method) and CaWO_4 .

Other fragmentations involving rupture of C–N and C–C bonds in benzotriazole **1** (Scheme 1, fragmentations *b* and *c*) as well as in the azepinones **2** and **3** took place, and undesired products were obtained. This kind of reaction was favored in virtually all scheelite-catalyzed pyrolysis, decreasing the selectivity of the process to the formation of the expected **3**. Thus, using experimental approach I, the best yields of this azepinone were obtained in the calcium scheelites-catalyzed reactions. In addition, these catalytic materials displayed greater surface areas. This feature, together with the presence of the Ca^{2+} ion, were found important in the formation of **3** through this packed experimental setup.

Using this experimental arrangement, it seems that the total number of active sites of the catalysts is too high because the

mass balance was over 50–60%, and the high degree of degradation of starting benzotriazole to volatile compounds as well as the favored fragmentation processes could be attributed to the exposure of molecules to a high concentration of catalytic active sites of catalysts in a very short time.

3.2.2. Catalytic Reactions Using a Supported Catalyst (Experimental Approach II). To minimize the total number of active sites and, consequently, undesired fragmentations and to improve the formation of **3**, we have decreased the amount of catalyst for the experiments, keeping a good surface area to promote the substrate gas–solid catalyst interaction. Thus, we evaluated experimental approach II, in which catalysts prepared by the dp method were deposited on the ceramic fiber support. This arrangement led to a ratio of catalyst/substrate between 1 and 2. Results obtained in this new catalytic system are shown in Table 2.

Table 2. Cfvp Reactions of **1** over Scheelites ABO₄; Experimental Approach II

catalyst ^a	% 1 ^b	% 3 ^b
SrMoO ₄	0	20
CaMoO ₄	40	54
BaMoO ₄	0	15
BaMoO ₄ ^c	20	65
SrWO ₄	13	82
CaWO ₄	15	50
BaWO ₄ ^d	10	87

^aCatalyst/substrate ratio was between 1 and 2. Temperature: 400 °C.

^bValues determined by ¹H NMR. ^cReused without heat treatment.

^dTotal conversion of **1** was achieved at 450 °C, yielding **3** (45%).

It was noted that the catalytic activity of SrMoO₄ did not change, and yields of **3** remained low. The main products were formed by multiple and nonselective fragmentations of starting benzotriazole. For CaMoO₄- and BaMoO₄-catalyzed reactions, the formation of **3** was increased (up to 45% yield); however, in the case of CaMoO₄, the conversion of **1** was only 60%. These results probably indicated that catalytic activity of molybdates remained high in terms of transformation of **1**; however, the catalysis has not yet been specific toward the desired process. To prove this assumption, cfvp was performed with reused BaMoO₄ without any activation treatment. Thus, the conversion of substrate decreased to 80%, but surprisingly, the yield of **3** increased to 65%, minimizing the formation of competitive products. This finding would indicate that the poisoning of the catalyst surface with consequent reduction of activity makes the process more selective to nitrogen extrusion reaction to give azepinone **3**, reducing other feasible processes.

In the case of tungstate-catalyzed pyrolysis, a great improvement in the formation of **3** was obtained. Thus, using SrWO₄ and BaWO₄, quantitative yields of **3** were achieved (>80%). Even the conversion of starting benzotriazole was not complete; the selectivity toward the nitrogen extrusion reaction followed by the dehydrogenation was substantially improved. In all cases, decarbonylation of **3** was insignificant, and **4** was obtained in trace yields (~1%). Thus, lower amounts of catalysts exposed to the gas phase substrate minimized the multiple rupture of this compound, giving selectively the elimination of molecular nitrogen in a typical [5 → 3 + 2] fragmentation.²⁹

The catalytic behavior can be analyzed in light of some considerations about the nature of the A and B cations. In

tungstates-catalyzed reactions the empty d orbitals of the B⁶⁺ cation seem to be significant in the selectivity of the thermal reaction. In addition, the selectivity to the formation of azepinone **3** as a function of the A²⁺ cation followed the order Ca²⁺ < Sr²⁺ ~ Ba²⁺. These metal ions have empty s and p orbitals (ns⁰, np⁰). It has been calculated that these empty orbitals may accept the electron density from the electronegative nitrogen atoms of the phenacyl benzotriazole **1** in the gas phase interaction (Figure 4), with the energy of adsorption

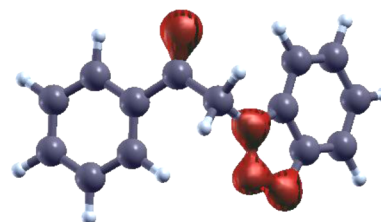


Figure 4. Distribution of the electronic density of phenacyl benzotriazole **1**. Red orbitals represent a negative electronic density.

being in the order Ca²⁺ < Sr²⁺ ~ Ba²⁺.³⁰ Thus, this indicates that the selectivity toward azepinone **3** is intimately related to the electron transfer from the substrate **1** to the A cation of the scheelite.

These catalytic performances were more pronounced for SrWO₄ and BaWO₄ since they favored the selective nitrogen extrusion reaction of **1** and further cyclization. In the case of cfvp experiments in the presence of fergusonite BaWO₄ supported on fiber, the catalytic behavior of the oxide was dependent on their morphology. Even acceptable yields of **3** were achieved using the vanadate prepared by the ultrasound technique; the more regular particles obtained by the microwave precipitation method showed a better catalytic profile, giving 84% yield of the desired azepinone at 400 °C (see Table 3). In both cases, the increment of the temperature

Table 3. Cfvp Reactions of **1** over BiVO₄; Experimental Approach II

catalyst ^a	T (°C)	% 1 ^b	% 3 ^b	% 4 ^b
BiVO ₄ ^c	400	35	63	2
BiVO ₄ ^c	450	20	40	0
BiVO ₄ ^d	400	15	84	1
BiVO ₄ ^d	450	0	52	1

^aThe catalyst/substrate ratio was between 1 and 2. ^bValues determined by ¹H NMR. ^cSynthesized by US method. ^dSynthesized by MW method.

decreased the selectivity toward **3**, favoring the other fragmentation process as it was described for scheelite-catalyzed systems.

The high activity displayed by this fergusonite-type oxide can also be explained by the charge transfer from the electronegative nitrogen atoms of the phenacyl benzotriazole **1** to the p orbitals (s orbitals are full) of Bi³⁺³⁰ that improve the interaction with the electronegative nitrogen atoms (N2 and N3) of the benzotriazole **1** (Figure 4).

4. CONCLUSION

In summary, scheelite ABO₄ and fergusonite BiVO₄ catalysts constitute good materials to promote the conversion of phenacyl benzotriazole **1** under cfvp conditions with high

selectivity to **3**. These oxides are stable and reusable, and their syntheses are easy and inexpensive. For cfvp systems, the catalytic activity was strongly dependent on the morphology of the oxide as a consequence of the synthetic method.

Using the catalytic material supported on the ceramic fiber, the selectivity of the process toward nitrogen extrusion of **1** was significantly enhanced. The controlled deposition of particles on the fiber improved the reactivity of the substrate and the selectivity of the process. Differences in the catalytic behavior were observed, depending on the nature of cations located in the mixed oxide. Thus, tungstates AWO_4 and BiVO_4 favored the formation of **3** with high selectivity. The selectivity to the formation of azeponone **3** as a function of A^{2+} cation followed the order $\text{Ca}^{2+} < \text{Sr}^{2+} \sim \text{Ba}^{2+}$.

In contrast, molybdates favored multiple C–C and C–N fragmentations of **1**. The use of inexpensive mixed oxides as specific catalysts in cfvp reactions constitutes a new and efficient “one-pot” procedure to synthesize the compound **3**, a precursor of potential bioactive dibenzazepinones.

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed experimental procedures and characterization analysis are summarized. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Thanks are given to Valeria Fuertes, Ph.D. for her significant assistance and Prof. Luis Cadús for the surface area (BET) determinations. Financial assistance from FONCYT, CONICET, and SECyT-UNC is gratefully acknowledged.

■ REFERENCES

- (1) Pozharskii, A.; Soldatenkov, A.; Katritzky, A. In *Heterocycles in Life and Society: An Introduction to Heterocyclic Chemistry, Biochemistry and Applications*, 1st ed.; Wiley: New York, 1997.
- (2) Peters, J-U; Galley, G.; Jacobsen, H.; Czech, C.; David-Pierson, P.; Kitas, E.; Ozmen, L. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 5918–5923.
- (3) Pegoraro, S.; Lang, M.; Dreker, T.; Kraus, J.; Hamm, S.; Meere, C.; Feurle, J.; Tasler, S.; Prütting, S.; Kuras, Z.; Visan, V.; Grissmer, S. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 2299–2304.
- (4) Ishida, M.; Muramura, M.; Kato, S. *Synthesis* **1989**, 562.
- (5) Moore, J.; Theuer, W. *J. Org. Chem.* **1965**, *30*, 1887–1889.
- (6) Paterson, W.; Proctor, G. *J. Chem. Soc.* **1962**, 3468–3472.
- (7) Moyano, E.; Eimer, G.; Lucero, P.; Chanquía, C.; Herrero, E.; Yranzo, G. *Appl. Catal., A* **2010**, *373*, 98–103.
- (8) Moyano, E.; Eimer, G.; Lucero, P.; Herrero, E.; Yranzo, G. *Org. Lett.* **2007**, *9*, 2179–2181.
- (9) Denis, J.; Gaumont, C. In *Gas Phase Reaction in Organic Synthesis*; Vallée, J., Ed.; Gordon and Breach Science Publishers: Amsterdam, 1997, 195–204.
- (10) Moyano, E.; Yranzo, G. *J. Org. Chem.* **2001**, *66*, 2943–2947.
- (b) Moyano, E.; del Arco, M.; Rives, V.; Yranzo, G. *J. Org. Chem.* **2002**, *67*, 8147–8150.
- (11) Angloher, G.; Bucci, C.; Cozzini, C.; Feilitzsch, F.; Frank, T.; Hauff, D.; Henry, S.; Jagemann, T.; Jochum, J.; Kraus, H.; Majorovits, B.; Ninkovic, J.; Petricca, F. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2004**, *520*, 108–111.
- (12) Han, Y.; Ueda, W.; Moro-Oka, Y. *J. Catal.* **1999**, *186*, 75–80.

(13) Muktha, B.; Madras, G.; Guru-Row, T. N. *J. Photochem. Photobiol. A* **2007**, *187*, 177–185.

(14) Klopogge, J.; Weier, M.; Duong, L.; Frost, R. *Mater. Chem. Phys.* **2004**, *88*, 438–443.

(15) Errandonea, D.; Manjon, F. J. *Mater. Res. Bull.* **2009**, *44*, 807–811.

(16) Wood, P.; Glasser, F. *Ceram. Int.* **2004**, *30*, 875–882.

(17) Ke, D.; Peng, T.; Ma, L.; Cai, P.; Jiang, P. *Appl. Catal., A* **2008**, *350*, 111–117.

(18) Liu, Y.; Huang, B.; Dai, Y.; Zhang, X.; Qin, X.; Jiang, M.; Whangbo, M. *Catal. Commun.* **2009**, *11*, 210–213.

(19) Wash, A.; Yan, Y.; Huda, M.; Al-Jassim, M.; Wei, S. *Chem. Mater.* **2009**, *21*, 547–551.

(20) Dhachapally, N.; Kalevaru, V.; Brückner, A.; Martin, A. *Appl. Catal., A* **2012**, *11*, 443–444.

(21) Yu, J.; Zhang, Y.; Kudo, A. *J. Solid State Chem.* **2009**, *182*, 223–228.

(22) Garcia Perez, U.; Sepúlveda-Guzmán, S.; Martínez-de la Cruz, A.; Ortiz, U.; Méndez, J. *J. Mol. Catal. A: Chem.* **2011**, *335*, 169–175.

(23) Zhu, Z.; Du, J.; Li, J.; Zhang, Y.; Liu, D. *Ceram. Int.* **2012**, *38*, 4827–4834.

(24) Liu, W.; Cao, L.; Su, G.; Liu, H.; Wang, X.; Zhang, L. *Ultrason. Sonochem.* **2010**, *17*, 669–674.

(25) Rietveld, H. J. *Appl. Cryst.* **1969**, *2*, 65–71.

(26) Jenkins, R.; Snyder, R. In *Introduction to X-Ray Powder Diffractometry*; Winefordner, J. D., Ed.; Wiley-Interscience: New York, 1996; Vol. 138, p 47.

(27) Pepino, A.; Peláez, W.; Moyano, E.; Argüello, G. *Eur. J. Chem.* **2012**, 3424–3430.

(28) Brown, L. In *Pyrolytic Methods in Organic Chemistry*; Wasserman, H., Ed.; Academic Press: New York, 1980, p 164.

(29) Rademacher, P. In *Advances of Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: London, 1999, Vol. 72, p 361.

(30) Lener, G.; Vélez, P.; Leiva, E.; Moyano, E.; Carbonio, R. In preparation