BRØNSTED SOLID ACIDS FOR IONONE SYNTHESIS

Verónica Díez, Carlos Apesteguía and Isabel Di Cosimo*

Catalysis Science and Engineering Research Group (GICIC)- INCAPE (UNL-CONICET), Santiago del Estero 2654,(3000) Santa Fe, Argentina
*e-mail: dicosimo@fiq.unl.edu.ar

Ionones are valuable chemicals. Whereas β-ionone is used in vitamin A synthesis, α- and γ-ionone are employed in fragrances. Ionones are produced from citral via a two-step process (Figure 1) that involves liquid catalysts. The second step, the cyclization of pseudoionone (PS) promoted by sulfuric acid gives ionone yields of 70-90 % but works using solid acids report much lower yields. In this work, we postulate different solid acid catalysts to convert PS into ionones in high yields. We investigate the effect of the acid species (Brønsted or Lewis) and reaction conditions on the ionone yield and isomer distribution.

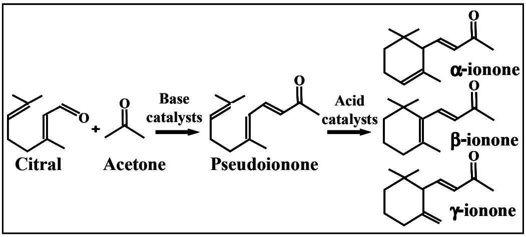

Figure 1: Two-step ionone synthesis

Table 1. Acid properties and catalytic results on solid acid catalysts.

Catalyst	S.A (m^2/g)	Acid Site Density, n_a [a] (μmol/g)	Catalytic Results [b] X_{PS} (%)	η_{IONONE} (%)
HBEA	630	611	20.1	7.7
SiO_2-Al_2O_3	560	319	21.8	5.3
HPA	9	534	3.9	1.2
Cs-HPA	143	47	38.3	25.1
HPAS-19	208	229	35.9	24.4
HPAS-27	203	258	67.1	50.9
HPAS-43	155	377	87.9	58.4
HPAS-59	144	566	93.0	68.0

[a] by NH_3 TPD; [b] at 6 h and 353 K

Four silica-supported tungstophosphoric acid catalysts (HPAS-*x; x*: wt.% of HPA) and Cs-HPA were prepared. Commercial HBEA, SiO_2-Al_2O_3 and HPA were also used. Total acid site densities (n_a) were measured by TPD of NH_3. The presence of Lewis and Brønsted surface acid species was determined by FTIR of pyridine (Py). PS cyclization was performed at 343-383 K and 250 kPa in a batch reactor, with typically a Toluene/PS = 71 molar ratio and a catalyst/PS = 56 wt. % ratio.

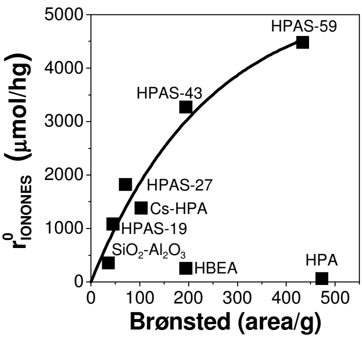

Figure 2: Initial ionone formation rate vs. Brønsted band area from Py adsorption

HBEA and SiO_2-Al_2O_3 presented Lewis and Brønsted surface acid sites whereas the HPA-based catalysts were essentially Brønsted acids. Table 1 shows that n_a, PS conversion (X_{PS}) and ionone yield (η_{IONONE}) increased with the HPA loading for the HPAS catalysts. Furthermore, a correlation was found between the initial ionone formation rate and the Brønsted acid site band area, Figure 2, thereby confirming that the reaction is promoted by this kind of surface sites. HBEA and unsupported HPA contained sites accessible for NH_3 and Py adsorption but not available for the reaction due to diffusional and spatial constraints. The best η_{IONONE} at 353 K was obtained on HPAS-59 which presented the highest density of available Brønsted sites. On the latter the η_{IONONE} reached 79 % in just 1.5 h at 383 K, Figure 3. Also, as shown in Figure 3, at 383 K the contribution of the α isomer was enhanced for reaction times longer than 1.5 h (time for 100 % PS conversion), reaching ~ 80 % of the total ionones at the end of the run, whereas β ionone remained constant. An isomerization process took place in which the least stable γ isomer converted to α-ionone.

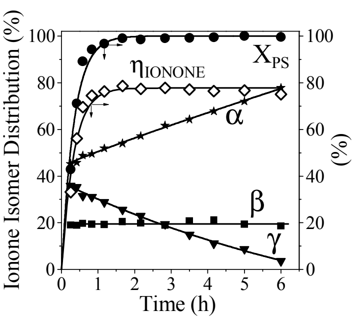

Figure 3: Effect of reaction time (T=383 K, HPAS-59)

Ionone synthesis is efficiently promoted on the Brønsted acid sites of silica-supported heteropolyacids. A 79 % ionone yield was obtained at 383 K in 1.5 h, a value comparable to that of the sulfuric acid-catalyzed ionone synthesis. The main isomer (α) is favored at high temperatures and reaction times.