

Ionone synthesis on solid acid catalysts

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Introduction

Ionones (α , β , γ) are valuable chemicals. The β -ionone is used in the synthesis of vitamin A, whereas α - and γ -ionone are employed in fragrances. Ionones are commercially produced from citral via a two-step process that involves liquid catalysts. In particular, the second step, the cyclization of pseudoionone (PS), is promoted by sulfuric acid. Few works report the use of solid acids for this step but yields (49 %) [1] are still lower than those of the homogeneous reaction (70-90 %). In this work we postulate two silica-supported acid catalysts to selectively convert PS into ionones: heteropolyacid (HPA) and triflic acid (TFA). Our goal was to investigate the effect of the acid species and reaction conditions on the ionone synthesis and on the ionone isomer distribution.

Materials and Methods

Four silica-supported tungstophosphoric catalysts (HPAS-*x*; *x*: wt.% of HPA) with HPA loadings between 19 and 59 wt.% were prepared by incipient wetness impregnation method. Similarly, a sample containing 8 wt.% of TFA (TFAS-8) was prepared. Acid site densities (n_a) were measured by TPD of NH_3 . The chemical nature of surface acid sites was determined by Infrared Spectroscopy (FTIR) of pyridine. Pseudoionone (Fluka, > 95 %) cyclization was performed at 343-383 K under autogenous pressure in a batch Parr reactor, using dehydrated toluene as a solvent with typically a Toluene/PS = 71 molar ratio and a catalyst/PS = 56 wt. % ratio.

Results and Discussion

The total acid site density, n_a , increased with the HPA loading (Table 1) in agreement with the measured H^+ content of each sample. Furthermore, pyridine FTIR experiments confirmed that surface acid sites are essentially Brønsted.

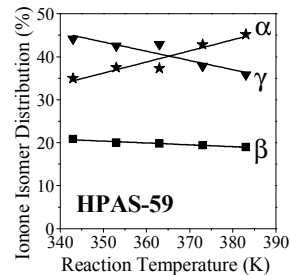


Figure 1: Effect of reaction temperature ($X_{\text{PS}} = 40\%$).

The effect of acid loading on the ionone synthesis was studied with the HPAS samples, Table 1. PS conversion (X_{PS}) increased with the acid loading. The effect of the HPA loading was limited to the catalyst activity since the selectivity to total ionones and the isomer distribution was independent of the HPA content at similar conversion levels. Thus, the highest final η_{IONONE} at 353 K was obtained on HPAS-59, which presented the highest Brønsted acid site density.

We also investigated the effect of reaction temperature and time using sample HPAS-59. The η_{IONONE} improved from 29 % at 6 h to 79 % at 1.5 h by increasing reaction

temperature from 343 to 383 K. Figure 1 shows that the contribution of the α isomer is enhanced at high temperatures. Similarly, at 383 K and for reaction times longer than 1.5 h (time for 100 % PS conversion), isomerization of the γ isomer into α -ionone was observed (Figure 2). Whereas β -ionone remained constant (20 %), α -ionone reached 80 % at the end of the run. These results are explained by the different isomer stability ($\beta > \alpha > \gamma$) due to the position

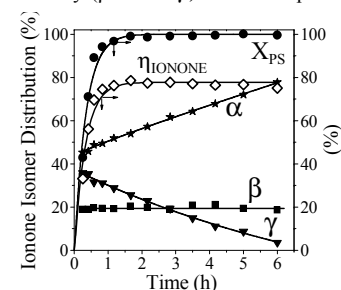


Figure 2: Effect of reaction time (T=383 K, HPAS-59)

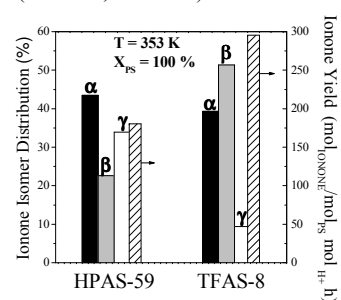


Figure 3: Effect of the acid species (HPA or TFA)

Table 1. Acid properties and catalytic results on HPAS solids.

Catalyst	Surface Area (m ² /g)	Acid Site Density, n_a^a (μmol/g)	Catalytic Results ^b	
			X_{PS} (%)	η_{IONONE} (%)
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.

of the double bond in the isomer molecules. Thus, β -ionone stabilized by the extended conjugated system, forms directly from PS and does not isomerize. The isomer distribution can be modified by the temperature and reaction time but β -ionone was obtained in low selectivity since this isomer requires stronger catalyst acidity.

Figure 3 compares the performance of HPAS-59 and TFAS-8 catalysts. Sample TFAS-8 was more active if ionone yields are compared per mol of H^+ and per hour. Clearly, the HPA catalyst produces mainly α -ionone (43 %), whereas on TFA, the most valuable β isomer contributes 51 %. The stronger acidic features of TFA ($H_0 = -14.6$) [2] compared to HPA ($H_0 = -13.2$) [3] explain these results.

Significance

Ionones are produced in high yields on silica-supported heteropolyacid catalysts: 79 % was obtained on a 59 wt. % HPA/ SiO_2 catalyst 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. The stronger silica-supported triflic acid shifts the isomer distribution toward the β isomer.

References

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