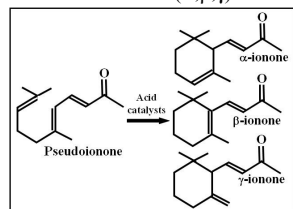


Effect of the Brønsted acid site strength on ionone isomer distribution during pseudoionone cyclization on solid catalysts

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Introduction

Ionones (α, β, γ) are valuable chemicals widely used in pharmaceutical and cosmetic industries. Ionones are commercially produced using strong and corrosive liquid acid catalysts such as H_2SO_4 and therefore, attempts have been made recently to replace this technology by solid acids. However, the most valuable isomer, β -ionone, has not been produced by heterogeneous catalysis. In this work we present silica-supported catalysts containing tungstophosphoric (HPA) and triflic (TFA) acids and an Amberlyst resin for ionone synthesis. Our goal was to investigate how the strength of the Brønsted acid surface species affects the activity and mainly, the ionone isomer distribution.



Materials and Methods

HPA/SiO₂ (HPAS) and TFA/SiO₂ (TFAS) catalysts with acid contents of 58.5 wt% and 8.2 wt%, respectively, were prepared by incipient wetness impregnation method using aqueous solutions of HPA and TFA. Commercial Amberlyst 35W resin was pretreated at 373K. The Lewis (L) or Brønsted (B) acid nature of the surface sites of TFAS and HPAS was determined by Infrared Spectroscopy (FTIR) of adsorbed pyridine. Pseudoionone, PS (Fluka, > 95%) cyclization was performed at 353 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 = 28-56 wt% ratio.

Results and Discussion

The HPA structure in HPAS sample was confirmed by XRD. Triflic acid on TFAS sample was identified by monitoring the IR SO₂²⁻ vibration band at 1417 cm⁻¹, which is regarded as the characteristic band of supported TFA. Characterization using FTIR of adsorbed pyridine confirmed that HPAS and TFAS samples are essentially Brønsted catalysts with a Brønsted site

Table 1. Acidic properties and catalytic results

Catalyst	Sg	Total acid site number (μmol/g)	Acid site nature		r_{IONONE}^0 (mol/h mol H ⁺)
			B	L	
TFAS	245	540 ^a	222 ^d	18 ^d	24.7
Amberlyst	39	5200 ^b	--	--	1.3
HPAS	144	610 ^c	450 ^e	56 ^e	4.9

^aby acid-base titration; ^bfrom manufacturer information; ^cby UV analysis; ^dpyridine evacuation at 353 K, ^epyridine evacuation at 373 K

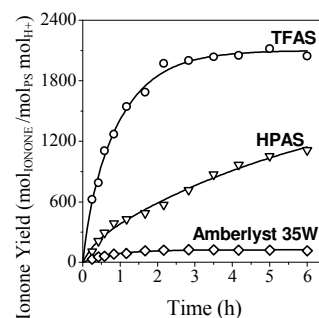


Figure 1. Ionone yield as a function of time at 353 K

catalysts produced initially α -, β - and γ -ionones, indicating that the three isomers are primary products formed directly from PS. However, isomerization reactions, i.e., isomer interconversion, took place during the catalytic runs proceeding to different extent depending on the catalyst (Figure 2), so that the final product distribution was significantly affected by the catalyst acidic properties. The stability order of ionone isomers is $\gamma < \alpha < \beta$; therefore, the least stable γ -ionone was isomerized to α and β isomers. On the strongest acid sites of TFAS the contribution of β -ionone increased with reaction time reaching an unprecedented $\approx 50\%$ at 6h. On the other hand, Amberlyst 35W gave α -ionone as the main isomer (61%) at the end of the run. Finally, on HPAS the ionone isomer distribution was rather constant during the run, giving similar amounts of α and γ isomers ($\approx 40\%$).

These results show that the kinetics of ionone isomer synthesis is affected by the catalyst surface proton strength and that strong Brønsted acid sites such as those of silica-supported TFA are able to promote β -ionone formation.

Significance

TFAS, HPAS and Amberlyst 35W catalysts convert efficiently PS into ionones. Catalyst activity and selectivity toward the three ionone isomers strongly depend on the surface acid site strength. Thus, α isomer is favored at high reaction times on Amberlyst resin while the stronger TFAS shifts the isomer distribution toward the β isomer.

contribution $B/(B+L) \geq 90\%$ (Table 1). Figure 1 shows the time evolution of ionone yields per H⁺ calculated from the total acid site number, for HPAS, TFAS and Amberlyst 35W catalysts. From these curves, the initial ionone formation rates (r_{IONONE}^0) were determined by calculating the slope at $t = 0$, Table 1. Results in Table 1 reveal that the ionone initial activity order is: TFAS \gg HPAS $>$ Amberlyst 35W. The catalytic activity results of the three catalysts reflect not only differences in the Brønsted site activity but also in the proton site strength. In fact, protons on TFA present the strongest acidity on a Hammett acidity function basis ($H_0 = -14.6$), in contrast to -13.2 on HPAS and -2.65 on Amberlyst 35W.

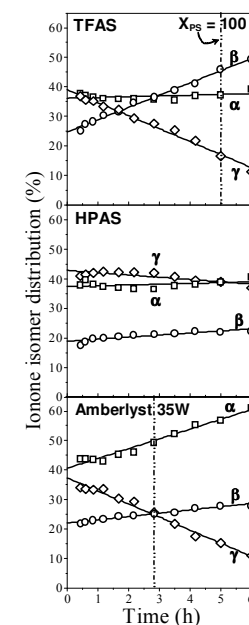


Figure 2. Ionone isomer distribution as a function of time. [$W_{\text{Amberlyst}} = W_{\text{HPAS}} = 1\text{g}$; $W_{\text{TFAS}} = 0.5\text{g}$]