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Kinetic and mechanistic study of the synthesis of ionone isomers from pseudoionone on Brønsted acid solids

V.K. Díez*, C.R. Apesteguía, J.I. Di Cosimo

Catalysis Science and Engineering Research Group (GICIC), INCAPE, UNL-CONICET, CCT CONICET Santa Fe, Colectora Ruta Nac. 168, km 0, Paraje "El Pozo", (3000) Santa Fe, Argentina

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ABSTRACT

The kinetics of the liquid-phase synthesis of α-, β- and γ-ionones from pseudoionone was studied on Brønsted acid solids. Four silica-supported tungstophosphoric acid catalysts containing different heteropolyacid loadings, as well as a silica-supported triflic acid sample and a commercial resin (Amberlyst 35W) were tested in a batch reactor at 343–383 K under autogenous pressure.

The final composition of the ionone isomer mixture depended on the catalyst acidic properties and operational conditions. The reaction pathways leading to the three ionone isomers were elucidated by postulating a heterogeneous Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model. First order rate expressions, participation of a single Brønsted acid site in each reaction step and a cationic cyclic intermediate shared by the three ionone isomers were the main model assumptions. It was found that α-, β- and γ-ionones form directly from pseudoionone by cyclization. However, the final concentration of α- and β-ionones is enhanced in consecutive pathways involving the isomerization of γ-ionone. The relative importance of the isomerization steps and the selective formation of α- or β-ionone depend on the Brønsted acid site strength and reaction temperature.

1. Introduction

Ionones (α, β and γ isomers) are widely used as pharmaceuticals and fragrances. The β-ionone isomer is used in the synthesis of vitamin A, while α- and γ-ionones are appreciated in the fragrance and cosmetic industries for their violet and fruity-woody scent, respectively [1,2]. The current commercial synthesis of ionones from citral takes place via a homogeneously catalyzed two-step process. Firstly, pseudoionone (PS) is obtained by aldol condensation of citral with acetone in the presence of diluted bases. Then, ionones are produced by cyclization of PS using strong mineral acids (H_2SO_4, H_3PO_4) as catalysts [3]. However, the use of mineral bases and acids entails concerns related to high toxicity, corrosion, and disposal of spent catalysts. Thus, in recent years new strategies have been postulated in the literature for ionone production in which liquid bases and acids are replaced by solid catalysts.

Time ago, we explored the second reaction step, i.e., the cyclization of PS to ionones on several solid acids such as unsupported tungstophosphoric acid (HPA), silica-supported HPA (HPAS), silica-supported triflic acid (TFAS), Cs-HPA, zeolite HBEA, SiO_2-Al_2O_3 and a commercial Amberlyst 35W resin [4–6]. The acidic nature (Lewis or Brønsted) of the active sites required for selective ionone synthesis was initially investigated [4]. In addition, the effect of the HPA loading and reaction conditions (temperature and reaction time) on catalytic activity and selectivity was studied on HPAS catalysts [5]. Finally, we investigated the effect of the acid site strength on ionone isomer selectivity by comparing the catalytic performance of three different Brønsted acid catalysts (HPAS, TFAS and Amberlyst 35W) [6]. The main findings of these previous works were that the reaction is efficiently promoted on catalysts containing a high density of strong Brønsted acid sites such as those of HPAS, TFAS, and Amberlyst 35W. In contrast, PS conversion was poorly promoted on Lewis acids such as SiO_2-Al_2O_3. In addition, it was found that ionone synthesis is favored at high reaction temperatures on HPAS catalysts so that the ionone yields at 383 K are comparable to those obtained by homogeneous catalysis using concentrated sulfuric acid.

Although the kinetic and mechanistic features of the ionone synthesis from PS have been investigated using homogeneous acid catalysis [7,8], they have not been discussed in detail using solid catalysts. In this work we investigate the kinetics and reaction mechanism involved in the formation of the three ionone isomers from PS on Brønsted acid solid catalysts. The kinetic performance of HPAS,

* Corresponding author.
E-mail address: verodiez@fiq.unl.edu.ar (V.K. Díez).

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TFAS and Amberlyst 35W catalysts was compared. In particular, we tested HPAS catalysts with different HPA loadings and at different temperatures. The reaction pathways leading to the different ionone isomers were discussed as well as how the selective formation of a particular isomer is affected by the catalyst acidic properties and reaction conditions. A complex reaction network was postulated and a heterogeneous Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model was proposed to interpret the catalytic data. Several kinetic parameters were calculated and statistically validated. The dependence of the kinetic parameters on the reaction temperature and catalyst acid properties was elucidated. The kinetic model successfully interprets the liquid-phase synthesis of ionone isomers promoted by different Brønsted acid solids.

2. Experimental

2.1. Catalyst synthesis

Four HPA/SiO_2 catalysts with different HPA loadings (18.8, 26.6, 42.5 and 58.5 wt.%) were previously prepared by the incipient wetness impregnation method [5]. The tungstophosphoric acid ($H_3PW_{12}O_{40}.xH_2O$, Merck, GR) was added to a commercial SiO_2 (Grace Davison, G62, 99.7) using aqueous solutions of HPA. Also, a silica-supported triflic acid catalyst (TFA/SiO_2) with an acid content of 8.0 wt.% was prepared by the same procedure using an aqueous solution of commercial TFA (CF_3SO_3H, Sigma-Aldrich, Reagent Grade). Details are given elsewhere [6]. The impregnated samples were dried at 353 K and then decomposed and stabilized at 523 K (HPA/SiO_2) and 383 K (TFA/SiO_2) for 18 h in N_2 (40 cm^3/min). The resulting silica-supported acid catalysts were denoted as HPAS-x and TFAS, where x is the HPA content expressed in wt.%. Amberlyst 35W resin pellets (Rohm and Haas) were crushed and sieved to retain particles between 180 and 480 μm. The resin was treated in N_2 (40 cm^3/min) at 373 K overnight before use.

2.2. Catalyst characterization

Chemical and spectroscopic techniques employed during catalyst characterization were thoroughly described in previous works [5,6]. BET surface areas (*SA*) were measured by N_2 physisorption at 77 K using an Autosorb Quantachrome 1-C sorptometer. Structural properties of HPAS-x samples were determined by X-ray diffraction (XRD) between 20° and 80° using a Shimadzu XD-D1 diffractometer equipped with Cu Kα radiation and a Ni filter. The chemical content of HPA in the calcined HPAS-x catalysts was determined by monitoring the tungsten content in a UV–vis spectrometer (Metrolab 1700). This quantitative method involves the calcination of the sample in an oven at 1073 K in order to transform $H_3PW_{12}O_{40}xH_2O$ in tungsten oxide (WO_3) and the subsequent digestion in an alkali solution. The solution containing WO_3 was finally analyzed by the UV–vis technique. More details are given elsewhere [9]. The TFA loading in the TFAS sample was measured by titration of the sample protons [6]. TFAS (0.3 g) was suspended in 75 ml of an aqueous solution of KCl (0.03 M) to release the triflic acid protons to the aqueous solution. The suspension was stirred for 20 min and then titrated with a 0.06 M KOH solution using phenolphthalein as the acid-base indicator.

The total acid site number (n_a, μmol/g) of HPAS-x samples was quantified by TPD of NH_3 preadsorbed at 373 K. Samples were thermally treated in He at 523 K, cooled down to 373 K and then exposed to a 1.01% NH_3/He flow to enable surface saturation. Weakly adsorbed NH_3 was removed by flushing with He. Finally, the sample temperature was increased from 373 K to 1073 K in a He flow. NH_3 concentration in the reactor effluent was monitored by a mass spectrometer (MS) detector in a Baltzers Omnistar unit. More experimental details are given elsewhere [5].

The chemical nature of surface acid sites was determined by Infrared Spectroscopy (IR) of pyridine adsorbed at room temperature and evacuated at increasing temperatures using a Shimadzu FTIR Prestige-21 spectrophotometer. Details are given elsewhere [6].

2.3. Catalytic testing

The liquid-phase cyclization of pseudoionone, PS (Fluka, > 95%) was carried out at 343–383 K under autogenous pressure (250 kPa) 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.

Before the catalytic test, catalysts were thermally treated ex-situ in a N_2 stream at the calcination temperature for 2 h to remove adsorbed water. After introducing the reactant mixture the reactor was sealed and flushed with N_2 and then the mixture was heated up to the reaction temperature under stirring (300 rpm). The catalyst powder was added to the reaction mixture to start the reaction. Reaction products were periodically analyzed during the 6-h reaction in a Varian Star 3400 CX gas chromatograph equipped with a FID and a Carbowax Amine 30 M capillary column. Main reaction products were ionones (α, β and γ isomers); in some experiments, unidentified compounds were detected in a concentration lower than 10%.

2.4. Kinetic modeling and statistical analysis

The reaction mechanism of the liquid-phase synthesis of α-, β- and γ-ionones from pseudoionone (PS) on Brønsted acid solids was studied using a heterogeneous Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model. The differential equations were solved numerically using the Runge-Kutta-Merson algorithm. The relative molar concentrations of all the species over the course of reaction were calculated and compared with the experimental values. The model parameter estimation was performed by non-linear regression, using a Levenberg-Marquardt algorithm, which minimizes the sum of the squared errors (*SSE*) [10] between the experimental data and the data predicted by the model according to Eq. (1):

$$SSE = \sum_{i=1}^{n} (C^*_{jcalc} - C^*_{jobs})^2 \quad (1)$$

where C^*_j is the relative concentration of compound j (C_j/C^0_{PS}), C^0_{PS} is the concentration of pseudoionone in the reactor at $t = 0$ and C^*_{jcalc} is the value calculated by applying the model, which is compared with the experimental value (C^*_{jobs}).

The coefficient of determination (R^2) gives the fitting quality [10] and was calculated using Eq. (2):

$$R^2 = \frac{\sum_{i=1}^{n} (C^*_{jcalc} - \overline{C}^*_{jobs})^2}{\sum_{i=1}^{n} (C^*_{jobs} - \overline{C}^*_{jobs})^2} \quad (2)$$

where $\overline{C}^*_{jobs}$ is the mean of measured values.

The discrimination between models was carried out using the model selection criterion (*MSC*) [11], according to Eq. (3):

$$MSC = \ln\left[\frac{\Sigma (C^*_{jobs} - \overline{C}^*_{jobs})^2}{\Sigma (C^*_{jobs} - C^*_{jcalc})^2}\right] - \frac{2p}{m} \quad (3)$$

where p is the number of parameters; m is the number of experimental observations. The *MSC* parameter is used to compare different models and results independent of the magnitude (scaling) of the data. When comparing different models, the larger the *MSC* value, the better the fit and the more appropriate the model for interpreting the data.