



Acetic acid removal from bio-oil on alumina-supported CaO and/or Ag catalysts

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Acetic acid removal from bio-oil by catalytic processes was investigated over alumina-supported calcium oxide and silver catalysts. A 20 wt.% CaO supported on γ -Al₂O₃ system (CaO-Al) was prepared by precipitation of CaCO₃ followed by calcination to obtain the supported oxide. A 10 wt.% Ag catalyst was prepared by impregnation on CaO-Al as support (Ag/CaO-Al). The conversion of acetic acid was tested in batch micro-reactors, with the purpose of screening the reaction conditions. Both CaO-Al and Ag/CaO-Al were active for the reaction, with the contribution of the metal phase increasing the conversion with respect to CaO-Al (75.7% vs. 58% at 200 °C). The Ag/CaO-Al catalyst was also tested in a batch reactor at two pressures, achieving a conversion of acetic acid of 97.5% at the lowest pressure (280 kPa). Based on the results, it is postulated that multiple pathways (catalytic decarboxylation, neutralization and ketonization) are responsible for acetic acid conversion.

1. Scope

Lignocellulosic biomass represents a sustainable source of organic carbon. With this resource, liquid fuels and other raw materials for the chemical industry can be produced¹. The pyrolysis of lignocellulosic biomass to bio-oils, followed by its catalytic upgrading to hydrocarbon fuels, is among the most employed transformation routes². Some possible applications of bio-oils can be affected by properties such as high acidity, high water content or instability for storage³. For example, in order to co-process a bio-oil in a refinery, one of the aspects that must be improved is the decrease of its acidity. The acidity of bio-oil is mainly due to volatile organic acids such as acetic and formic acids, being the first one which is in higher concentration⁴. Acidity is determined by pH measurement. The total acid number (TAN) used to measure the acidity of crude oils has recently been adapted for bio-oils. The pH of untreated biomass bio-oils is typically 2.5-3, while the TAN for oils of biological origin may be as high as 100⁴.

As a contribution to the subject, in this work the reaction of elimination of acetic acid using alumina-supported CaO and/or Ag catalysts is studied. Taking into account that acetic acid is the carboxylic acid found in greater proportion in bio-oils, it was selected as model compound for this study.

2. Results and discussion

In a first series of tests, the reaction was carried out in stainless steel batch micro-reactors. Approximately 20 mg of catalyst and 1.5 mL of a 1% (w/v) solution of acetic acid dissolved in n-decane under Ar atmosphere were used for each assay with CaO-Al and Ag / CaO-Al. The catalytic performance was evaluated by placing the reactors in an oven with a continuous stirring system, using temperatures in the range of 150 to 300°C for 2 h. At the end of the reaction, the products were analyzed by gas chromatography (SHIMADZU GC-2014 with FID). The percentages of removal of acetic acid are shown in Table 1.

It can be seen that the CaO-Al system has an appreciable activity, which decreases with increasing temperature. These are promising results, since the alumina-supported active phase would allow the subsequent development of a conformed catalyst, decreasing the possibility of leaching and thus increasing the amount of total solids in the bio-oil. The addition of silver (Ag/CaO-Al) increases the conversion of acetic acid by ca. 20% with respect to the CaO-Al system, reaching the maximum value at 200°C. Next, the

catalytic activity was evaluated in an autoclave batch reactor (Berghof BR 100) with magnetic stirring. The operating conditions were: mass of catalyst 370 mg, volume of acetic acid solution 30 mL, temperature 200°C and reaction time 2 h. Two pressure values, 280 and 400 kPa, were used. Table 2 shows the results obtained. It is observed that while with the CaO-Al catalyst conversion is practically independent of the working pressure, the Ag/CaO-Al system showed a higher conversion at the lower pressure, obtaining 97.5% acetic acid removal.

Table 1. Percentage conversion results in micro-reactor

Catalyst	Reaction temperature (°C)			
	150	200	250	300
CaO-Al	69.0	58.0	48.7	48.2
Ag/CaO-Al	69.4	75.7	55.7	60.9

Table 2. Percentage conversion results in pressure batch reactor

Catalyst	Acetic acid conversion (%)	
	P=280 kPa	P=400 kPa
CaO-Al	77.3	76.3
Ag/CaO-Al	97.5	70.0

Three possible mechanisms are proposed for this reaction: neutralization, decarboxylation and ketonization reaction.

Samples collected after reaction, were analyzed by TEM and XRD in order to identify the reaction products and to elucidate a catalytic reaction pathway. Figure 1 shows the diffractograms obtained for the fresh (f) and used (s) CaO-Al and Ag/CaO-Al catalysts. For the first one, in both (s) and (f) samples, the calcium oxide diffraction lines are observed at 26.7° and 37.3°. Both Ag/CaO-Al catalyst samples show the Ag⁰ diffraction lines at 38.37°, 44.54° and 64.69°. In both used catalysts, the presence of hydrated calcium acetate is revealed by the diffraction lines at 7.62°, 10.39°, 11.98°, 25.41° and 27.21°. This result would be indicating that the neutralization reaction pathway is the main one for the CaO-Al system, whereas for the Ag/CaO-Al catalyst besides the neutralization there is an acetic acid removal by a ketonization mechanism. This last fact is explained by the dependence of the conversion on the pressure (Table 2) and by the appearance of bands assignable to acetone in the FTIR spectra (not shown).

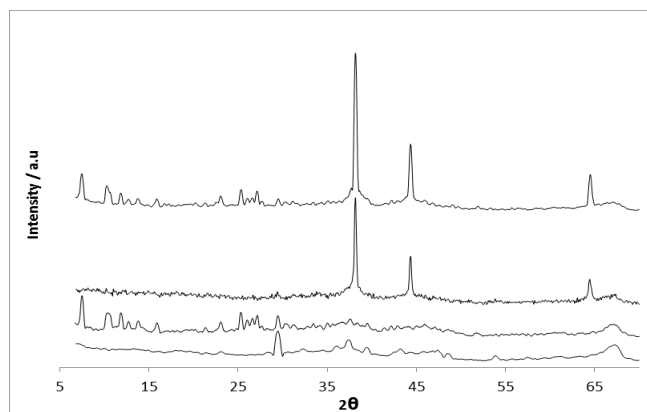


Figure 1. Diffractograms of: CaO-Al (f); CaO-Al (s); Ag/CaO-Al (f) and Ag/CaO-Al (s) (bottom to top).

3. Conclusions

The CaO-Al catalyst was able to efficiently decompose CH₃COOH at 150°C, but this capacity decreased with increasing temperature. The addition of silver led to a maximum conversion of *ca.* 75% at 200°C. When tested in an autoclave-type reactor, the Ag/CaO-Al catalyst reached a CH₃COOH conversion of 97.5%. In both used catalysts, calcium acetate hydrated was identified as reaction product by XRD. It is proposed the existence of a mixed neutralization and ketonization mechanism for the elimination of CH₃COOH.

References

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