Solid acid catalysed conversions of oleochemicals
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Activity and Selectivity of Silica-Alumina Catalysts in Gas Phase Esterification of Acetic Acid and Ethanol

Abstract

Esters form an important product category, for instance for the synthesis of intermediates for fragrances, flavors and detergents. Mostly esterification reactions are carried out in batch processes using homogeneous catalysts. In the search for potentially better solid acid catalysts, we have studied the influence of acidic properties of a variety of silica-alumina based solid acid catalysts on the activity and selectivity. To this end the gas phase esterification of ethanol and acetic acid is used as a model system and is investigated by means of a combination of NH$_3$-TPD and kinetic studies. The catalysts studied include microporous zeolite Beta and H-ZSM-5, mesoporous silica-aluminate MCM-41, and amorphous silica-alumina catalysts, all with a varying Si/Al ratio. The major side reactions, i.e. ethanol dehydration towards diethyl ether and ethene, are independently studied as well. It is demonstrated that the esterification reaction predominantly proceeds over strongly acidic sites. The selectivity of reaction is found to depend both on the conversion and on the acetic acid to ethanol molar ratio, but not on the acidity of the active sites. Ethanol dehydration is shown to proceed over both weakly and strongly acidic sites and is promoted by a high Al content in silica-aluminas.
Introduction

Esterification is an important process in the oleochemical industry and in the production of flavors and fragrances. Most commercial esterification processes are currently conducted as homogeneously catalyzed batch processes, using for instance homogeneous acids or Sn-octoate as a (Lewis acidic) homogeneous catalyst [1].

The catalyst is conventionally removed after reaction by adsorption on bleaching earth, giving rise to waste problems. This can be circumvented by the use of Brønsted acidic catalysts, but this in turn leads to potential corrosion problems and to formation of salts. Heterogeneous catalysts would facilitate separation, reduce waste, minimize product quality problems and allow for the development of continuous processes. Therefore, a variety of solid acid catalysts have been investigated for their activity and selectivity in esterification.

Esterification catalysts

Many catalysts have been tested in esterification, like ion exchange resin [2], H-ZSM-5 [3], zeolite Y [4, 5], niobic acid [6], sulfated oxides [7-9], hydrous zirconium oxide [10] and supported heteropolyacids [11]. Several of these studies focused on the acid strength of the active sites in esterification.

Corma et al. [4] conclude for the liquid phase esterification of phenyl acetic acid and ethanol over HY (partially exchanged by Na+) that strongly acidic sites are needed. These are assumed present when the Si/Al molar ratio of the HY zeolite exceeds a value of fifteen. These authors show that the initial esterification rate over three Na-HY zeolites correlates well with the pyridine infrared adsorption at 1545 cm\(^{-1}\) after evacuation at 623 K, but not with the same peak after evacuation at 453 K. Therefore, only the strongest sites, having none or only one Al as next nearest neighbor, seem to be active. The increasing hydrophobicity at a
higher Si/Al ratio of the catalyst is proposed by Corma as an additional parameter to explain the increased activity of zeolite H-Y after dealumination.

Lu et al. [9] conducted experiments with Ti-Al-O/\(\text{SO}_4^2\)- as catalyst for liquid phase esterification of 2-ethylhexanol and phthalic anhydride. These authors identify weakly, medium and super acidic sites using pyridine-TPD, showing that the number of intermediate acidic sites correlates well with the rate of esterification. These sites in case of super acidic sulfated oxides may well be identical in acidic strength as the strongly acidic sites of zeolite Y as studied by Corma.

In contrast to Corma, Santacesaria et al. [5], using the same zeolite HY catalysts in the gas phase esterification of acetic acid and ethanol, found a non-linear relation between the number of strongly acidic sites and the activity of ion-exchanged Y zeolites. The latter authors propose esterification to proceed by two simultaneous reaction paths, the rate of one of them correlating with catalyst acidity. This would also explain why they fail to observe a complete deactivation with very high amounts of pyridine in poisoning experiments.

Chu et al. [11] studied the gas phase esterification of acetic acid and ethanol over carbon-supported heteropolyacids (PW\textsubscript{12} and SiW\textsubscript{12}). These authors conclude from NH\textsubscript{3}-TPD experiments of four different HPA/C catalysts that weakly acidic sites are responsible for ethyl acetate formation. However, while the number of weakly acidic sites varies significantly among the catalysts, the conversion varies only marginally. Chu et al. did not find a similar result for the esterification of acetic acid with butanol, but attribute this to an assumed different reaction mechanism.

**Ethanol dehydration**

The most important side reactions in esterification are ethanol dehydration in a bimolecular reaction towards diethyl ether, and in a monomolecular reaction towards ethene (Figure 4.1). Alcohol dehydration is extensively reported in literature [12-15], in particular
for ethanol dehydration [16-20]. Corma et al. [4] claim that ethanol dehydration does not correlate to the strength of the acid sites. Many authors suggest that a dual site mechanism (acid-base pair) is operative, involving a surface ethoxide, in the dehydration of ethanol to ethene over γ-alumina [16, 17, 19]. Surface alkoxy species are also proposed as intermediates for the dehydration of butanol to butene over H-ZSM-5 [13]. According to Arai et al. [16], ether formation over γ-alumina proceeds via such species. Olah et al. [12] propose a mechanism for the ether formation over Nafion-H, involving a nucleophilic attack of alcohol on an oxonium ion formed on a Brønsted acidic site.

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\begin{align*}
\text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{OH} & \quad \xrightarrow{a} \quad \text{CH}_3\text{COCH}_2\text{CH}_3 + \text{H}_2\text{O} \\
\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{OH} & \quad \xrightarrow{b} \quad \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{H}_2\text{O} \\
\text{CH}_3\text{CH}_2\text{OH} & \quad \xrightarrow{c} \quad \text{H}_2\text{C}=\text{CH}_2 + \text{H}_2\text{O}
\end{align*}
\]

*Figure 4.1: Schematic representation of the studied reaction and side-reactions; a. esterification of ethanol and acetic acid, b. formation of diethyl ether, and c. dehydration of ethanol to ethene.*

**Scope**

Presently, we set out to assess the influence of acidic properties of silica-alumina catalysts on the activity and selectivity in esterification. The gas phase reaction of acetic acid and ethanol is chosen as the model reaction, as these are conveniently carried out in steady state continuous experiments, and where transport limitations are easily avoided. As the reaction of acetic acid and ethanol is much studied, a comparison of our data with those from literature is possible.
In this study, amorphous catalysts (silica-aluminas), crystalline materials (H-ZSM-5, H-Beta), as well as mesoporous hexagonally structured materials (MCM-41) were tested. Ethanol dehydration experiments, in the absence of acetic acid, are conducted to study the activities of the catalysts in side-reactions. NH$_3$ – TPD is used to determine the acid strength distribution.

**Experimental**

**Gas-phase reactions**

Steady-state gas phase esterification reactions of acetic acid with ethanol were carried out using a standard flow set-up. Several series of catalysts were tested in the temperature range of 398-473 K. Lower temperatures were not used as these are not relevant from an industrial point of view and secondly because at low temperature the equilibrium of the gas-phase dimerization of acetic acid is favorable to the formation of dimers of acetic acid. The influence of gas phase dimers of acetic acid on the activity of the catalyst is not known and therefore the experimental conditions are chosen as to restrict the presence of dimers to 2 vol. % at most. For this reason a low reactant concentration is used, i.e. 0.5 vol. %. The equilibrium between monomers and dimers of acetic acid, as determined by Hawes [21], is shown in Figure 4.2.

Reactants were added to a nitrogen flow using a thermostatted saturator. Vapor pressures were calculated according to Reid [22]. Acetic acid p.a., ethanol p.a., 1-butanol p.a. and pyridine p.a. were obtained from Aldrich.

Six parallel reactors are used in one experiment. The flow through each reactor was set at 50 ml/min. Each reactor contains typically 50 mg of catalyst ($d_p = 150$-$200$ $\mu$m), $\text{VHSV} = 30000$ hr$^{-1}$, $F/W = 13.4$ (mol ethanol /hr·kg). One of the reactors is used as a blank to monitor the reactant concentrations and to verify the absence of gas phase reaction. In this study, no reaction was ever observed in the absence of a catalyst in the reactor. In this respect, gas phase
esterification reactions behave distinctly different from liquid phase esterifications, which are auto-catalyzed by the carboxylic acid.

![Figure 4.2: Fraction of dimers (%) of acetic acid in the gas phase versus the temperature, calculated according to Hawes [21]; □ 10 mbar, ◇ 50 mbar, and △ 100 mbar total acetic acid partial pressure.](image)

Experiments with ethanol as the sole reactant are conducted for all catalysts to investigate the activity of the catalysts in the side-reactions. Dehydration experiments were performed under the same conditions as employed in esterification.

The analysis of the reactants and products proceeds by GC (Carlo Erba 6000 Vega series 2). Both a FID and a HWD detector were used for detection of both the organic compounds and the produced water.

**NH$_3$-TPD**

The acid strength distribution of the solid acids is determined by NH$_3$-TPD. The temperature at which NH$_3$ desorbs from the acid site of the catalyst indicates its acid strength [23, 24]. NH$_3$ is adsorbed at 323 K from 50 ml/min 5% NH$_3$ in He, following a pre-treatment at either 523 K or 773 K in an inert flow overnight. Desorption is conducted in a He flow of 50 ml/min, while increasing the temperature from 323 K to 773 K at a rate of 10 K/min.
References


