

Oxidation of Ethanol over Zeolite Supported Silver Catalysts

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Introduction

Acetaldehyde plays an important role in the chemical industry. It is used as an intermediate for the production of acetic acid, and acetic anhydride. Currently, it is manufactured via the liquid-phase oxidation of ethylene using Wacker catalyst. Some acetaldehyde is also produced by ethanol partial oxidation and acetylene hydration.

The partial oxidation of ethanol to acetaldehyde has been intensively studied during the last few years. Product distribution and stability depends on the nature of the active metal or oxide used and the support[1]. Supported vanadia catalysts are found to be efficient for the selective oxidation of ethanol to acetaldehyde[2]. Acetaldehyde was the only product detected over Co/CeO₂ catalyst, while several byproducts were produced on Pt/CeO₂ and Pd/CeO₂[3]. Cu/Co ion exchanged Y-zeolite selectively produced acetaldehyde[4] while over Cu/Co ion exchanged ZSM-5, ethanol oxidation produced mainly CO₂ with acetaldehyde as a minor product[5].

Silver is established as a good catalyst for the oxydehydrogenation of alcohol[6]. The aim of this work is to investigate the effect of different zeolite supports on the selective oxidation of ethanol over silver catalysts.

Materials and Methods

The catalysts were prepared by dry impregnation of ZSM-5, Y-Zeolite, H-Mordenite, alumina and silica, with an aqueous solution of AgNO₃. Catalysts were dried at 110°C overnight, then reduced at 300°C using 50 vol% H₂ for 10h.

A 10mm LD-tubular flow reactor was used to study the gas phase reaction. Temperature of the reactor was controlled by a thermocouple placed in the middle of the catalyst bed. 0.7g of catalyst (0.5-0.8mm) was mixed with silica carbide and placed in the middle of the reactor, and supported by quartz wool from both ends. Liquid ethanol was pumped into an evaporator/mixer, counter current configuration and at 150 °C using a liquid mass flow controller. The ethanol/argon mixture/pre-heater was then fed into a mixer where air was added to adjust the reactor feed composition.

All catalysts were tested in the range 200 to 350°C. The GHSV and operating pressure were kept constant at 9860h⁻¹ and 1 atm respectively. The reactor effluent was condensed using ice and analyzed offline. The liquid sample was analyzed using HF-IFAP Agilent capillary column with FID detector, while the tail gas was analyzed using Porapak Q packed column with TCD detector and Alumina Plot Varian Capillary column with FID detector. TEM and XPS methods were used for catalyst characterization.

Results and Discussion

Temperature programmed studies of ethanol dehydration over H-Mordenite showed that diethyl ether, DEE, was produced at lower temperature whereas ethylene production increased to become the main product at 300°C. The TPR results show a decrease in the dehydration activity due to the addition of silver metal.

The product distribution from ethanol oxidation over 10wt% Ag on H-Mordenite is shown in table 1. The other by products were propionaldehyde, propyl acetate, ethyl acetate, and methanol. Neither CO nor CO₂ were detected in the exit gas stream.

Table 1. Ethanol oxidation. $\text{EOH} = 28\text{vol}\%$, Air = $15\text{vol}\%$

Catalyst	Temp., °C	Yield, %		
		Ethylene	DEE	Acetaldehyde
10wt% Ag on Alumina ($100\text{m}^2/\text{g}$)	220	0	0.5	8.6
	250	0.3	2	9.2
10wt% Ag on H-Mordenite	275	0.7	8	9.4
	300	4	19.6	10.4

The maximum ethanol conversion obtained over the alumina support was only 34% compared to 78% over H-Mordenite. DEE production increased with temperature over the alumina support, whereas it decreased to almost zero at 300°C for the mordenite supported catalyst. Ethylene formation over the mordenite supported silver catalyst was much higher dehydration due to the greater acidity of mordenite compared to alumina.

Significance

The partial oxidation of ethanol over H-mordenite supported silver catalyst shows high activity and selectivity to acetaldehyde and ethylene. The results demonstrate that changing the support material significantly enhance the catalyst performance for the production of acetaldehyde from a sustainable feedstock.

References

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