

NOTE

GREEN-OIL FORMATION AND SELECTIVITY CHANGE IN SELECTIVE HYDROGENATION ON TITANIA-SUPPORTED AND UNSUPPORTED PALLADIUM CATALYST FOR ACETYLENE REMOVAL FROM ETHYLENE-RICH STREAM

Dong Keun LEE

Department of Chemical Engineering, Gyeongsang National University,
900, Kajwa-dong, Chinju 660-701, Korea

(Received 23 November 1989 • accepted 25 May 1990)

Abstract—Green-oil accumulation during the selective hydrogenation of acetylene was measured on titania-supported and unsupported catalyst, and changes in the selectivity for ethylene formation with green-oil accumulation were observed. Selectivity decrease was observed on the titania-supported catalyst where green-oil accumulated continuously after induction time, while the green-oil accumulation on the unsupported catalyst resulted in a slight increase in selectivity.

INTRODUCTION

Ethylene produced by cracking process is invariably contaminated with appreciable amounts of acetylene, and the acetylene concentration has to be reduced to a very low level in many polymerization processes [1,2]. Selective catalytic hydrogenation of acetylene to the useful ethylene is a process widely used to purify the ethylene, but in many cases excess ethylene as well as the acetylene is hydrogenated to ethane, thereby resulting in serious ethylene loss [3]. Palladium metal is known to be most suitable as a catalyst for acetylene hydrogenation with the minimum ethylene loss [4-7], and alumina-supported palladium catalysts are widely used in commercial acetylene-removal process. According to our invention [9], titania-supported palladium catalyst was proved to be highly selective for acetylene removal in the presence of excess ethylene. During the hydrogenation, oligomers (so-called green-oil) accumulate on catalysts [10-13], to reduce the catalytic activity. Green-oil is thought to accumulate on the supported and unsupported palladium catalysts in different manners, and selectivity will also depend on the pattern of green-oil accumulation. In this study, green-oil accumulation on titania-supported and unsupported catalyst was measured in a gravimetric flow system, and selectivity was discussed and interrelated with green-oil accumulation.

EXPERIMENTAL

Titania-supported palladium catalyst was prepared through the method in reference [9] and had 0.1% palladium loading. Palladium black (Strem Chemicals) was used as the unsupported catalyst. A gravimetric flow system was used to measure the amount of green-oil accumulated. About twenty milligram sample was loaded in a platinum container and was reduced with hydrogen at 300°C for 4h. Hydrogen stream was then replaced by helium and the sample was kept at the temperature for 2h. After the sample was cooled to 120°C (reaction temperature) under helium stream, reaction mixture (1% C_2H_2 , $H_2/C_2H_2 = 2$, balance C_2H_4) was flowed over the catalyst sample and the exit stream was analyzed by a G.C. (HP5710A) with Porasil B column and FID detector. Acetylene conversion was kept to be 90% for all the catalysts.

RESULTS AND DISCUSSION

Figure 1 and 2 show typical plots of the selectivity and weight increase vs. time on the titania-supported and unsupported catalyst, respectively. The selectivity was defined as the mole percentage of ethylene "produced" in the mixture of ethylene and ethane by the reaction. On the titania-supported catalyst no apparent increase in weight is observed during the first 1h after which a rapid increase occurs, while on the unsup-

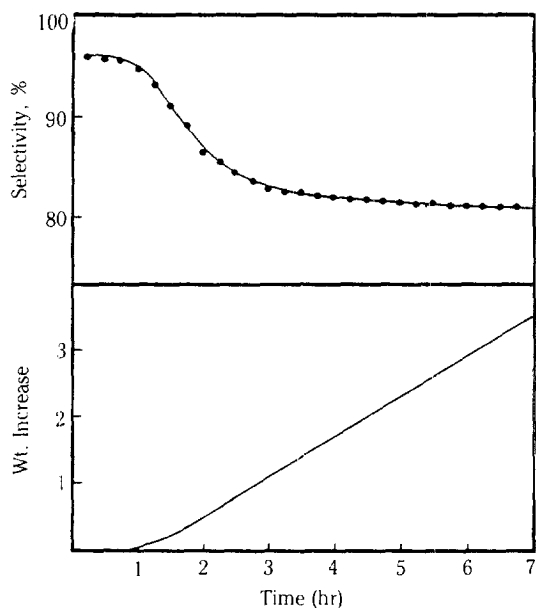


Fig. 1. Changes in selectivity and green-oil accumulation with reaction time in the titania-supported palladium catalyst.

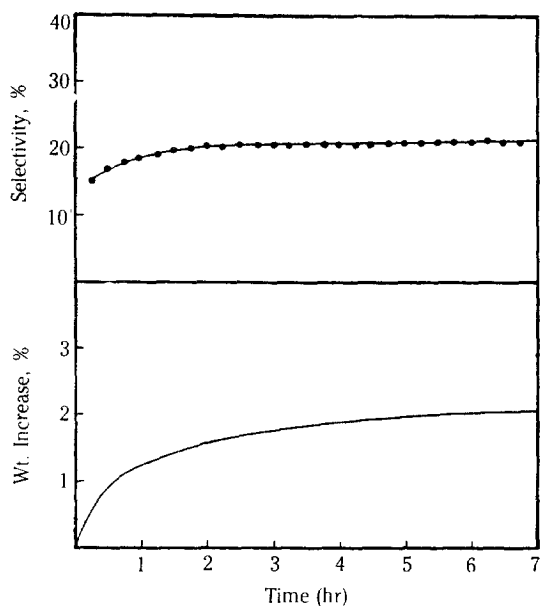


Fig. 2. Changes in selectivity and green-oil accumulation with reaction time in the unsupported palladium catalyst.

ported catalyst a rapid and significant increase is observed at the beginning of reaction after which weight increases slowly. According to the results of Sarkany et al. [14] green-oil formation was proved to be due to the dissociatively chemisorbed acetylene on palladium surface. The induction period preceding the onset of rapid weight increase would be required in order for enough dissociatively chemisorbed acetylene to oligomerize on the palladium surface. Why is the dissociative chemisorption and/or the subsequent onset of oligomerization difficult? The reason cannot be answered at present and further studies are being done in our laboratory.

The slow green-oil accumulation after the rapid and significant weight increase on the unsupported catalyst may probably be due to the saturation of palladium surface. On the titania-supported catalyst, however, the weight increases continuously after induction time. The amount of the accumulated green-oil ranged upto 30 mg/g-cat. Most of the green-oil will be adsorbed on the support, and the continuous increase in weight seems to be due to continuous migration of a primarily formed green-oil onto the nearby support.

In the unsupported catalyst selectivity increases with increasing green-oil accumulation. But the selectivity decreases on the titania-supported catalyst. Two site mechanism proposed by McGown et al. [15] seems to be a plausible explanation for the selectivity

change with green-oil accumulation on the unsupported catalyst. There existed two different active sites on palladium surface; one for the hydrogenation of both acetylene and ethylene, the other for the ethylene hydrogenation only. Green-oil will be formed primarily on the acetylene hydrogenation site because green-oil is based on dissociatively chemisorbed acetylene [14]. Acetylene, owing to its strong adsorption, may successfully compete with the accumulated green-oil upto a certain coverage. The chemisorbed acetylene is likely to push the primarily formed green-oil to the ethylene hydrogenation site, resulting in the suppression of ethylene hydrogenation. Accordingly the selectivity seems to increase with increasing accumulation of green-oil on the unsupported catalyst.

On the titania-supported catalyst, however, the selectivity change cannot be explained by the aforementioned two-site mechanism solely because the selectivity decreases with increasing accumulation of green-oil. Sarkany et al. [13] suggest hydrogen spillover through green-oil. The consequent enrichment of hydrogen in the vicinity of the Pd-support interface may enhance the hydrogenation of the excess balance ethylene adsorbed on the support. The decreasing selectivity with increasing accumulation of green-oil in the titania-supported catalyst is believed to be mainly due to the hydrogenation of the excess balance ethylene on the titania surface.

ACKNOWLEDGEMENT

This paper was supported by 1988 non-directed research fund, Korea Research Foundation.

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