Dehydrogenation of Paraffins using PtSn/Mg(Al)O: Catalyst Design and Characterization

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Introduction

Ethene, a basic building block chemical and the monomer for polyethylene, can be produced by dehydrogenation of ethane [1]. While chromia-based catalysts have been used for this purpose, they suffer from poor steam resistance and low thermal stability. For this reason, there has been an ongoing interest in developing supported Pt catalysts as an alternative. The challenge is develop a catalyst exhibiting high alkene yield, with minimal catalyst deactivation.

The effectiveness of an alkane dehydrogenation catalyst depends on the composition of the support and the active component. Gamma alumina, a conventional catalyst support, has high surface area, but its acidic sites lead to alkene conversion to coke. By contrast, Mg(Al)O is a moderately basic support, exhibiting high thermal stability and steam resistance, which make it good candidate support for alkane dehydrogenation catalysts [2]. Pt is chosen as the active component because of high activity for ethane dehydrogenation, and Sn is alloyed with Pt to increase ethene selectivity [3]. The goal of this research was to prepare, characterize, and investigate catalysts containing Pt and Sn supported on Mg(Al)O. By careful investigation of all aspects of catalyst preparation, insights were gained into the factors affecting catalyst stability, activity, and selectivity.

Materials and Methods

Hydrotalcite was synthesized by co-precipitation of $Mg(NO_3)/Al(NO_3)_3$ and $NaOH/Na_2CO_3$. After calcination at 700°C, a Mg(Al)O mixed oxide was formed. Pt and Sn were deposited onto the support using organometallic precursors. The synthesized catalysts were characterized using SEM/EDX, TEM, XRD, XAS, BET, TGA-DSC, and H_2 and CO_2 chemisorption. Catalytic tests were carried out in a tubular fixed-bed quartz reactor. Insights into the mechanism were also obtained from isotopic labeling experiments.

Results and Discussion

High surface area hydrotalcite, 300 m^2/g, was obtained by optimizing synthesis parameters, e.g., starting Mg/Al ratio, reaction temperature, co-precipitation speed, stirring condition, aging temperature and aging time. After calcination, the resulting Mg(Al)O support had a relative high surface area of 200 m^2/g and contained mesopores (117 nm). The surface basicity of Mg(Al)O correlated with Al content.

Addition of Sn to Pt/Mg(Al)O increased the selectivity to C_2H_4 but reduced the overall conversion of C_2H_6. The particle size of Pt was found to have no effect on the selectivity at a given conversion, but increasing particle size decreased the activity for a fixed Pt loading. Fig. 1 shows a TEM image of a typical PtSn catalyst. Fig. 2 shows a typical catalytic test result, showing high activitity and good stability, with more than 99% selectivity towards C_2H_4. Increasing the Sn/Pt ratio (0-0.9 at/at) increased the ethene selectivity, and the rate of ethene formation went through a maximum at Sn/Pt ~ 0.3.

Information about the mechanism of ethane dehydrogenation, as well as methane formation and catalyst coking were obtained from reaction rate studies and isotopic labeling experiments. The apparent activation energy of ethane dehydrogenation is 102 kJ/mol, and the rate of ethene formation is first order with respect to ethane. Hydrogen, co-feed with ethane, had a strong effect on catalyst activity and by-product formation, with methane and carbon being the main byproducts. Experiments in which $^{13}C_2H_4$ was co-fed with $^{12}C_2H_6$ indicated that methane was produced from both ethane and ethene. Experiments in which D_2 and C_2H_6 were fed showed D exchange into both ethene and ethane, with ethene exhibiting the greater level of exchange.

XAS characterization showed that Pt was fully reduced upon catalyst reduction in H_2. A portion of the Sn is reduced and is present as an alloy with Pt, but the remainder of the Sn was retained as SnO_2, most likely distributed on the support. With successive reduction and oxidation cycles, progressively more of the Sn appears to alloy with the Pt, contributing to a reduction in the activity of the catalyst.

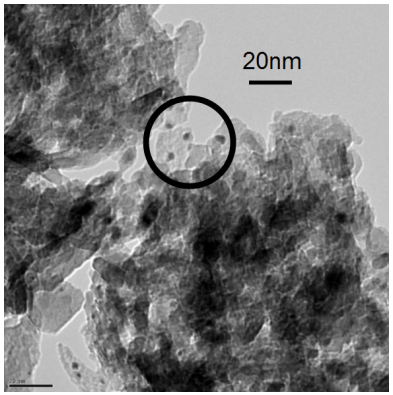

Figure 1. TEM image of PtSn nanoparticles supported on Mg(Al)O

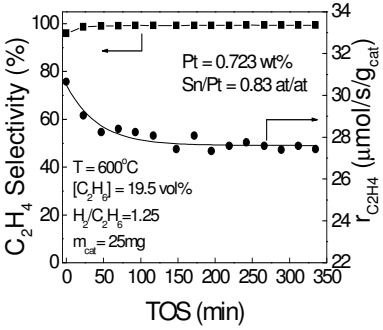

Figure 2. Catalytic activity and selectivity of PtSn-Mg(Al)O vs TOS

Significance

The results of this study provide critical insights into the role of catalyst composition and manner of preparation on the activity, selectivity, and stability of PtSn/Mg(Al)O catalysts for ethane dehydrogenation to ethene. High ethene selectivity and catalyst stability can be achieved by keeping the Sn/Pt at ~ 0.3.

References

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