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Effect of lanthanide promoters on zirconia-based isosynthesis catalysts prepared by surfactant-assisted coprecipitation

Nicholas E. McGuire, Narasimharao Kondamudi, Lucia M. Petkovic, Daniel M. Ginosar*

Interfacial Chemistry Department, Idaho National Laboratory, Idaho Falls, ID 83401, USA

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ABSTRACT

This work examines the characteristics and performance of lanthanide-promoted zirconia catalysts for synthesis of isobutene from syngas (isosynthesis). Several mixed-metal-oxide catalysts employing a range of modifier species are considered. The catalysts examined include lanthana-promoted zirconia (La-ZrO_2), ceria-promoted zirconia (Ce-ZrO_2) and lanthana–ceria–zirconia (LaCe–ZrO_2). The addition of metal promoters to zirconia is known to have an effect on the physicochemical properties of the catalyst which in turn affects catalytic performance for isosynthesis. In this work, catalyst properties are characterized via a number of diagnostic techniques including N_2 physisorption, X-ray diffraction, and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis following pyridine chemisorption. Isosynthesis activity is evaluated in a packed bed reactor configuration and the results are analyzed in terms of the physicochemical characteristics of the catalysts. Catalyst activity test results indicate that such modifiers have a strong effect on carbon monoxide conversion and selectivity to isobutene.

1. Introduction

Isosynthesis is a catalytic reaction that selectively converts synthesis gas (a mixture of hydrogen and carbon monoxide) to a product rich in branched hydrocarbons, in particular isobutene and isobutane. Isobutene has a variety of different uses but one current application of interest is oligomerization into C_8+compounds [1]. Such compounds are used as gasoline octane enhancers, jet fuel, and feedstock for plastics production. Similarly, isobutane is used as a feedstock in commercial alkylation processes [2].

Early work on isosynthesis by Pichler and Ziesecke [3] focused on using difficult to reduce oxides such as thoria, zirconia, and ceria as catalysts. They found that thorium oxide catalysts show high syngas conversions and high selectivity to isobutene at severe operating conditions. However, the radioactivity of thoria catalysts limits its use in large-scale industrial reactors. Zirconia-based catalysts are also active for isosynthesis and are widely regarded as the best non-radioactive catalyst for carrying out isosynthesis at both mild and severe conditions. Because the intrinsic isosynthesis activity of zirconia is lower than that of thoria, the properties of zirconia catalysts are often modified using catalyst promoters to improve product yield.

Recent research on isosynthesis focuses on promoting zirconia catalysts with various metal oxides to improve syngas conversion and product selectivity to isobutene. Promoters recently tested in the literature include cerium oxide [4,5], titanium oxide [6], samarium oxide [7] and aluminum oxide [8]. Researchers experimenting with the different oxides have achieved a variety of results and the range of results is often attributed to the altered physicochemical properties of the modified zirconia catalyst.

One such property is the redox property of the catalyst. Jackson and Eckerdt initially studied the effects of oxygen vacancies on isosynthesis activity by doping zirconia catalysts with yttrium and calcium oxides [9]. Several researchers have recently studied mixed ceria–zirconia catalysts for isosynthesis and found increased selectivity to C_4 hydrocarbons [5,10]. Researchers suggest that the increase in C_4 production is due to the increased oxygen mobility of the catalyst enhancing the condensation reaction [5]. The lattice oxygen mobility of cerium oxide is well documented [11,12].

Rare earth metal oxides have also been examined as possible alternatives to thoria or zirconia catalysts for isosynthesis. Kieffer et al. tested a number of rare earth metal oxides and palladium-promoted catalysts under isosynthesis conditions [13]. In particular, lanthanum oxide catalysts showed a high selectivity to isobutene. The enhanced selectivity was attributed to the increased formation on the surface of the intermediate product, methanol.

Overall surface area is also an important property to consider in the design of an effective isosynthesis catalyst. Zirconia catalysts synthesized by conventional techniques typically have surface area values on the order of 90–100 $m^2\ g^{-1}$. Originally developed for synthesizing catalysts for *n*-butane isomerization, surfactant-assisted

* Corresponding author. Tel.: +1 208 526 9049; fax: +1 208 526 8541.
E-mail address: daniel.ginosar@inl.gov (D.M. Ginosar).

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