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Synthesis of CeO_2 and $CeZrO_2$ mixed oxide nanostructured catalysts for the iso-syntheses reaction

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ABSTRACT

The different CeO_2 oxides and mixed oxide $CeZrO_2$ showed nanosized structures and morphologies in particular distinct structural and surface properties. These catalysts were effective in the iso-synthesis reaction. The flowerlike CeO_2 (F) and the mixed oxide ($CeZrO_2$) showed the highest selectivity toward isobutene and isobutene and low methane formation. The turnover frequency (TOF) related to the total basicity and total acid sites are equal for all catalysts within a factor less than 2 and did not change with the oxygen lattice capacity (OSC), which confirms that the reaction is structure insensitive. The selectivity of total hydrocarbon and of CO_2 are independent of the basic sites. However, the selectivity of total iso-C_4 exhibits a linear relationship with the basic sites. The mixed oxide ($CeZrO_2$) presented the strongest basic sites and thus the highest selectivity to iso-C_4. Significant is the influence of Lewis acid sites on the selectivity of isobutene increasing and isobutane decreasing both linearly with Lewis acid sites. The ratio isobutene/isobutane presented a linear relationship with the Lewis acid sites which are directly related to OSC capacity of reducible oxides.

1. Introduction

Syntheses gas derived from natural gas and nowadays from renewable biomass sources is promising for producing valuable aggregated products as well as hydrogen for energy or fuels specially designated to improve the quality. In particular, isobutene is an important feedstock for producing oxygenated compounds. It is produced from petroleum products which becomes limited or inadequate in near future. One potential source is based on renewable resources. From biomass or biogas the main products are methane and CO_2, which can be transformed through dry reforming to synthesis gas (CO and H_2) and subsequently converted to branched chain hydrocarbons, especially isobutene and isobutane through hydrogenation of carbon monoxide, named by Pichler and Ziesecke, as isosynthesis reaction [1]. The selective conversion of synthesis gas on metal oxides to produce alcohol, isobutane, isobutene and other derivatives has been studied by many authors under severe reaction conditions [1–4].

Shi et al. [5] studied the isosynthesis using oxides, like Samaria (SmO_2) under mild conditions, at temperatures around 450 °C and 50 atm. This catalyst presented good selectivity to iso-C_4 (above 50%). Besides ceria (CeO_2) also provided good selectivity to isobutene in C_4 hydrocarbons [6]. Some reducible oxides such as ceria promote the catalytic activity and selectivity of isobutene. Therefore, it is a suitable catalyst for isosynthesis. Mostly, zirconia and ceria have been tested for isosynthesis.

In fact, Khaodee et al. [7,8] and Reddy and Khan [9] studied the isosynthesis reaction on zirconia and ceria catalysts showing higher activity and selectivity of isobutene than the commercial catalysts. Khaodee et al. [7,8] studied the effects of preparation method and catalyst composition on the catalytic performance for the isosynthesis on ZrO_2–CeO_2 oxides mixtures and the influence of acid–base properties, as well as, the surface area on the selectivity of isobutene.

Su et al. [10], Postula et al. [11] and Feng et al. [12] observed higher catalytic performance of isobutene with zirconia oxide and concluded that the activity and selectivity depended on the acid sites and base/acid ratio, respectively, which was confirmed by Lu et al. [13]. Maruya et al. [14] claim that branched carbon chains compounds of CO hydrogenation are formed on oxide catalyst which are less or non reducible oxides.

The CeO_2 and CeO_2-based materials have been investigated for this reaction. The higher performance of cerium oxide is assigned to the redox property ($Ce^{4+} \leftrightarrow Ce^{3+}$) promoting oxygen vacancies in

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