PROPYLENE PRODUCTION THROUGH THE CO_2-ASSISTED OXIDATIVE DEHYDROGENATION OF PROPANE OVER MODIFIED SILICA BASED CATALYSTS

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Propylene (C_3H_6) is one of the most important building blocks of the petrochemical industry as it is essential for the production of a wide range of chemicals such as polypropylene, acrylonitrile and propylene oxide. In recent years, the catalytic oxidative dehydrogenation of propane (C_3H_8) using a mild oxidant such as CO_2 (CO_2-ODP) has gained interest as an efficient and eco-friendly process for C_3H_6 production because it not only produces propylene but also utilizes the CO_2 emissions, thus contributing to the mitigation of the greenhouse effect. Furthermore, adding CO_2 in the gas stream can shift the equilibrium towards C_3H_6 production by consuming the produced H_2 via the Reverse Water-Gas Shift (RWGS) reaction, while simultaneously can inhibit coke deposition by promoting the reverse Boudouard reaction, thus preventing catalyst deactivation. However, depending on the catalyst and reaction conditions employed, the reactions of propane hydrogenolysis and propane or propylene decomposition may also take place, resulting in a decrease of propylene yield and possibly coke formation, which has a significant impact on the life-time of catalyst. Thus, the physicochemical characteristics of catalyst and operating conditions should be properly selected. In the present study, the production of propylene via the CO_2-ODP reaction was studied over 10%M_xO_y-SiO_2 (M: Ga, Cr, Ca, Sn) catalysts. The effect of the physicochemical properties of catalysts on their ability to promote both high propane conversions and propylene yields was investigated and discussed. An attempt was made to optimize the operating parameters (temperature, space velocity and CO_2:C_3H_8 molar ratio) in order to increase the process efficiency.

Composite metal oxide powders 10 wt.% M_xO_y-SiO_2 (M: Ga, Cr, Ca, Sn) were prepared employing the wet impregnation method and characterized with respect to their specific surface area and pore volume, phase composition and crystallite size as well as surface basicity and acidity by means of B.E.T., X-Ray Diffraction (XRD), temperature programmed desorption of CO_2 (CO_2-TPD) and pyridine adsorption/desorption experiments, respectively. Catalytic performance tests were carried out in a fixed-bed flow reactor loaded with 0.5 g of catalyst and using a feed stream consisting of 5%C_3H_8+25%CO_2 (in He) with a total flow rate of 50 $cm^3\ min^{-1}$.

Results showed that the surface acidity and basicity were affected by the nature of M_xO_y additive, which in turn affected the conversion of propane to propylene which was in all cases higher compared to that of bare SiO_2. Specifically, both $X_{C_3H_8}$ and $Y_{C_3H_6}$ were notably increased by a factor of 5 and 6.8, respectively, at temperatures of practical interest following the order (bare) $SiO_2 < SnO_2\text{-}SiO_2 \sim CaO\text{-}SiO_2 < Ga_2O_3\text{-}SiO_2 < Cr_2O_3\text{-}SiO_2$. Propane conversion, reaction rate and selectivities towards propylene and carbon monoxide were maximized for the Ga- and Cr-containing catalysts characterized by moderate surface basicity, which were also able to limit the undesired reactions leading to ethylene and methane byproducts (Fig.1). High surface acidity was found to be beneficial for the CO_2-ODP reaction, which, however, should not be excessive to ensure high catalytic activity. The time on stream stability tests conducted over Ga_2O_3-SiO_2 and Cr_2O_3-SiO_2 catalysts showed that the former one exhibited sufficiently stable performance after about 22 hours on stream, while the latter presented a decrease of initial propane conversion during the first 5 hours which was smoothed out for longer time of catalyst interaction with the gas stream. However, both catalysts exhibited excellent stability with respect to the selectivity towards propylene production.

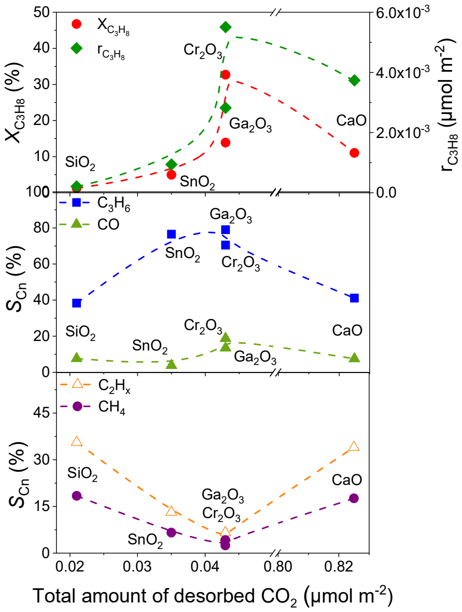

Figure 1. Propane conversion, reaction rate and products selectivities at 610 °C as a function of the total amount of desorbed CO_2 during CO_2-TPD experiments for SiO_2 and 10%M_xO_y-SiO_2 catalysts.

Decreasing the weight gas hourly space velocity (WGHSV) resulted in a significant improvement of both propane conversion and propylene yield as well as a suppression of undesired products formation. Increasing CO_2 concentration in the feed did not practically affect propane conversion, while led to a decrease of propylene yield. The ratio of propylene to ethylene selectivity was optimized for CO_2:C_3H_8 = 5:1 and WGHSV=6,000 mL g^{-1} h^{-1}, most possibly due to facilitation of the C–H bond cleavage against that of C–C bond. DRIFTS studies indicated that the adsorption/activation of CO_2 under reaction conditions was enhanced by the addition of Cr_2O_3 or Ga_2O_3 on SiO_2 surface due to the higher surface basicity characterized these samples. Results of the present study provided evidence that the efficient conversion of propane to propylene is feasible over silica-based composite metal oxides provided that catalyst characteristics have been optimized and reaction conditions have been properly selected.

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