CO_2-assisted oxidative dehydrogenation of propane over Ga_2O_3-SiO_2, Ga_2O_3-TiO_2 and Ga_2O_3-Al_2O_3 catalysts

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Introduction. Among various processes that have been proposed for the production of propylene (C_3H_6), which ranks among the most critical building blocks for the industrial production of numerous chemical compounds, is the oxidative dehydrogenation of propane (C_3H_8) using a mild oxidant like CO_2 (ODP-CO_2). This approach is considered to be attractive due to (a) the abundant availability of C_3H_8 contained in shale gas condensates which can be easily extracted in large scale and (b) the utilization of CO_2 which participates both in C_3H_8 conversion towards C_3H_6 and the consumption of H_2 via the RWGS reaction, contributing to the reduction of CO_2 emissions and therefore, the mitigation of global warming [1]. In the present study, the influence of the support nature (Al_2O_3, TiO_2, SiO_2) on the activity and stability of supported Ga_2O_3 catalysts was investigated for the CO_2-ODP reaction.

Experimental. Gallium based composite metal oxides (10%Ga_2O_3-M_xO_y) were synthesized by the incipient wetness impregnation method and characterized employing BET, XRD, CO_2-TPD, TPO, TGA, TEM and SEM techniques. Catalytic performance tests were carried out in the temperature range of 500-750 °C using a CO_2:C_3H_8 molar ratio of 5:1.

Results and discussion. Catalytic activity was found to be higher when gallium oxide was dispersed on alumina support. Although this catalyst was characterized by the highest acid site density, surface acidity does not seem to be the key physicochemical property determining ODP activity. A moderate surface basicity was found to be beneficial for the achievement of high C_3H_6 yields at temperatures of practical interest. Ga_2O_3-TiO_2 and Ga_2O_3-SiO_2 exhibited sufficient stability for 35 hours on stream at 660 and 710 °C, contrary to Ga_2O_3-Al_2O_3 which although was found to be stable at 710 °C it was gradually deactivated when the reaction occurred at 600 °C. Coke formation was favored over Ga_2O_3-Al_2O_3 catalyst which may be related to the higher surface acidity of this sample and be responsible for its deactivation with time. SEM images and elemental mapping obtained from both the as prepared and used samples showed that Ga and M (M: Si, Ti, Al) were uniformly present even after prolonged catalyst interaction with the gas stream. EDS analysis indicated that carbon formation was accelerated with increasing reaction temperature. No carbon formation was detected by conducting TEM and XRD experiments over all "spent" catalysts providing evidence that the so formed carbon was amorphous.

Significance of work. The significance of this work lies in (a) the development of active catalysts with sufficient stability for 35 hours on stream contrary to previous studies where a rapid catalyst deactivation was observed and (b) the identification of key physicochemical properties that determines catalytic activity and catalysts' tendency to coke formation.

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References

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