Propylene production via oxidative dehydrogenation of propane with carbon dioxide over composite metal oxides

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Introduction. Propylene (C_3H_6) is a versatile precursor for the formation of various derivatives (e.g. polypropylene, acrylic acid, acrylonitrile, cumene etc.) used in our daily life and thus, it is considered as a key component of the chemical industry [1]. Oxidative dehydrogenation of propane (C_3H_8) in the presence of CO_2 has recently gained interest as an alternative approach for the selective production of C_3H_6. This approach has the advantage that CO_2 participates both in (a) C_3H_8 conversion toward C_3H_6 and (b) hydrogen consumption via the Reverse Water-Gas Shift (RWGS) reaction [2]. Removing hydrogen from the gas stream can overcome the equilibrium limitations of C_3H_8 dehydrogenation, resulting in higher C_3H_6 yields. However, depending on the catalyst and reaction conditions employed, the reactions of C_3H_8 hydrogenolysis and C_3H_8 or C_3H_6 decomposition may also take place, resulting in a decrease of C_3H_6 yield and possibly surface carbon formation. Thus, in order for this method to be effective, the physicochemical characteristics of catalyst and operating reaction conditions should be properly selected.

Experimental/methodology. Composite metal oxide powders 10 wt.% M_xO_y-TiO_2 and 10 wt.% M_xO_y-SiO_2 (M: Ga, Cr, Ca, Sn) were prepared employing the wet impregnation method by using commercial TiO_2 or SiO_2 powder and an aqueous solution of the M_xO_y precursor salt. The impregnation was followed by drying at 120 °C for 24 h and subsequent calcination at 600 °C for 3 h. Catalysts were characterized employing nitrogen physisorption at -196°C and X-Ray Diffraction (XRD). Catalytic performance tests were carried out in the temperature range of 550-750°C using a CO_2:C_3H_8 molar ratio equal to 5:1.

Results and discussion. Results showed that the addition of metal oxides on TiO_2 or SiO_2 surface results in higher C_3H_8 conversions (X_{C3H8}) compared to bare TiO_2 or SiO_2. In the case of M_xO_y-TiO_2 catalysts, catalytic performance is improved following the order TiO_2 (none)< SnO_2 < Cr_2O_3 < Ga_2O_3 < CaO, whereas in the case of M_xO_y-SiO_2 catalysts, the activity order was found to be SiO_2 (none) < CaO < Ga_2O_3 < SnO_2 < Cr_2O_3. In all cases the main products detected were C_3H_6, CO, CH_4 και C_2H_4. Selectivity toward C_3H_6 (S_{C3H6}) was found to be higher for Ga_2O_3-TiO_2, Cr_2O_3-TiO_2, Cr_2O_3-SiO_2 and SnO_2-SiO_2 catalysts and progressively decreases with increasing temperature for all catalysts examined with the exception of the CaO containing samples, where S_{C3H6} remains stable in the entire temperature range examined. Carbon monoxide selectivity also decreases with increasing temperature above 660 °C and was found to be higher for CaO-TiO_2 and CaO-SiO_2 catalysts. Production of both CO και C_3H_6 indicates that, under the present experimental conditions, the desired reaction of oxidative dehydrogenation of propane takes place whereas part of the produced CO may be due to the RWGS reaction. Selectivities toward CH_4 και C_2H_4 exhibit similar behavior with temperature and increases slightly for T>650 °C, most possibly due to enhancement of their production via C_3H_8 hydrogenolysis and C_3H_8 or C_3H_6 decomposition reactions. Comparison of the results obtained for the two series of catalysts investigated implied that M_xO_y-SiO_2 catalysts are more active than M_xO_y-TiO_2 and exhibit significantly higher improvement compared to bare SiO_2 than that obtained for M_xO_y-TiO_2 samples. This is also the case for propylene yield which was found to be optimum for SnO_2-SiO_2 sample reaching the value of 30% at 730°C. DRIFTS studies have been also performed over selected catalysts in order to identify the nature and population of active surface intermediates and investigate the reaction pathway.

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