Utilization Of CO_2 As A Mild Oxidant For Propylene Production Via Oxidative Dehydrogenation Of Propane

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1. Introduction

Propylene (C_3H_6) is a versatile precursor for the formation of various derivatives used in our daily life (e.g. polypropylene, isopropanol, acrylonitrile etc.) and thus, it is consider as a key component of the chemical industry [1]. One of the traditional methods used for propylene production is the reaction of propane (C_3H_8) dehydrogenation, which is strongly endothermic and equilibrium limited [2]. The reaction requires high temperatures, and therefore high energy consumption, suffering from fast catalyst deactivation as well as low C_3H_8 conversions and C_3H_6 selectivities [3]. Oxidative dehydrogenation of propane in the presence of molecular oxygen has been proposed as an alternative pathway, which is an exothermic reaction, with no thermodynamic limitations, and operable at low reaction temperatures. The main drawback of the process is the deep oxidation of both C_3H_8 and C_3H_6 toward carbon monoxide (CO) and carbon dioxide (CO_2), resulting in low propylene yields [3]. Thus, replacing of molecular oxygen by a milder and readily available oxidant, such as CO_2, has recently gained interest as an alternative approach for selective propylene production [3]. This approach has the advantage that CO_2 participates both in (a) propane conversion toward propylene and (b) hydrogen consumption via the RWGS reaction, which can overcome the equilibrium limitations of propane dehydrogenation, resulting in higher propylene yields. Moreover, carbon monoxide produced via both reactions is a valuable byproduct, which can be utilized in chemical synthesis. The major benefit of the proposed process is the utilization of CO_2, the emissions of which in the atmosphere have increased rapidly during the last decades and, in nowadays, it is considered as one of the main greenhouse gases resulting in global warming and therefore, major climate changes [4]. 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 surface carbon formation [5]. Thus, the physicochemical characteristics of catalyst and operating conditions should be properly selected. In the present study the oxidative dehydrogenation of propane (ODP) with CO_2 was studied over $10\%M_xO_y$-TiO_2, $10\%M_xO_y$-Al_2O_3 and $10\%M_xO_y$-SiO_2 (M: Ga, Cr, Ca, Sn) catalysts. The ability of composite metal oxides to promote both high propane conversions and propylene yields with respect to the nature of M_xO_y additive and the support was investigated and discussed.

2. Experimental

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Composite metal oxide powders 10 wt.% M_xO_y-TiO_2, 10 wt.% M_xO_y-Al_2O_3 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, Al_2O_3 or SiO_2 powders as supports and an aqueous solution of the M_xO_y precursor salt ($Ga(NO_3)_3 \cdot 6H_2O$, $Cr(NO_3)_3$, $Ca(NO_3)_2 \cdot 4H_2O$, $SnCl_2 \cdot 2H_2O$). The impregnation was followed by drying at 120 °C for 24 h and subsequent calcination in air at 600 °C for 3 h. Catalysts were characterized employing X-Ray Diffraction (XRD) and B.E.T measurements. Catalytic performance experiments 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 cc/min. In a typical experiment the catalyst was first preheated under He flow at 450 ^oC for 1 h followed by a switch of the gas stream to the reaction mixture. The concentrations of reactants and products are then determined using a gas chromatograph. Similar measurements are obtained following a stepwise increase of temperature up to 750 ^oC.

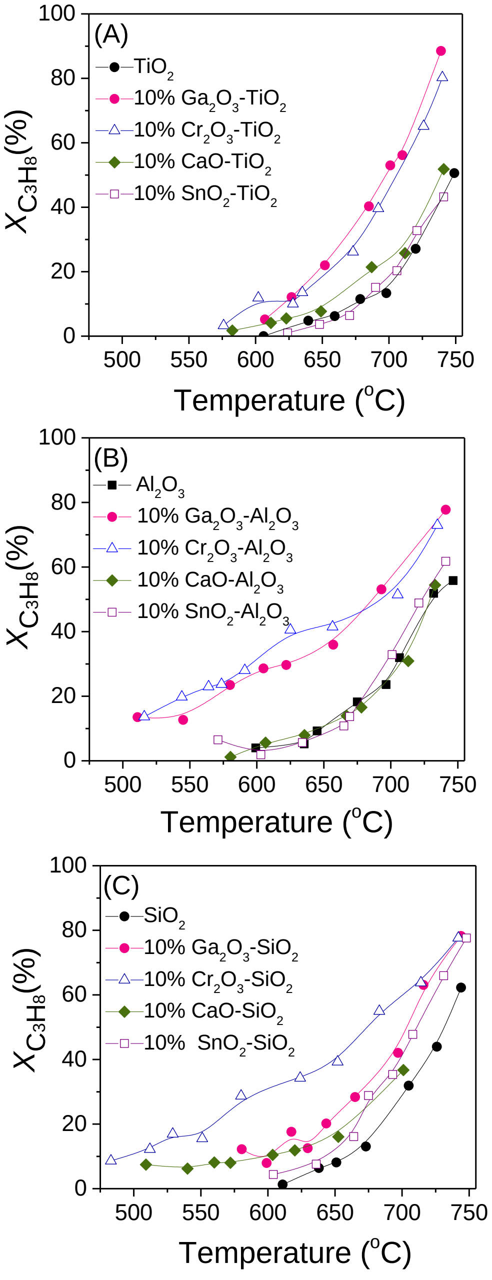

Figure 1. Conversion of propane as a function of reaction temperature obtained over (A) M_xO_y-TiO_2 (B) M_xO_y-Al_2O_3 and (C) M_xO_y-SiO_2 for the ODP reaction.

3. Results

The specific surface area (SSA) of composite metal oxides was determined with the BET method. The SSA of bare TiO_2, Al_2O_3 and SiO_2 were found equal to 36.9, 95.7 and 222.1 m^2 g^{-1}, respectively. In the case of TiO_2-based oxides the SSA was varied between 33.9 m^2 g^{-1} for CaO-TiO_2 and 47.9 m^2 g^{-1} for Ga_2O_3-TiO_2. The addition of Cr_2O_3, Ga_2O_3, SnO_2 and CaO on Al_2O_3 surface resulted in a reduction of the SSA compared to that of bare alumina and was found equal to 77.9, 73.1, 71.1 and 35.7 m^2 g^{-1}, respectively. The SSA of SiO_2-based oxides was varied between 109.9 m^2 g^{-1} for CaO-SiO_2 and 220.9 m^2 g^{-1} for Cr_2O_3-SiO_2. XRD results showed that the diffractograms obtained for the Al_2O_3-based oxides are characterized by the crystallographic peaks attributed to cubic Al_2O_3. In the case of TiO_2-based oxides the presence of both anatase and rutile phases were identified in the obtained XRD spectra, whereas for SiO_2-based oxides no sharp peaks corresponding to SiO_2 were discerned. The presence of SiO_2 was only confirmed by some relatively broad peaks in the case of bare SiO_2, Ga_2O_3-SiO_2 and CaO-SiO_2 samples.

Results of catalytic performance experiments showed that the addition of metal oxides on TiO_2, Al_2O_3 or SiO_2 surface results, generally, in higher C_3H_8 conversions (X_{C3H8}) compared to bare TiO_2, Al_2O_3 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 < CaO < Cr_2O_3 < Ga_2O_3 (Fig. 1A). The addition of metal oxides on TiO_2 surface also results in higher propylene yields compared to bare TiO_2, with Ga_2O_3-TiO_2 sample reaching the value of 17.7% at 710 ^oC. In the case of M_xO_y-Al_2O_3 catalysts, catalytic activity is significantly improved for Ga_2O_3-Al_2O_3 and Cr_2O_3-Al_2O_3 samples (Fig. 1B) whereas propane conversion curves for SnO-Al_2O_3 and CaO-Al_2O_3 were found to be identical with that of bare Al_2O_3. Propylene yield was found to be higher for Cr_2O_3-Al_2O_3 sample reaching the value 19.5% at 625 ^oC. The catalytic performance for M_xO_y-SiO_2 catalysts increases in the order SiO_2 (none) < CaO < SnO_2 < Ga_2O_3 < Cr_2O_3 (Fig. 1C). Propylene yield is also improved with the addition of M_xO_y on SiO_2 surface, with SnO_2-SiO_2 exhibiting the superior value of 30% at 730 ^oC. 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 the catalysts containing Ga_2O_3 and Cr_2O_3 and progressively decreases with increasing temperature for all catalysts examined with the exception of the CaO containing samples where S_{C3H6} remains almost stable in the entire temperature range examined. Carbon monoxide selectivity also decreases with increasing temperature above 660 ^oC and was found to be higher for CaO-TiO_2 catalysts. Production of both CO and 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 temperatures higher than 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. For M_xO_y-SiO_2 catalysts S_{CH4} and S_{C2H4} at a given temperature decrease significantly when a metal oxide is added on SiO_2 surface implying that the aforementioned side reactions are suppressed with the use of SiO_2-based composite oxides. This is also the case for Ga_2O_3-Al_2O_3, Cr_2O_3-Al_2O_3 and CaO-TiO_2 samples at low reaction temperatures. Comparison of the results obtained for the three series of catalysts investigated showed that Al_2O_3- and SiO_2-based composite oxides exhibit higher C_3H_8 conversions compared to M_xO_y-TiO_2 samples. Propylene yields are generally higher when M_xO_y is dispersed on TiO_2 or SiO_2 surface compared to Al_2O_3 with the exception of Ga_2O_3-Al_2O_3 catalyst which exhibited optimum performance with Y_{C3H6} =19% already at 600 ^oC.

4. Conclusions

Results of the present study showed that catalytic performance for the ODP reaction with CO_2 is significantly improved with the addition of metal oxides on TiO_2, Al_2O_3 or SiO_2 surface. Both catalytic activity and C_3H_6 yield depend strongly on the nature of M_xO_y with the Ga_2O_3 and Cr_2O_3 containing samples exhibiting superior performance. Simultaneous production of both C_3H_6 and CO indicates that oxidative dehydrogenation of propane and RWGS reaction take place in parallel. The undesired reactions of C_3H_8 hydrogenolysis and C_3H_8 or C_3H_6 decomposition leading to CH_4 and C_2H_4 production can be significantly suppressed with the addition of the appropriate metal oxide on TiO_2, Al_2O_3 or SiO_2 surface.

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