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Selection of optimum chromium oxide-based catalysts for propane oxidehydrogenation

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Abstract

Propane oxidative dehydrogenation has been studied at 350–500 °C, 1.0 bar and feed flow rate of 75 cm^3/min over several supported chromium oxide-based catalysts. Effects of various chromium loadings, different supports, catalyst precursors and reaction conditions were investigated in an attempt to select an optimum catalyst for the reaction. Chromium oxides of different loadings ranging from 0.1 to 20 wt.% on γ-Al_2O_3 were tested. At 450 °C, 10 wt.% loading exhibited propane conversion of 19%. γ-Al_2O_3 gave the best performance when MgO, TiO_2, SiO_2 and γ-Al_2O_3 were tested as supports. As a precursor, $Cr(NO_3)_3{\cdot}9H_2O$ exhibited the best results compared with $K_2Cr_2O_7$, $CaCr_2O_7$, $Na_2Cr_2O_7$, $Cr_2SO_4{\cdot}12H_2O$ and CrO_3. Effects of reaction temperatures and feed compositions were also evaluated on a 10 wt.% Cr-Al-O catalyst. The maximum selectivity to propene obtained was 61% while the yield was 18%. The 10 wt.% Cr-Al-O catalyst was characterized by X-ray diffraction patterns (XRD), temperature-programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS) which confirmed the presence of both Cr^{3+} and Cr^{6+} in the calcined catalyst and, also, the predominance of Cr^{3+} in the spent catalyst.

Keywords: Oxidative dehydrogenation; Propane; Propene; Ethene; Chromium oxide catalysts; XPS; XRD

1. Introduction

Catalytic oxidative dehydrogenation of propane has received extensive research efforts in recent years. This drive is partly due to increasing demand of propene in the international market. Another motivation for the attempt to convert propane to propene is the general tendency of the petrochemical industry to utilize the abundant, cheap and environment-friendly alkane as feedstocks. Several promising catalytic systems for the reaction have emerged. The most studied catalysts for propane conversion are based on vanadium [1,2], metal molybdates [3,4] and phosphates [5]. So far, all catalysts in the open literature need further studies to improve their performances. On some of these catalysts, a selectivity of 63% was obtained at a propane conversion of 7% [6] and propene yield of 23.9% at selectivity of 38% [7]. Previous attempts to improve V-Mg-O catalyst did not result in significant change [8]. Other catalytic systems such as metal molybdates gave maximum propene yield of 15% [4]. This was improved to 16–18% on B-Al-O catalyst [9]. Design of catalysts to give high propene yields at propene selectivities higher than 70%, for instance, is believed to be a challenging task in this area of research [9–11].

In an earlier study, the activities of some γ-Al_2O_3 supported transition metals oxides for propane

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oxidative dehydrogenation (POD) was investigated [12]. The catalysts were found to catalyze the reaction at 350–450 °C, 1 bar and feed flow rate of 75 cm^3/min. The feed was composed of a mixture of C_3H_8, O_2 and He at a molar ratio of 4:1:10, respectively. Among the catalysts, alumina supported chromium oxide was found to exhibit good performance. At 350 °C, the propane conversion was 8.5% and selectivity to C_3H_6 was 41.4% and at 450 °C, the conversion was 16.7% and selectivity to C_3H_6 was 54.1%. Chromium oxide on different supports has also been reported to be active and selective in the oxidative dehydrogenation of isobutane at relatively low temperatures (200–300 °C) [13,14]. Chromium and vanadium have been shown to promote the catalytic performance of niobium oxide for POD [8]. Recently, chromium oxide-based catalysts have been reported to be active in oxidative dehydrogenation of ethane [15]. Apart from these, studies of oxidative dehydrogenation of alkanes on Cr-based catalytic systems are scarce in the literature.

In this paper, supported chromium oxide catalysts have been tested for POD. Studies were conducted on the effects of chromium loadings, different supports, precursors and reaction conditions on the performance of the catalysts in an attempt to select an optimum catalyst for the reaction. In order to have more understanding of the activity and selectivity, X-ray diffraction patterns (XRD), temperature-programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS) have been used to characterize samples of the catalysts.

2. Experimental

2.1. Catalysts preparation

All catalysts were prepared using the impregnation method. Catalysts of different loadings were prepared by impregnating γ-Al_2O_3 (200 m^2/g, 50–200 μm, Riedel De Haen AG31182) with chromium(III) nitrate-hydrate ($Cr(NO_3)_3\cdot 9H_2O$, Riedel De Haen 12232) in a continuous stirred vessel. The content of the vessel was dried over night at 100 °C and calcined at 600 °C for 3 h. The chromium content was varied to obtain catalysts of different loadings of chromium(III) oxide, viz. 0.1, 0.2, 0.5, 2.0, 5.0, 10.0 and 20.0 wt.% on the γ-Al_2O_3. Unsupported chromium(III) oxide was also prepared.

Table 1
Catalysts with their compositions, supports and precursors prepared using impregnation method

Catalyst	Composition (wt.%)	Support	Precursor
0.1% Cr-Al-O	0.1	γ-Al_2O_3	$Cr(NO_3)_3\cdot 9H_2O$
0.2% Cr-Al-O	0.2	γ-Al_2O_3	$Cr(NO_3)_3\cdot 9H_2O$
0.5% Cr-Al-O	0.5	γ-Al_2O_3	$Cr(NO_3)_3\cdot 9H_2O$
2.0% Cr-Al-O	2.0	γ-Al_2O_3	$Cr(NO_3)_3\cdot 9H_2O$
5.0% Cr-Al-O	5.0	γ-Al_2O_3	$Cr(NO_3)_3\cdot 9H_2O$
10% Cr-Al-O	10.0	γ-Al_2O_3	$Cr(NO_3)_3\cdot 9H_2O$
20% Cr-Al-O	20.0	γ-Al_2O_3	$Cr(NO_3)_3\cdot 9H_2O$
Unsupported Cr_2O_3	–	N/A	$Cr(NO_3)_3\cdot 9H_2O$
10% Cr-Mg-O	10.0	MgO	$Cr(NO_3)_3\cdot 9H_2O$
10% Cr-Si-O	10.0	SiO_2	$Cr(NO_3)_3\cdot 9H_2O$
10% Cr-Ti-O	10.0	TiO_2	$Cr(NO_3)_3\cdot 9H_2O$
CrN	10.0	γ-Al_2O_3	$Cr(NO_3)_3\cdot 9H_2O$
CrK	10.0	γ-Al_2O_3	$K_2Cr_2O_7$
CrCa	10.0	γ-Al_2O_3	$CaCr_2O_7$
CrNa	10.0	γ-Al_2O_3	$Na_2Cr_2O_7$
CrO	10.0	γ-Al_2O_3	CrO_3
CrS	10.0	γ-Al_2O_3	$Cr_2SO_4\cdot 12H_2O$

Using chromium nitrate as a precursor, a group of 10 wt.% catalysts was prepared by impregnating the precursor on different supports, e.g. MgO (BDH, AnalaR), SiO_2 (Sigma, S-5631), and TiO_2 (BDH). Using γ-Al_2O_3 as a support, various 10 wt.% catalysts were prepared from different precursors; $K_2Cr_2O_7$ (Fluka), $CaCr_2O_7$ (BDH), $Na_2Cr_2O_7$ (BDH), CrO_3 (BDH) and $Cr_2SO_4\cdot 12H_2O$ (Fisher). The catalysts with their compositions, supports and precursors are summarized in Table 1. For simplicity, catalysts are represented as X wt.% Cr-M-O, where X is the weight percent and M is the metal in support.

2.2. Catalysts characterization

2.2.1. X-ray diffraction

Powder XRD patterns were recorded at room temperature using a Cu Kα radiation and a Siemens diffractometer. A suitable amount of the catalyst sample was mixed with vaseline and the mixture was evenly distributed on a thin glass plate and put into the diffractometer.

2.2.2. X-ray photoelectron spectroscopy

The XPS spectra were measured and recorded by a VG Scientific ESCA-3 photoelectron spectrometer using Al Kα radiation (1486.6 eV) operating at 13 kV and 10 mA. The operating pressure was less than 2.6×10^{-11} bar. A take-off angle of 45° was used. The C 1s peak from the carbon surface deposit at 284.8 eV was used as a reference for the binding energy.

2.2.3. *Temperature-programmed reduction*

TPR experiments were carried out in a system supplied by Ohkura Riken Co. Ltd. (model TP-2000). At first, 150 mg of catalyst sample was placed in a quartz tube (8.0 mm o.d.) reactor and was held in the middle by quartz wool plugs. The samples were pretreated in flowing dry air (30 cm^3/min). The temperature was raised to 400 °C at a heating rate of 10 °C/min and held at 400 °C for 2 h, and then cooled to ambient temperature. The gas mixture used for reduction was 5% H_2 in Ar at a flow rate of 20 cm^3/min. The temperature was increased linearly from room temperature to 1030 °C at a heating rate of 10 °C/min and then retained isothermally for 15 min. Water formed either by reduction or from dehydration process was trapped by a 5 Å molecular sieve. The hydrogen concentration was determined with a thermal conductivity detector (TCD). The TCD and molecular sieve trap were thermostated at 50 ± 0.1 °C. The temperature of the catalyst and the TCD current response were continuously monitored and recorded on a dedicated personal computer (NEC model PC9821-Xe10).

2.3. *Catalysts testing*

The method for testing the catalysts was reported elsewhere [12]. All catalysts were tested using a feed flow rate of 75 cm^3/min (molar ratio of C_3H_8:O_2:He = 4:1:10) at atmospheric pressure. The effect of reaction temperature was investigated up to 500 °C on one catalyst sample. At 450 °C, the effects of varying the partial pressure of propane and oxygen in the feed were further studied. Both fuel-rich (i.e. oxygen was the limiting reactant) and fuel-lean (i.e. propane was the limiting reactant) sides with respect to flammability limit for the propane/oxygen mixture have been considered. The propane partial pressure was varied from 0.07 to 0.53 bar at a fixed oxygen pressure of 0.07 bar. Then propane pressure was fixed at 0.27 bar while oxygen pressure was varied from 0.07 to 0.20 bar. Triplicate runs of each experiment were conducted. The highest variations between identical runs were about ±6%. The values reported in the paper are the average values for each experiment. Carbon balances were typically better than 95%. Conversion is defined as the mole fraction of feed carbon present in the reaction products relative to feed carbon, while selectivity is the fraction of product carbon in a particular product relative to reacted feed carbon.

3. Results

3.1. *Catalysts characterization*

The XRD pattern of the 10 wt.% Cr-Al-O catalyst, produced from chromium nitrate, shows the dominant reflections attributed to γ-alumina and those of chromium(III) oxide. Fig. 1a and b show the XPS curve-fitted multiplex spectra in the Cr 2p region of the calcined and spent 10 wt.% Cr-Al-O catalyst, respectively. Fig. 1a for the calcined catalyst shows the presence of both Cr^{3+} (main contribution at a binding energy of about 577 eV) and Cr^{6+} (binding energy of about 579 eV). Spin–orbit splitting [16], due to the unpaired d-electron in the valence levels, results in two peaks for each chromium species (curves A and B for Cr^{3+} and curves C and D for Cr^{6+}). These values are consistent with the results obtained for a similar system in the literature [17]. Fig. 1b shows the predominance of Cr^{3+} in the spent catalyst, thus indicating the reduction of Cr^{6+} to Cr^{3+} (only curves A and B for Cr^{3+} are present). Similar observation was reported in the literature where the Cr^{6+} was reduced to Cr^{3+} in the reaction environment [17]. It appears that dispersed Cr^{3+} is the active species in the reaction. The Cr/Al ratio of 0.2 suggests that Cr_2O_3 was well dispersed in the sample. This is approximately the same Cr/Al ratio in the catalyst bulk as in the preparation. The amount of Cr_2O_3 required for monolayer has been reported to be about 12 wt.% [18]. This depends on the preparation method, calcination temperature and nature of dopants [10]. Such factors have been shown to cause different components ratios between the bulk and surface of the catalysts [10].

Fig. 2 shows the TPR profile for (i) 10 wt.% Cr-Al-O and (ii) 10 wt.% Cr-Mg-O. Their peak maxima temperatures are 285 and 429 °C, respectively. The Cr-Mg-O shows a small peak at 360 °C. The profile of the Cr-Mg-O indicates that there are two

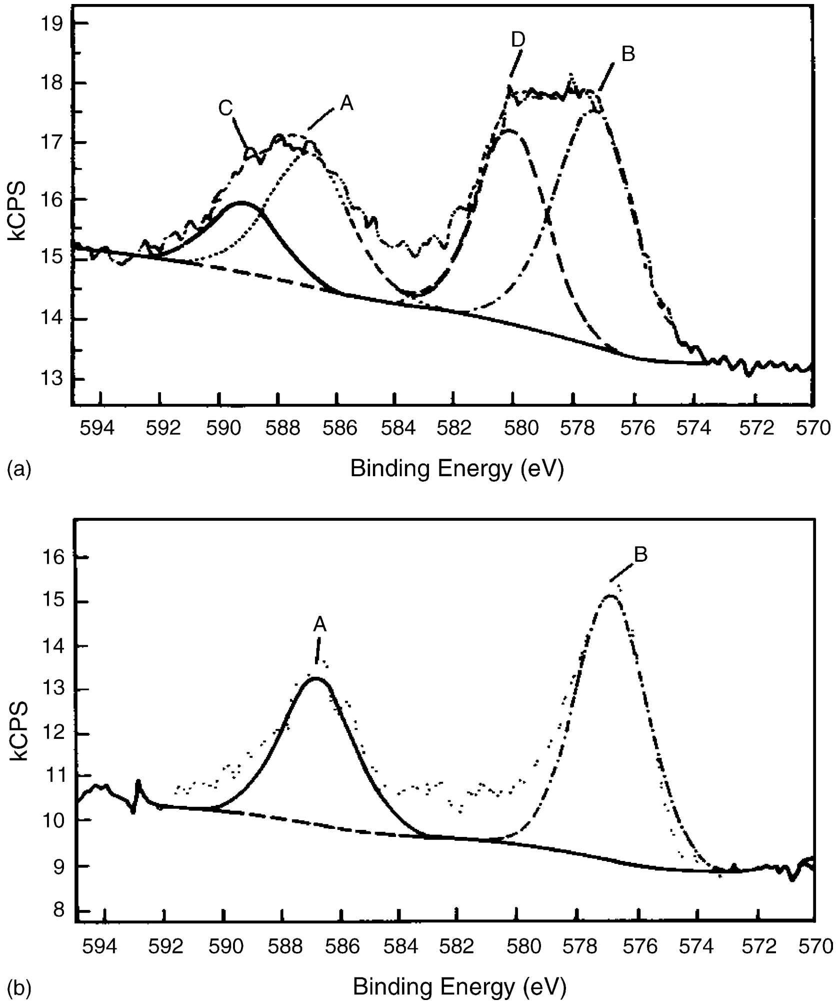

Fig. 1. XPS multiplex spectrum for: (a) calcined 10 wt.% chromium(III) oxide/γ-Al_2O_3 catalyst; (b) spent 10 wt.% chromium(III) oxide/γ-Al_2O_3 catalyst.

distinct chromium sites of lower reducibility than Cr-Al-O. These may be attributed to chromium species having different dispersions and coordination symmetry in the catalyst.

3.2. Catalytic tests

Figs. 3–8 show the results of catalytic activities of the tested samples. The effects of loading of the active component (Fig. 3), nature of supports (Fig. 4), type of chromium precursor (Fig. 5) and reaction conditions (Figs. 6–8) have been investigated. The major products were propene, ethene, CO_2 and CO. The differences of the amounts of the active components seems to be more important at high reaction temperatures. The reducibility of the catalysts due to the nature of chromium–support interactions determine the propane conversions and products distribution. For instance, catalysts prepared from alkali and alkaline earth metals-based precursors exhibited lower performance than those prepared from chromium nitrate or oxide (see Fig. 5). When the reaction temperature was varied from 350 to 500 °C on 10 wt.% Cr-Al-O, propane conversions increased with corresponding

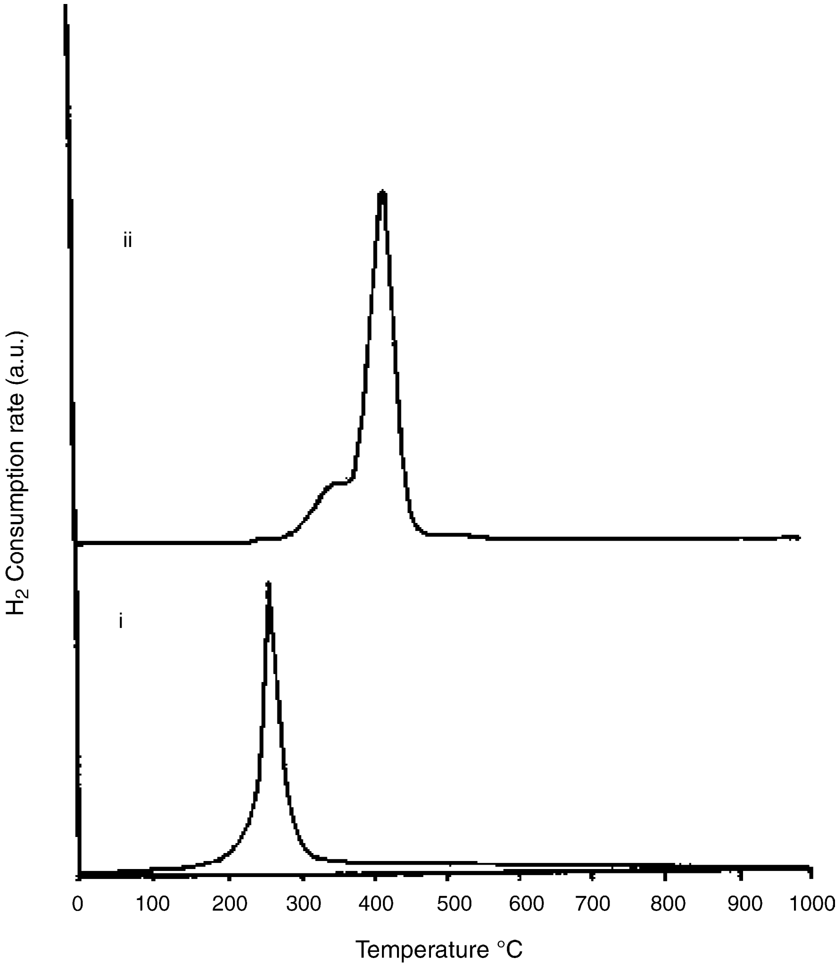

Fig. 2. TPR profile of 10 wt.% chromium(III) oxide on supports: (i) γ-Al_2O_3; (ii) MgO.

decrease of propene selectivity (Fig. 6). At high temperature (500 °C) other oxygenates might have formed. The catalyst atmosphere is important in determining the yield to desired products as shown in Figs. 7 and 8.

4. Discussion

4.1. Effects of loading of chromium oxide

Fig. 3 shows the variation of propane conversion with reaction temperature for X wt.% chromium on γ-Al_2O_3, where X is 0.1, 0.2, 0.5, 2.0, 5.0, 10.0 or 20.0 wt.% of chromium impregnated on the support. The reaction run on quartz granules of similar sizes of the catalyst showed negligible conversion at the same reaction conditions. The performance of unsupported catalyst (denoted CrU) is also shown on the same plot for comparison. At 350 °C, the bulk (unsupported) chromium oxide exhibited a negligible propane conversion of 1.2%, which increased at higher temperatures to reach 8.8%. The increase in activity could be attributed to the increase in the Cr^{3+}/Cr^{6+} ratio and/or increase in activity of the lattice oxygen with the temperature. As suggested by the XPS results, Cr^{3+} is the active component. The conversion was markedly improved by depositing the chromium oxide on γ-Al_2O_3. It is clear that there is an uneven increase in degrees of conversion and selectivities to propene

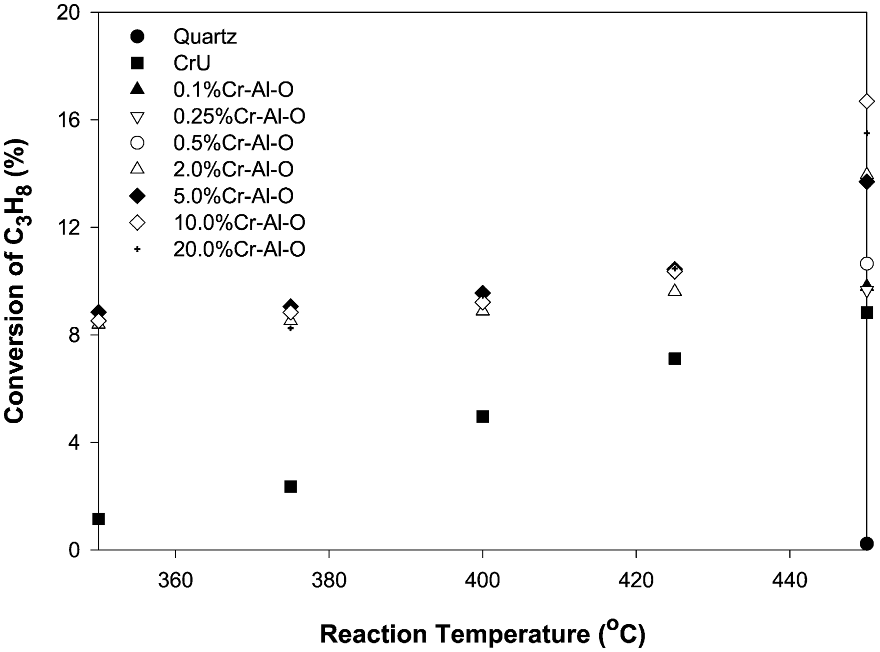

Fig. 3. Propane conversion as a function of temperature over catalysts of different chromium(III) oxide loadings at 350–450 °C.

with the increase in chromium loading. There are no significant differences in the activity among the supported catalysts up to 425 °C, perhaps due to lower activity of the lattice oxygen resulting from interaction with support. However, at high temperatures, activity of the lattice oxygen increased, resulting in significant differences in the conversions. For instance, the propane conversion on the 0.5 wt.% catalyst is 9.7%

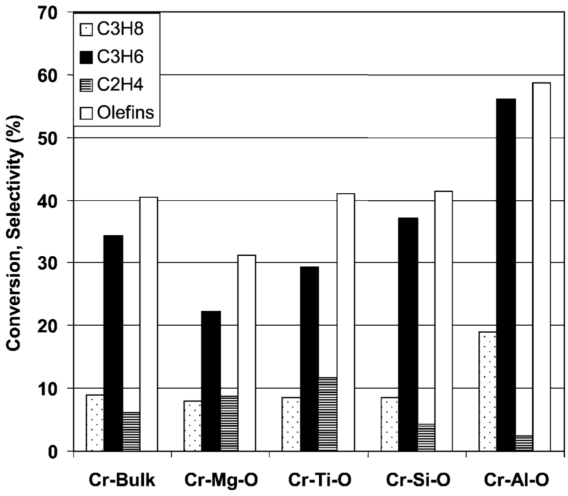

Fig. 4. Propane conversion and product selectivities on 10 wt.% chromium(III) oxide over different supports at 450 °C.

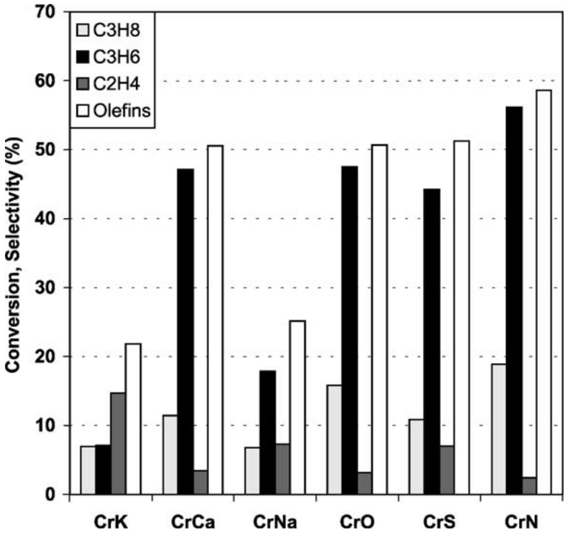

Fig. 5. Propane conversion and product selectivities on 5 wt.% Cr-O-Al of different precursors.

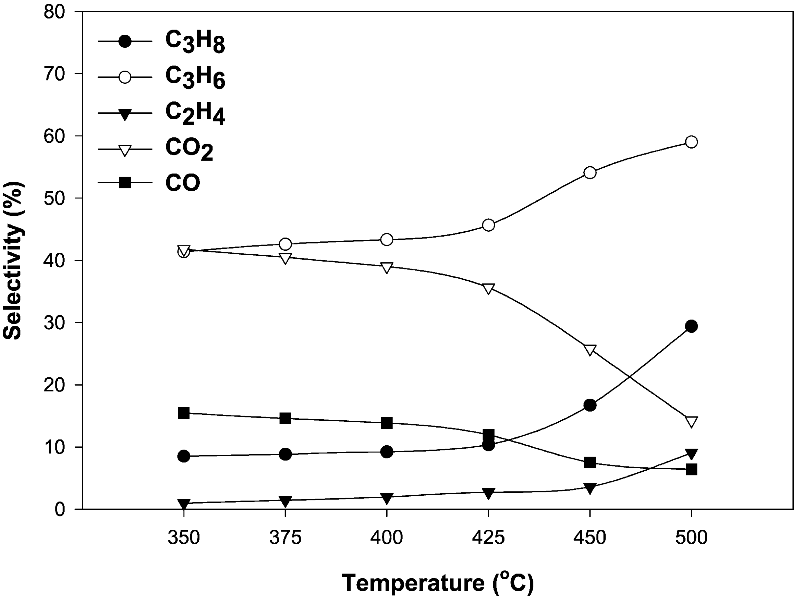

Fig. 6. Propane conversion and product selectivities as functions temperature from 350 to 500 °C, at 1 bar over 10 wt.% Cr-Al-O.

while it is 16.7% on the 10 wt.% catalyst at 450 °C. In addition to temperature effects, catalyst loading becomes more important. Low loadings (0.1–0.5 wt.%) give low conversion of about 8% while higher loadings (2.0–20.0 wt.%) exhibit higher conversions. Propane conversion increased with the amount of chromium oxide on the support up to 10 wt.% catalyst where the value is 17% at 450 °C. Conversion, then, dropped to a

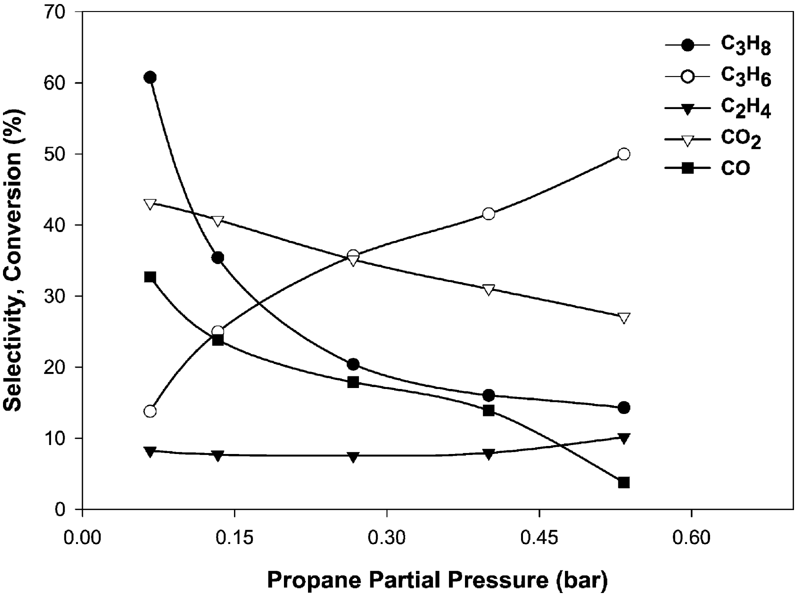

Fig. 7. Propane conversion and product selectivities as functions propane partial pressure at $P_O = 0.07$ bar $T = 450$ °C, over 10% Cr-Al-O.

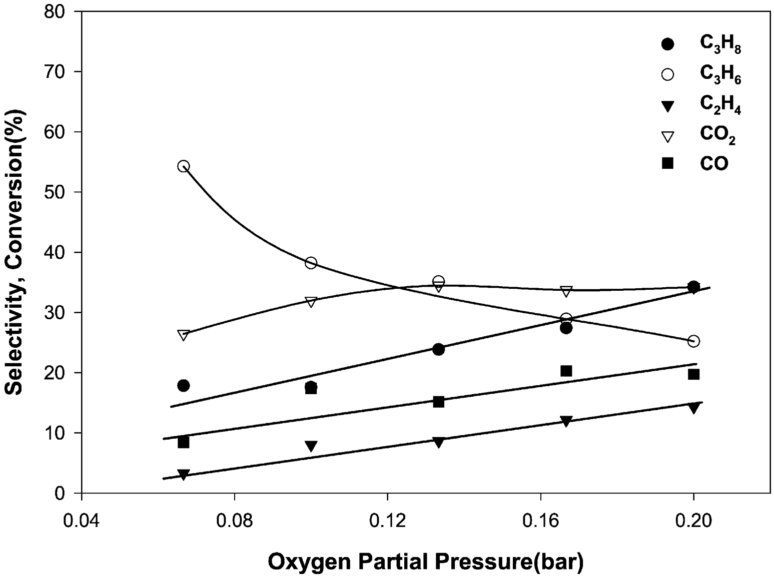

Fig. 8. Propane conversion and product selectivities as functions oxygen partial pressure at $P_{C_3} = 0.27$ bar $T = 450\,^{\circ}$C, over 10 wt.% Cr-Al-O.

lower value of 15% for the 20 wt.% catalyst. These results reflect the importance of the loading of the active component and suggest an optimum catalyst loading of about 10 wt.%.

In the following sections, we attempted to explore ways to improve the performance of the catalyst by investigating the effect of the support, precursors, reaction temperature and feed compositions.

4.2. Effects of supports

The role of the support on the reaction was investigated by comparing the performances of the Cr_2O_3 supported on MgO, SiO_2, TiO_2 and γ-Al_2O_3 in addition to unsupported catalyst. Fig. 4 shows the propane conversion and product selectivity at 450 °C. It is interesting to observe that the unsupported (bulk) Cr_2O_3 showed better propane conversion than MgO, TiO_2 and SiO_2 supported catalysts at the conditions of the experiment. The propane conversion are Cr-Mg-O (8%) = Cr-Ti-O (8%) < Cr-Si-O (8.5%) < CrU (9%) < Cr-Al-O (19%) at 450 °C. This shows γ-Al_2O_3 to have the best performance among the supports. The behaviors of Cr-Al-O and Cr-Mg-O may be partly associated with the different nature of Cr–O–support bridging oxygen species associated with the MgO and γ-Al_2O_3. This is suggested by the TPR profiles of Cr-Mg-O and Cr-Al-O as shown in Fig. 2. Probably, the lower propane conversion and selectivity to propene shown by Cr-Mg-O originates from electrophilic attack by more reducible oxygen on propyl species and/or propene leading to CO_x [4].

4.3. Effect of precursors

As previously mentioned various precursors, namely, $K_2Cr_2O_7$, $CaCr_2O_7$, $Na_2Cr_2O_7$, CrO_3 and $Cr_2SO_4{\cdot}12H_2O$, and $Cr(NO_3)_3{\cdot}12H_2O$ (for brevity, are denoted by CrK, CrCa, CrNa, CrO, CrS and CrN, respectively) were used to synthesize the catalyst (10 wt.% Cr-Al-O). Propane conversion and product selectivities at 450 °C are shown in Fig. 5. These may be ranked based on respective propane degree of conversions at 450 °C as CrNa (6.8%) < CrK (7.0%) < CrS (10.9%) < CrCa (11.4%) < CrO (15.8%) < CrN (19%). The low degree of conversion of the CrK, CrCa and CrNa could be associated with the presence of alkali and alkaline earth metals. Earlier TPR and XPS studies have shown that these metals contaminants decreased the activities of V- and Mo-based catalysts [19]. Similar effect could be present in this case. The metals might have occupied some active sites on the surface of the catalysts. Alternatively, the presence of the metals such as K (in $K_2Cr_2O_7$) could stabilize Cr^{6+} with corresponding decrease in Cr^{3+} that is suggested to be the active species. This would decrease the degree of conversion and selectivity in the reaction.

4.4. Effects of reaction conditions

Fig. 6 shows the effect of reaction temperature (350–500 °C) on products distribution for the 10 wt.% Cr-Al-O catalyst. Both propane conversion and propene selectivity increase with reaction temperature. In a previous study, it was observed that high propene yields could be achieved at low propane feed concentration (<5%) [20]. This feed concentration may not be practical due to the expected high cost of separation, recycle of the diluent added to eliminate temperature effects or hot spot in the catalyst bed, etc. However, in fundamental investigations, the low concentration may be used since the main aim is to design high-yield catalytic systems for the reaction and to be able to suggest the important factors that affect the system. In this work, relatively higher propane feed concentration was used. To investigate the effect of propane and oxygen concentration in the feed, their respective partial pressures were varied. Initially, at 450 °C, the propane partial pressure (P_{C_3}) was varied from 0.06 to 0.53 bar while the oxygen partial pressure (P_O) was fixed at 0.07 bar as shown in Fig. 7. The conversion of propane decreases from 60% at P_{C_3} of 0.03 bar to 14% at 0.53 bar. The selectivity to C_3H_6 increases from about 14 to 50% in the same P_{C_3} range. It is, also, observed that the selectivity to CO_x decreases as the amount of propane increases in the feed. The selectivity to C_2H_4 shows a very slight increase in the partial pressure range. This indicates that production of ethene has no significant dependence on propane partial pressure. Probably, it is produced through consecutive reaction such as splitting of propene. Finally, the partial pressure of propane (P_{C_3}) was fixed at 0.27 bar while P_O was varied from 0.07 to 0.20 bar at 450 °C. Fig. 8 shows the effect of P_O variation on the performance of the catalyst. Propane conversion increases while selectivity to propene decreases with increase in P_O. The selectivity to both C_2H_4 and CO increases with the partial pressure. The selectivity to CO_2 increases then levels off. The high amounts of C_3H_6 and CO_2 at low conversions suggest that the two are primary products. The increase in selectivity to CO_2 with oxygen partial pressure indicates that it is also produced from consecutive reactions. Both C_2H_4 and CO appear to be essentially secondary products. Their respective amounts are low at low conversions. They are probably produced by attack on electron-rich propyl species and/or propene molecules by surface adsorbed oxygen. The latter was reported to facilitate formation of highly active oxygen species that is involved in such electrophilic attack [21]. A recent study on the reaction pathways in catalytic propane oxidation has shown that carbon oxides and ethene production may occur through parallel–consecutive reaction with respect to propene production [22]. This depends on the reaction temperature and feed compositions. Further studies need to be performed to establish the reaction network and kinetics for a wide range of conditions.

5. Conclusions

A number of chromium(III) oxide-based catalysts have been screened and found to be active and selective in propane oxidative dehydrogenation at moderate reaction conditions. Propane conversion and selectivity to propene increased with increase in chromium loadings up to 10 wt.% and dropped thereafter. The catalyst prepared from chromium nitrate gave better performance than those prepared from other precursors. Among the various supports investigated, γ-Al_2O_3 exhibited the best performance. There is a strong influence of the oxygen partial pressure in the feed stream on the conversion and selectivity in the reaction. Reducing environment due to low oxygen favored higher selectivity to propene. Chromium oxide (10 wt.%)/γ-Al_2O_3 exhibited propene yield of 18% at 500 °C. This shows that this catalyst is very promising for oxidative dehydrogenation of propane.

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