

Propane Dehydrogenation over Alumina Supported Chromia Catalysts Shivaji Thapliyal and Goutam Deo*

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Abstract

Different alumina-supported chromia catalysts were prepared by varying the chromium oxide loading from 3.6 to 17 $\mu\text{mol Cr/m}^2$. Previous characterization studies on the catalysts revealed that the monolayer limit was $\sim 9 \mu\text{mol Cr/m}^2$. The different catalysts were tested and found to be active for the dehydrogenation (DH) of propane. Propene was formed on all the chromia supported catalyst samples. The rate of propane converted increased with chromium oxide content till monolayer limit and then decreased. Interestingly, this behaviour paralleled the rate of propane converted during the oxidative dehydrogenation (ODH) of propane suggesting that the active sites for the DH and ODH reactions originate from the same surface chromium oxide species.

Key words: Dehydrogenation, Chromia, Alumina, Propane, Propene, Surface active sites, Catalyst, Precursor, Surface area, Loading, Oxidative Dehydrogenation

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1. Introduction

Dehydrogenation of alkanes into their corresponding alkenes is an industrially significant procedure as the demand of alkenes has increased. Alkenes, especially ethane and propane, are important feedstocks for the petrochemical industry. Several transition and noble metal oxides have been successfully employed as catalysts for dehydrogenation reactions. The commonly used catalysts are supported or unsupported Pt, Pd, Sn, V-Mg, Co, Bi or Sb based oxides.

Chromia-based catalysts have been the subject of study for various petrochemical and environmental applications [1]. Commercially, Al_2O_3 -supported Cr_2O_3 is used for the dehydrogenation of alkanes. When chromia is supported on another metal oxide (e.g. Al_2O_3 , TiO_2 , SiO_2 , ZrO_2 , etc), its structure is changed and it is found that the catalytic activity/selectivity is improved. Characterization techniques, such as, XRD, Raman, UV-VIS, TPR, XPS and ESR have been used to study supported chromia catalysts [1,2]. These

techniques have revealed that the supported chromia catalysts have two-dimensional surface species below monolayer concentration and it is believed that these are the active sites in most reactions.

Several studies have focused on the DH of alkanes over alumina supported chromia catalysts. Rossi et al. [3] studied propane DH on chromia-alumina and suggested that mononuclear Cr^{+3} with two coordinative vacancies is the active site for DH of propane. They compared the catalytic activity of chromia-alumina with that of chromia-zirconia and discussed the possible reasons for the substantially higher activity of the latter. Gorriz and Cadus [4] studied propane DH and coke formation over a series of alumina-supported chromia catalyst. They found that the calcined catalysts contained Cr^{+6} and Cr^{+3} in proportions that depended on the overall chromia content. The coke formation on CO-prerduced catalysts was fast and could be related to the level and stability of the conversion to propene.

They also found that both activity and selectivity of the catalysts were determined by the dispersion of chromia and by the effect of chromia content on the porous structure of the catalysts. Mentasty et al. [5] also conducted catalytic dehydrogenation of propane using chromium oxide supported on different commercial alumina. They reported that the tendency of Cr^{3+} to form aggregates, such as Cr_2O_3 , was induced by the support. The features of the support were said to exert an influence upon chromium stabilization both in its oxidation states $6+$ and $3+$ and in the coordination of surface chromia species. Furthermore, the total acid sites and the oxidized chromium were described to have a marked effect on activity and selectivity at initial operation times. Rossi et al. [6,7] studied propane DH on chromia-zirconia catalysts and found that at temperatures higher than 773 K, the catalyst prereduction is not significant. At 723 K, however, the catalyst prereduction affects the initial rate and its trend with time-on-stream. Deactivation of the catalyst occurred due to coke formation, which decreased by adding hydrogen or water to the reactants and increased by adding propane. It was also found that Cr^{+3} was the active species and that the O^{2-} ions adjacent to Cr^{+3} active species are also involved in the DH reaction.

In the present study, the DH of propane is performed over a series of chromia-alumina catalysts to investigate the effect of chromium oxide loading on the activity of the catalyst. Furthermore, the DH of propane is performed at a single temperature for a chromium loading to investigate deactivation over time. Finally, the DH of propane is compared with the ODH of propane that takes place at lower temperatures.

2. EXPERIMENTAL

2.1. Catalyst Preparation

The incipient wetness impregnation method was employed to make the

alumina-supported chromia catalysts. Chromium nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Aldrich, 99.98% purity) was used as the precursor and alumina (Condea) was used as the support. Incipient volumes of double distilled water were used to pre-treat the support following which it underwent calcinations at 873 K for 8 h. This pretreated support is referred to as $\text{Al}_2\text{O}_3 - 600$. In order to prepare catalysts with different loadings of chromium oxide, the pretreated support and incipient volumes of solution containing predetermined amounts of precursor were intimately mixed. First, the mixture was kept in a dessicator overnight and then dried for 8 h at 383 K, and for another 8 h at 523 K. The samples then underwent calcinations at 873 K for 6 h. The resultant samples were denoted as x % CrAl-600, where x % is the weight % loading corresponding to Cr_2O_3 . Additional details are provided elsewhere [8].

2.2. Reaction Procedure

The prepared catalyst samples were tested for the DH of propane at atmospheric pressure in a down-flow quartz reactor. The reactor had an inlet of 10 mm i.d. and a length of 15 cm. The outlet was of 5 mm i.d. and a length of 15 cm. The inlet and outlet sections were joined together by a tapered region. It was just above this tapered region that the catalyst bed was placed on quartz wool. The catalyst bed contained a physical mixture of 0.05 g catalyst and appropriate amount of quartz glass powder to form a bed height of 1 cm. The reactor was placed vertically in a tubular furnace. A thermocouple located inside the reactor just above the catalyst bed served to measure the temperature. The thermocouple provided the input to a PID temperature controller (FUJI Micro-controller X Model PXZ 4). The exit gases were transferred for online analysis to a Gas Chromatograph (AIMIL-NUCON 5765) equipped with a methanizer. The hydrocarbon analysis is done in FID mode employing an activated alumina column.

Propane and nitrogen flow was adjusted using electronic flow controllers (Bronkhost Hi-Tec). A molar ratio of propane to nitrogen of 1:4 and a total flow rate of 50 ml/min was maintained. Reaction runs were performed at different temperatures starting from 823 to 873 K.

In order to calculate the conversion, the inlet and outlet concentrations are noted from which the moles propane fed and consumed are calculated. Consequently, the conversion is calculated. The conversion is given as:

$$\text{conversion (\%)} = 100 (n_c/n_f)$$

where, n_c and n_f are the number of moles of propane consumed and fed, respectively.

The activity is also calculated and is given as:

$$\text{activity} = \text{conversion} \times (F_{AO}/W)$$

where, F_{AO} is the molar flow rate of propane fed and W is the mass of catalyst used.

3. Results and Discussion

The BET surface areas of pure alumina and the $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ samples were obtained and are tabulated in Table 1. It is seen that for the CrAl-600 samples, the surface area first decreased with loading and then remained relatively constant. The plugging of pores has been cited as a reason for the initial decrease in surface area [9]. The surface concentration of chromium oxide in the catalyst samples, in $\mu\text{mol Cr}/\text{m}^2$, is also been specified in Table 1.

Table 1. BET surface area of different samples

Samples	Surface Area (m^2/g)	Concentration ($\mu\text{mol Cr}/\text{m}^2$)
Al_2O_3 -600	201	-
5% CrAl-600	185	3.6
10% CrAl-600	156	8.4
15% CrAl-600	141	14.0
20% CrAl-600	155	17.0

These CrAl-600 catalyst has been characterized by various techniques and discussed in detail elsewhere [2,8]. The XRD patterns for the CrAl-600 samples have major peaks at 46.1 and 67.8 ° and an additional broad peak between 36 and 38 °. These peaks are due to the γ - Al_2O_3 support. Additional peaks for the 20% CrAl-600 sample appear at 24.8, 32.8 and 54.6 ° due to Cr_2O_3 crystals. XPS studies on the CrAl-600 samples reveal only Cr, Al, O and C in the samples. Additionally, trace amounts of F, Cl and Sn are detected. In the UV-VIS spectra, two peaks at 276 and 370 nm, corresponding to Cr^{6+} , are observed for 5 and 10 % loadings. These peaks are also seen for the 15% CrAl-600 sample but with lesser intensity. Broad peaks are observed at 460 and 600 nm once the loading exceeds 15% Cr_2O_3 , which corresponds to the chromium ion in the +3 oxidation state. Raman spectroscopy reveals the presence of Cr_2O_3 crystals at 15% and higher chromia loadings. Chromium is present as Cr^{+3} species in Cr_2O_3 crystals consistent with the UV-VIS results. Below 15 % loading Raman features of molecularly dispersed chromia are observed. Thus, the molecularly dispersed chromium oxide species is in the +6 oxidation state.

In summary, the chromium oxide species is molecularly dispersed till bulk Cr_2O_3 formation takes place above monolayer coverage. Below monolayer coverages, chromium oxide in the +6 oxidation state is the predominant species. Presence of minor amounts of Cr^{5+} has also been suggested from the EPR spectra [2]. Upon surface moisture being removed, the chromium oxide on alumina is present as tetrahedral monomeric and polymeric Cr^{+6} oxide species under fully oxidized conditions different from those present under ambient conditions. Moreover, surface coverage below monolayer loadings does not influence the ratio of the two Cr^{+6} oxide species.

The DH of propane reaction was performed using 5, 10, 15 and 20% CrAl-

600 samples at temperatures starting from 823 to 873 K and at a propane mol % of 20. Furthermore, DH of propane using the 15% CrAl-600 sample was performed at a single temperature for an extended period of time to study the deactivation characteristics. Propene is the only product formed. The values of propane conversion are given in Table 2. The conversion values revealed that propane conversion first increased with chromium loading in the CrAl-600 samples and then decreased. The 15% CrAl-600 sample gave maximum conversion for all temperatures considered in the present study. The physical characterization studies suggest that the maximum amount of surface chromia species is present for the 15% CrAl-600 sample. A small amount of bulk Cr_2O_3 is also formed at this loading. When the chromium oxide loading increases beyond 15%, the amount of Cr_2O_3 increases. Consequently, propane conversion decreases since Cr_2O_3 is less active than molecularly dispersed chromium oxide species [2,8].

Table 2. Propane conversion (%) for CrAl-600 samples at different temperatures.

$y_{\text{propane}} = 0.2; m = 0.5 \text{ g}$

Samples	Conversion (%)		
	833 K	843 K	873 K
5% CrAl-600	0.91	1.98	2.87
10% CrAl-600	1.51	3.90	5.79
15% CrAl-600	2.50	5.56	5.99
20% CrAl-600	1.38	3.19	4.24

The deactivation of propane conversion reaction studies revealed that propane conversion decreased steadily over time as shown in Fig. 1 (semi-log plot). For 15% CrAl-600 at 853 K, the conversion decreased steadily from ~4.7% to ~2.8% in a time span of 200 mins.

The same CrAl-600 catalysts have also been studied for the propane oxidative

dehydrogenation (ODH) reaction [2,8]. The temperature was varied from 653 K to 733 K and the propane: oxygen: nitrogen ratio was ~3:1:4. The active center for this reaction was proposed to be the Cr^{6+} redox site. For comparison purposes the ODH (at 673 K) and DH (at 853 K) activities are plotted versus chromia loading in Figure 2. Figure 2 reveals a remarkable parallel between the variations of activity versus chromia loading, x% CrAl-600. Previous studies have proposed that the active sites for propane DH are the Cr^{3+} oxide species [3]. The parallel between the DH and ODH activities suggests that the Cr^{6+} oxide species present under fully oxidized conditions are the precursors to the Cr^{3+} oxide species required for the DH reaction. Furthermore, the linear increase in activity with chromia loading till monolayer coverage suggests a constant turnover frequency (mole propane converted per mole chromium per unit time) of the surface chromia oxide species for both the DH and ODH reaction. Thus, the Cr^{6+} oxide species undergoes a redox cycle during the ODH reaction and is reduced to Cr^{3+} oxide species, which is the active species for the DH reaction.

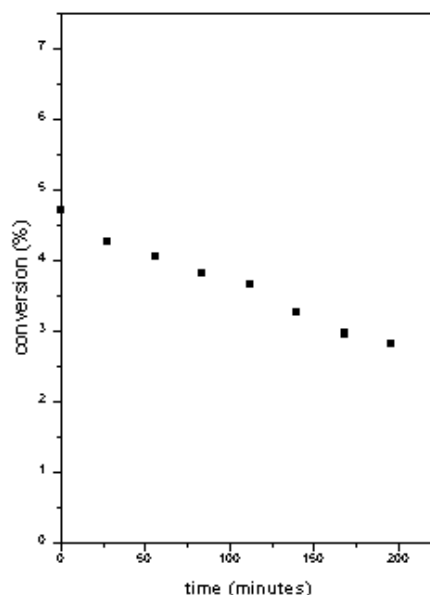


Figure 1: Conversion (%) versus time for 15% CrAl-600 at 853 K.

$y_{\text{propane}} = 0.2; m = 0.5 \text{ g}$

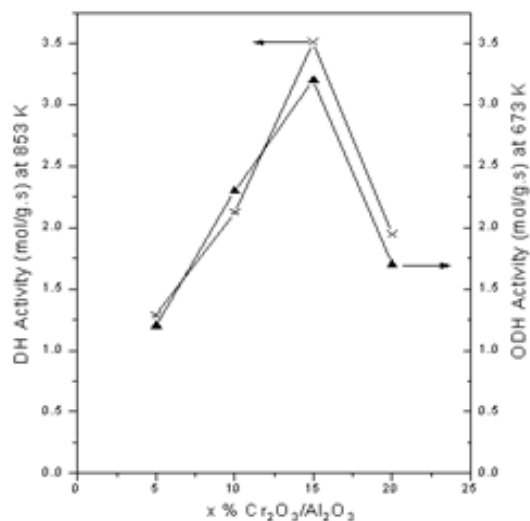


Fig.2. Comparison of activity for Dehydrogenation (DH) and Oxidative Dehydrogenation (ODH) of Propane as a function Cr₂O₃ loading, for a series of Cr₂O₃/Al₂O₃ catalysts.

4. Conclusions

A series of alumina supported chromia oxide catalysts were prepared by varying the chromium oxide loading from below to above monolayer coverages. These catalysts were found to be active for the DH of propane and propene was formed on the surface chromia sites. The activity for DH initially increased with chromia loading, for below monolayer coverage samples, and then decreased for those samples with above monolayer coverages. A parallel was observed between the DH and ODH activity, which suggests that the active sites originate from the same species.

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