Effects of reducibility on propane oxidative dehydrogenation over γ-Al_2O_3-supported chromium oxide-based catalysts

B.Y. Jibril [a,]*, S.M. Al-Zahrani [a], A.E. Abasaeed [a], and R. Hughes [b]

[a] *Chemical Engineering Department, King Saud University, PO Box 800, Riyadh 11421, Saudi Arabia*
[b] *Chemical Engineering, University of Salford, Maxwell Building, The Crescent, Salford, Manchester M5 4WT, UK*

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Alumina-supported chromium oxide and binary mixed oxide catalysts of the form Cr–M oxide/γ-Al_2O_3 (where M is Ni, Co, Mo, W, Ho, La, Li, Cs or Bi) were found to catalyze the oxidative dehydrogenation of propane at 300–450 °C. The basic characters of the metals were found to determine partly the selectivity to propylene. Cr–Mo/γ-Al_2O_3 proved to be the most promising. It exhibited a propylene yield of 10.3% at 450 °C. The connections between the selectivity and reducibility of the catalyst were explored. TPR results showed that addition of molybdenum to chromium increased the temperature of reduction maxima. Thus the selectivity to propylene was improved by a decrease in the tendency of the catalyst to undergo a redox cycle. Further, an X-ray photoelectron spectroscopy study conducted on a sample of the catalysts showed that the basicity of the catalysts increased with increase in molybdenum. Catalysts with appropriate Cr/Mo ratios exhibited lower selectivity to over-oxidation product than those containing either chromium or molybdenum alone.

KEY WORDS: oxidative dehydrogenation; propane; propylene; chromium oxide; molybdenum oxide; TPR; XPS.

1. Introduction

Oxidative dehydrogenation of lower alkanes is a potential alternative or complementary route to alkenes. The reaction is exothermic whereas the nonoxidative dehydrogenation is endothermic. Therefore, the latter reaction takes place at high temperatures for favorable thermodynamic equilibrium. The high temperatures often lead to cracking and formation of coke. This makes it necessary to frequently shut down the reactor for decoking and/or catalyst regeneration. These difficulties are minimized in oxidative dehydrogenation since there are no thermodynamic equilibrium limitations and the reaction takes place at much lower temperature. However, it is still difficult to design a catalytic system that gives high yield in the reaction because both alkanes and alkenes have tendencies towards oxidation to CO_x [1]. This situation poses a challenge and serves as a motivation for developing new and/or improving the existing catalytic systems for the reaction. To this end, catalytic propane oxidative dehydrogenation (POD) has been the subject of extensive research efforts that have led to the discovery of several promising catalysts. The most studied catalytic systems for the reaction are based on vanadium [2–4], metal tungstates [5], metal molybdates [6,7] and metal phosphates [8,9]. Recently, rare earth vanadates have been reported to have better performance than the much-studied V–Mg–O [10]. Ni–Co–Mo was also shown to be as promising as V-based catalysts [6].

In a previous study, we reported the performances of some supported metal oxide catalysts for the reaction, among which chromium oxide was found to be promising [11]. This study focuses on the attempt to modify some of the catalyst's properties in order to improve its performance. It is generally accepted that oxidative dehydrogenation takes place through the classical Mars–Van Krevelen mechanism where the catalyst donates lattice oxygen to take part in the oxidation reaction [3,12]. The gas-phase oxygen reoxidizes the reduced catalyst. This concept of a redox cycle in selective oxidation catalysis was propounded earlier by Grasselli and co-workers at SOHIO/BP [13]. The redox character of the catalyst is among the important factors upon which optimum catalyst activity and selectivity are based. Therefore, the reducibility of the catalyst surface is critical in determining the catalyst's performance [14,15]. In addition, it is important to have a catalyst of appropriate basicity to facilitate the desorption of olefins [6,14].

The redox character could be modified by addition of some metals to the base metal [16]. This is because the lattice oxygen migration could be influenced by such addition. Mixing certain metals with the base catalyst might also improve the selectivity to propylene (i) by modifying the oxidation state and electronic structure of the chromium center, (ii) by modifying its behavior through structural site isolation or (iii) due to stabilization of a lower chromium oxidation state. Therefore, the optimized catalyst should consist of a group of elements that are able to change their valance states on appropriate supports to give a desired redox and acid–base character

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* To whom correspondence should be addressed.
E-mail: baba@ksu.edu.sa

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[2,3,17–19]. Based on the foregoing, here we report results of a study of the reaction on alumina-supported chromium oxide-based multi-component catalysts. The catalysts are 10%Cr–M–Al–O (where M is Ni, Co, Mo, W, Ho, La, Li, Cs or Bi).

2. Experimental

2.1. Catalyst preparation

The supported metals oxides were prepared by the impregnation method. For each catalyst, an aqueous solution of a predetermined amount of the precursor was added gradually to a crystallizing dish containing a predetermined amount of the support to obtain the required weight percent of active component on the support. For instance, 59.6 g of $Cr(NO_3)_3{\cdot}9H_2O$ was added to 102 g of γ-Al_2O_3 to obtain 10 wt% chromium oxide on the support. The content of the crystallizing dish was continuously stirred, while the excess deionized water was evaporated at about 70 °C. A thick paste was obtained which was then dried in an oven at 100 °C overnight. The catalyst was calcined in air at 600 °C.

Other metals were respectively added to chromium to obtain catalysts of the form 10 wt% Cr–M oxides on γ-Al_2O_3 (where M is Ni, Co, Mo, W, Ho, La, Li, Cs or Bi), with weight ratio Cr:M of 3:2. The precursors for the metals Ni, Co, Mo, W, Ho, La, Li, Cs and Bi were $Ni(NO_3)_2{\cdot}6H_2O$ (BDH 29322), $Co(NO_3)_2{\cdot}6H_2O$ (Mallinckrodt), MoO_3 (Fluka), $(NH_4)_{11}W_{12}O_{41}{\cdot}5H_2O$ (BDH), $Ho(NO_3)_3{\cdot}5H_2O$ (Aldrich 22,968.7), $La(NO_3)_3{\cdot}6H_2O$ (BDH 29009), $LiNO_3{\cdot}2H_2O$, $CsNO_3$ (BDH 27570) and $BiNO_3$ (BDH), respectively. In the subsequent discussion the catalysts are represented as Cr- and Cr-M for the alumina-supported chromium oxide and mixed oxides of chromium and other metal M. Further, $Cr_xMo_{(1-x)}/\gamma$-Al_2O_3 (where $x = 0$–1) were prepared from the chromium and molybdenum precursors mentioned above.

2.2. Catalyst characterization

Temperature-programmed reduction (TPR) of a sample of the catalysts, Cr-, Cr-Mo(4:1), Cr-Mo(4:2), Cr-Mo(2:4) and Mo-, was performed. This was done in a quartz tubular reactor using 10% H_2 in nitrogen at a flow rate of about 50 cm^3/min and a heating rate of 5 °C/min. Catalyst samples (100 mg) were pretreated in flowing O_2 (50 cm^3/min) at 500 °C and cooled in O_2. The consumption of H_2 was measured using a thermal conductivity detector (TCD) and the signal transferred to a data acquisition computer. The water was removed with a molecular sieve trap. X-ray photoelectron (XP) spectra of a sample of the catalysts, CrMo(1:4) and CrMo(4:1), were obtained. The XP spectra were measured and recorded using a VG Scientific ESCA-3 photoelectron spectrometer using an X-ray source (of AlKα radiation) operating at 13 kV and 10 mA. BET surface areas and pore volumes were measured using a Micromeritics 2400 instrument.

2.3. Catalyst testing

The catalysts were tested in a fixed-bed quartz laboratory reactor, operated at atmospheric pressure in the temperature range 300–450 °C. The feed was a 75 cm^3/min mixture of C_3H_8, O_2 and He, molar ratio 4:1:10. In some experimental runs the feed composition was varied. The gases were high-purity, propane (99.99%), oxygen (99.99%) and helium (99.99%) obtained from Linde. They were supplied from cylinders at laboratory temperature, passed through microfilters for additional purification and delivered to the reactor preheat zone. In each case, the catalyst was pretreated in a stream of oxygen for 30–45 min at 450 °C. The line was then evacuated with helium at the same temperature for 30 min. Thereafter, the reactant gases were metered through the reactor at the desired temperatures.

The gas flows were controlled by Omega electronic mass flow controllers. The temperature of the catalyst bed was monitored by a thermocouple placed on the reactor wall from outside. A temperature controller (Omega CN3000) was used to monitor the temperature. The actual temperature of the catalyst bed was calibrated in a separate experiment using a second thermocouple positioned in the center of the catalyst bed. This is the reaction temperature reported in this work. The reactor was a 70 mm long quartz tube of 7 mm internal diameter (i.d.) tapered to a 2 mm i.d. This removes the reaction gases from the reaction zone as fast as possible, thereby minimizing possible gas-phase reactions. One gram of 20–40 mesh size granules of each of the catalysts was each placed in the reaction zone of the reactor and supported on quartz wool directly above the junction of this section with the bottom.

A gas chromatograph (GC; HP6890) was used for online analysis of both the feed and products streams. The products flowed directly through a heat-traced line to the GC sampling valve. The hydrocarbons CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, C_4H_{10} and C_4H_8 were separated using a HP-PLOT column and analyzed with a flame ionization detector (FID), while O_2, CO and CO_2 were separated using MS and HayeSep-R columns and analyzed with a TCD. All GC analyses were performed online using HP Chemstation software provided with the equipment.

A blank test without a catalyst or quartz granules in the reactor showed negligible conversion of propane under the reaction conditions. For the kinetic study, preliminary measures were performed in which the mass and the particle sizes of the catalyst were varied. Conditions were chosen so that the transport phenomena do not limit the reaction rates. For some experiments triple runs were performed to ensure reproducibility. The variations among the runs were about ±3%. In these cases results reported are the average values. Carbon balances were typically better than 95%. The performance of each catalyst is reported based on the following: conversion is defined as the mole fraction of feed carbon present in the reaction products, while selectivity is the fraction of product carbon in a particular product.

3. Results and discussion

3.1. Catalyst characterization

TPR experiments were performed on a sample of the catalysts. Figure 1 shows the TPR patterns of (i) Cr- and (ii) Cr-Mo(4 : 1) while figure 2 shows those of (i) Mo-, (ii) Cr-Mo(4 : 2) and (iii) Cr-Mo(2 : 4). The temperatures of the reduction peak maxima (T_M) are summarized in table 1. Sharp peaks below 600 °C and broad peaks at 600–900 °C are observed. The sharp peaks show that once transformation starts, it converts one compound into another rapidly. The broad peak indicates gradual transformation to a group of domains of different oxides. This shows that the catalysts are readily susceptible to redox perhaps due to formation of other compounds at temperature higher than 600 °C [20,21].

The result shows that the Cr- catalyst is readily reducible compared with the others. As can be observed from table 1, the Cr- exhibits a peak at $T_M = 285$ °C while Mo- shows peaks at $T_M = 475$, 532, 556, 736, 842 and 901 °C. For Mo-, a shoulder may be observed in the region 380–390 °C. On mixing chromium and molybdenum oxides, different reduction patterns are observed. The reduction site associated with chromium is shifted to higher temperature ($T_M = 367$–385 °C) due to interaction with molybdenum. Similarly, the reducibilities of molybdenum sites are modified. Clearly, the interactions of the chromium and molybdenum have complex effects on the overall reducibilities of the catalysts as indicated by the shift of T_M. In addition, shoulders may be observed in the regions 700–800 °C for Cr-Mo(4 : 1) and 530–560 °C for Cr-Mo(2 : 4). There are convolutions of T_M at high temperatures to a peak centered at about 750 °C. This indicates that phases associated with these peaks disappeared in the presence of chromium. The complex pattern is perhaps due to the tendency of chromium and molybdenum to intermix, thereby enhancing the stabilization of different forms of chromium oxides, molybdenum oxides and/or their mixture at the surface and in the lattice of the support. This suggests the ability of molybdenum to reduce the agglomeration of chromium oxides on the surface, thereby decreasing the overall catalyst reducibilities.

Table 2 gives the XP spectroscopy (XPS) data of a representative sample of the catalysts—CrMo(4 : 1) and CrMo(1 : 4). The surface atomic ratio of Cr/Mo is influenced by the relative amounts of chromium and molybdenum. The catalyst with high Cr/Mo ratio in the preparation (= 4.00) has a low dispersion of

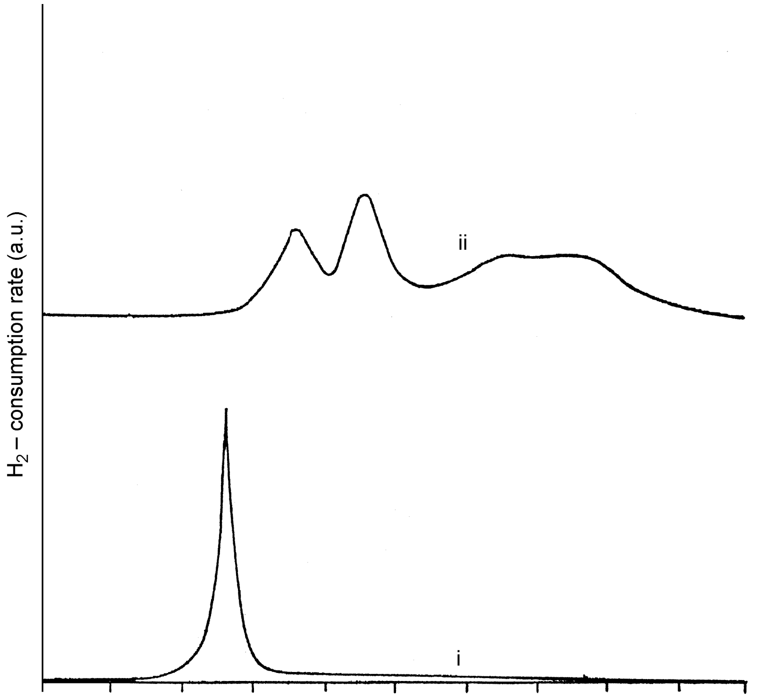

Figure 1. TPR profile for (i) Cr- and (ii) Cr-Mo(4 : 1).

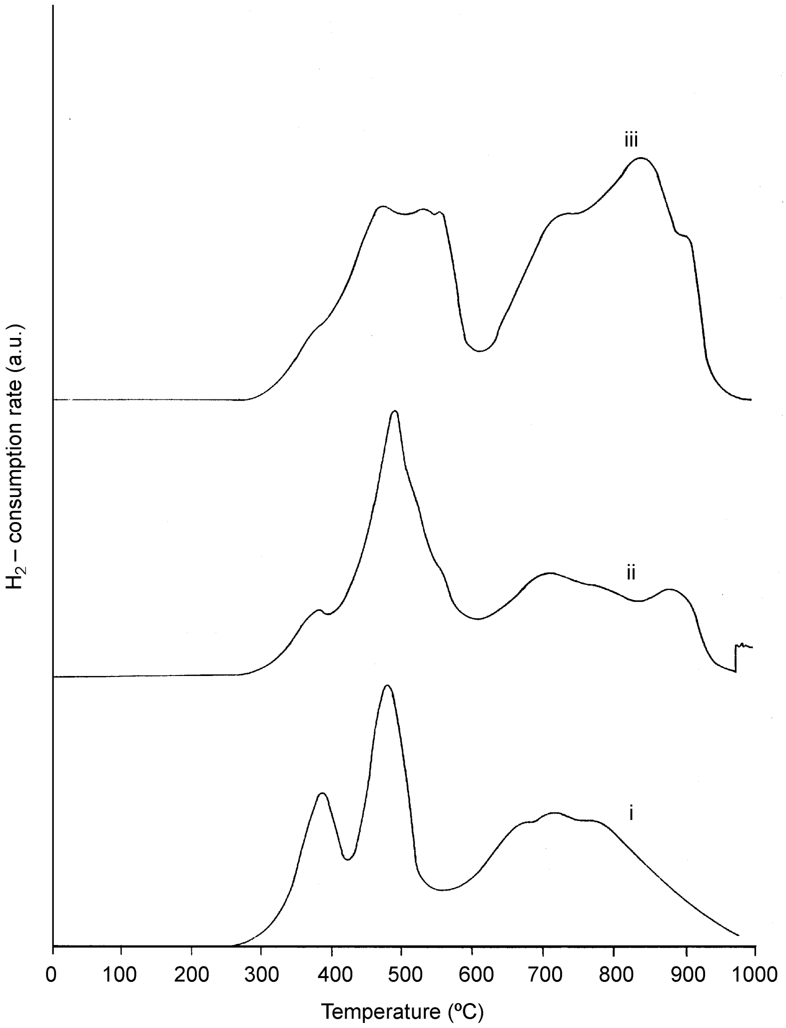

Figure 2. TPR profile for (i) Cr-Mo (4 : 2), (ii) Cr-Mo(2 : 4) and (iii) Mo-.

chromium on the catalyst surface (Cr/Mo ratio of about 1.13) after calcination. The catalyst with low Cr/Mo ratio (= 0.25), however, shows almost same ratios on the surface. The almost same surface ratios (XPS data and catalyst preparation) in the case of CrMo(1 : 4) indicate an increase in the degree of dispersion perhaps due to the presence of molybdenum. For the catalysts, the Al $2p$ binding energy (BE) does not show a dependence on the ratios unlike those for Mo $3d_{5/4}$, Cr $2p_{3/2}$ and O $1s$. The BEs for Mo $3d_{5/4}$ and Cr $2p_{3/2}$ increase but that of O $1s$ decreases for a sample with a higher amount of Mo. Higher BE for the chromium and molybdenum with a decrease in the Cr/Mo ratio suggests less susceptibility for the species to be oxidized. Therefore, the ratio is important partly because of its effect on the reduction–oxidation tendency of constituent species in the catalyst. Probably, the predominance of molybdenum on the surface is responsible for the reduction in surface oxygen associated with over-oxidation to CO_x. Table 3 shows the BET surface areas and pore volumes for a sample of the catalysts.

Table 1
Temperature (°C) of reduction peak maxima (T_{Mi}) for a sample of the catalysts

Sample	T_{M1}	T_{M2}	T_{M3}	T_{M4}	T_{M5}	T_{M6}	T_{M7}
Cr-	285	–	–	–	–	–	–
CrMo(4 : 1)	367	456	665	–	–	–	–
CrMo(4 : 2)	385	478	687	719	775	–	–
CrMo(2 : 4)	385	492	–	716	–	886	–
Mo-	–	475	532	556	736	842	901

3.2. *Chromium oxide catalyst*

The catalysts studied are found to catalyze the reaction at 300–450 °C, 1 atm and a feed flow rate of 75 cm^3/min (C_3H_8, O_2 and He, mole ratio of 4 : 1 : 10). The major products are propylene, ethylene and CO_x (CO_2 and CO). Figure 3 shows the conversion and product distribution as a function of reaction temperature for the Cr- catalyst. At 350 °C the conversion is 8.5% (selectivity to olefins of 42.3%) while at 450 °C the conversion increases to 16.7% (selectivity to olefins

Table 2
XPS data for a sample of the catalysts

Sample	Atoms on the surface (%)					Binding energy (eV)			
	O	Cr	Mo	Al	Cr/Mo ratio	Al 2*p*	Mo $3d_{5/4}$	Cr $2p_{3/2}$	O 1*s*
CrMo(1 : 4)	73.2	3.5	14.3	9.0	0.24	74.4	232.7	577.5	530.8
CrMo(4 : 1)	69.9	6.1	5.4	18.6	1.13	74.4	232.5	577.4	531.0

of 57.6%). It is interesting to observe the increase in selectivity to propylene with increase in conversion (or temperature). This is contrary to the general observations of a decrease in selectivity to olefins with increase in conversion of propane, although there are some reports that showed an increase in both selectivity and conversion in the oxidative dehydrogenation reactions [22,23]. This observation may be explained on the basis of the reducing environment on the surface of the catalysts caused by the low supply of oxygen in the reaction. As the reaction temperature increases, the reactivity of the lattice oxygen increases thereby enhancing the rate of abstraction of hydrogen from propane with subsequent loss of oxygen. This is observed in the increase in conversion with temperature. More oxygen is needed to replenish the lattice oxygen lost from the catalyst. Since there was a low supply of oxygen (propane/oxygen = 4), the surface became reduced. On the reduced surface there is low tendency towards attacking the propyl species and/or the propylene molecules. This results in an increase in selectivity to propylene with increase in conversion (or temperature) in the reaction.

Table 3
BET surface area and pore volume of the alumina-supported 10 wt% Cr-M (M as defined in the text) and $Cr_xMo_{(1-x)}$ ($x = 0$–1)

Sample	Total (BET) surface area (m^2/g)	Pore volume (cm^3/g)
Cr-Ho	146.6	0.350
Cr-Ni	140.8	0.350
Cr-Co	139.0	0.360
Cr-Bi	146.2	0.390
Cr-W	131.0	0.163
Cr-Mo	136.1	0.343
Cr-Cs	145.3	0.382
Cr-Li	104.5	0.290
Cr-La	104.5	–
Cr-	113.0	0.181
CrMo(4 : 1)	100.2	0.152
CrMo(4 : 2)	93.4	0.137
CrMo(4 : 3)	77.6	0.119
CrMo(3 : 4)	62.1	0.096
CrMo(2 : 4)	57.9	0.089
CrMo(1 : 4)	45.5	0.072
Mo-	51.9	0.079

The effect of oxygen supply on the reducibility of the catalyst was further investigated by varying the partial pressure of both oxygen and propane in the feed. At 450 °C the propane partial pressure (P_{C_3}) was varied from 0.06 to 0.53 atm while the oxygen partial pressure (P_O) was fixed at 0.07 atm. Then P_{C_3} was fixed at 0.27 atm while P_O was varied from 0.07 to 0.20 atm. Figure 4 shows the effect of variation of P_{C_3} on the rates of propane consumption and production of propylene, ethylene, CO_2 and CO for the reaction. A higher P_{C_3} value makes the environment or the catalyst surface reducing in line with the following discussion. The rate of propane consumption increases at higher partial pressure to about double the value at lower pressure. The rates of C_3H_6 production increase from about 2.8×10^{-7} to 19.3×10^{-7} mol/g-cat/s in the P_{C_3} range. The increase in both rates of propane and propylene is probably due to a lower amount of oxygen that may attack the electron-rich center of the propylene. It is observed that the rates of C_2H_4 and CO_2 show less significant change than CO as the amount of propane increases in the feed. Figure 4 is further discussed below in comparison with figure 7.

Figure 5 shows the effect of variation of P_O on the performance of the catalyst. The pressure was varied from 0.07 to 0.2 atm. The rate of propane consumption shows a continuous increase with increasing P_O. The rates of the products also increase with the partial pressure of oxygen. The rates of CO_x show a more significant increase than in figure 4, perhaps as a result of a decrease in the rate of propylene due to higher electrophilic attacks by greater amounts of oxygen species. The relatively higher amounts of C_3H_6 and CO_2 than C_2H_4 and CO at low rate of propane consumption suggest that the two are primary products. Propylene is unstable in the presence of a high amount of oxygen in the gas phase. Both C_2H_4 and CO appear to be essentially secondary products. Their respective amounts are negligible at low propane consumption. They are probably produced by attack on electron-rich propyl species and/or propylene molecules by surface-adsorbed or highly reactive lattice oxygen. The surface oxygen was reported to facilitate formation of highly active oxygen species that is involved in such electrophilic attack [24].

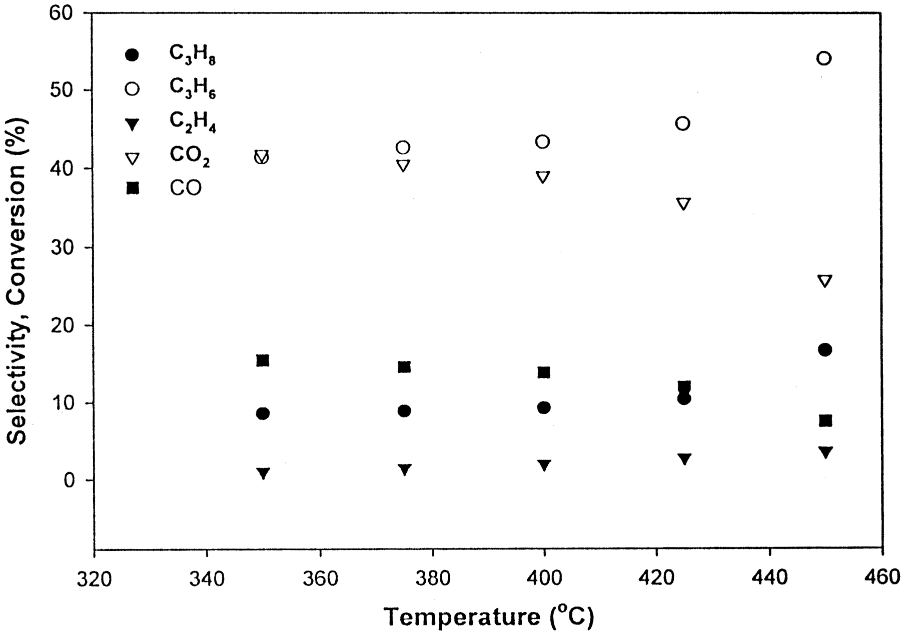

Figure 3. Propane conversion and product selectivities on Cr-.

Such reactivity of oxygen is suggested by low values of T_M for the catalyst.

3.3. Binary chromium oxide-based catalysts

The catalyst composition was varied in an attempt to modify the redox and/or acid–base properties in order to improve the performances. It has been shown that these properties are central in determining the catalyst activity and product distribution [14,25]. The reducibility of the catalyst will be strongly determined by the nature of the metal–oxygen bond. This in turn may be influenced by the presence of another metal in the catalyst. A possible surface-adsorbed oxygen species and acid–base character may also be controlled by addition of some basic and amphoteric metals known to reduce oxygen mobility in the oxidic materials [16]. The metals added have a wide range of properties. For instance, some of them are known to possess no surface oxygen species [26]. The oxides of some are more acidic while others are more basic compared with the base chromium oxide, as discussed below.

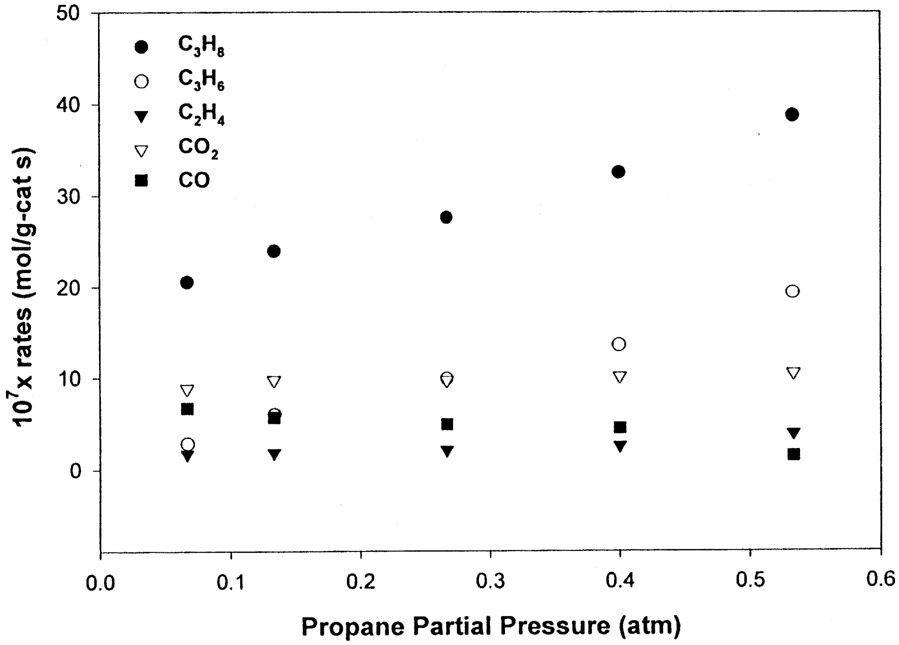

Figure 4. Rates of consumption of C_3H_8 and production of C_3H_6, C_2H_4, CO_2 and CO as functions of P_{C_3} at $P_O = 0.07$ atm and $T = 450\,^{\circ}C$ over Cr-.

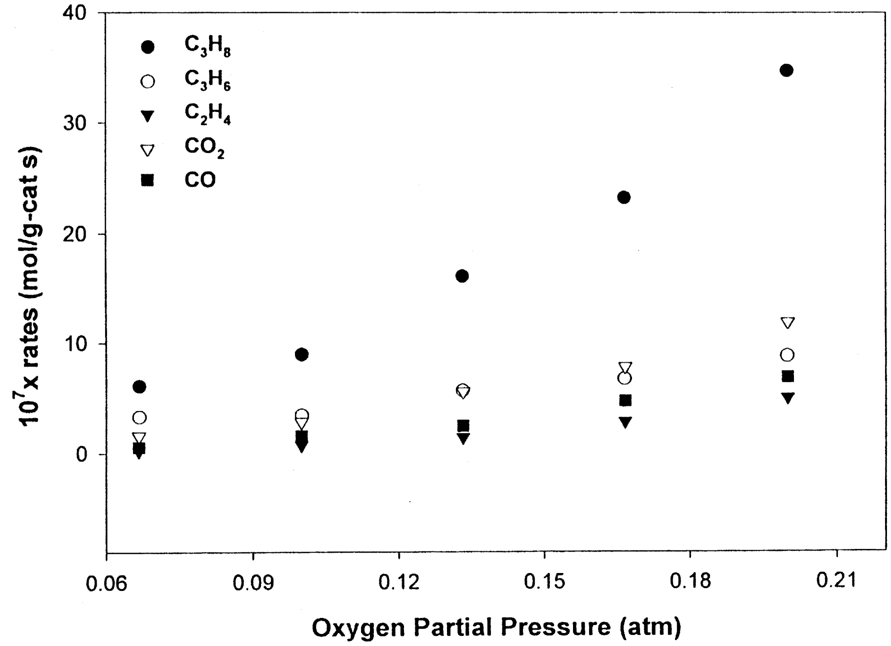

Figure 5. Rates of consumption of C_3H_8 and production of C_3H_6, C_2H_4, CO_2 and CO as functions of P_O at $P_{C_3} = 0.27$ atm and $T = 450$ °C over Cr-.

The propane conversion and selectivity to propylene at 450 °C on the Cr-M oxide/γ-Al_2O_3 (where M is Ni, Co, Mo, W, Ho, La, Li, Cs or Bi) catalysts are shown in figure 6. The performances (conversion/selectivity) may be discussed based on the nature of the metals added. At equal propane conversions, the catalysts Cr-Mo (16.8%/62.0%), Cr-La (16.4%/47.7%), Cr-Cs (16.3%/58.0%), Cr-W (16.7%/49.5%) and Cr-Bi (16.9%/48.5%) exhibit different selectivities to propylene from the base Cr- (16.7%/54.1%). The difference in selectivity to propylene between the base and Cr-Mo catalyst suggests that addition of the metal changes the acid–base character and/or the nature of surface reducibility, since these properties were shown to be responsible for changing the selectivity to olefins [27,28]. As shown by the TPR results in figures 1 and 2, the Cr-Mo is less reducible than the Cr-only catalyst. Thus, the decrease in reducibility has increased the selectivity to propylene at isoconversion.

The oxide of chromium was reported to have surface-adsorbed oxygen species while oxides of molybdenum, bismuth and tungsten showed no such oxygen species

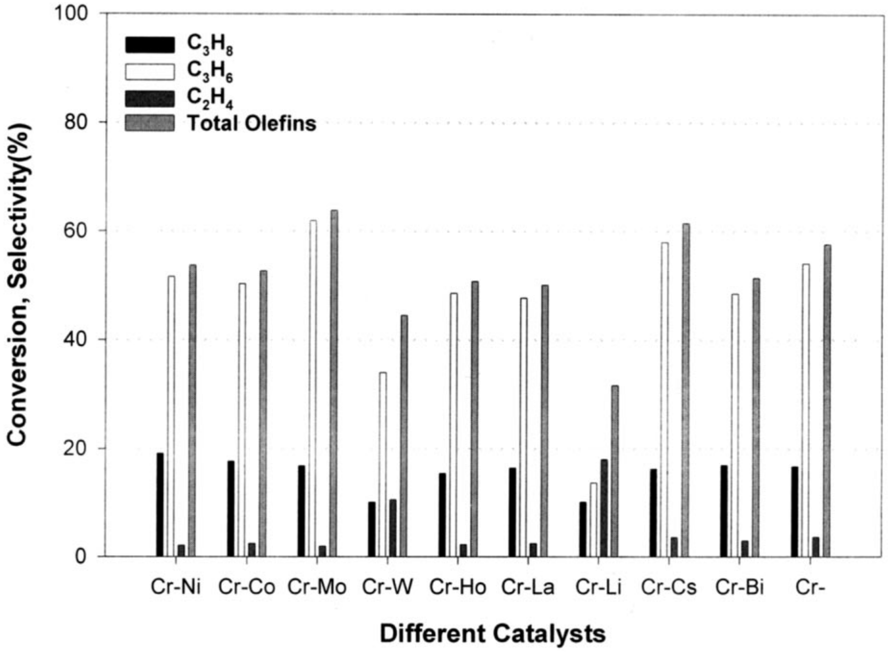

Figure 6. Propane conversion and olefin selectivities on Cr-M catalysts at 450 °C.

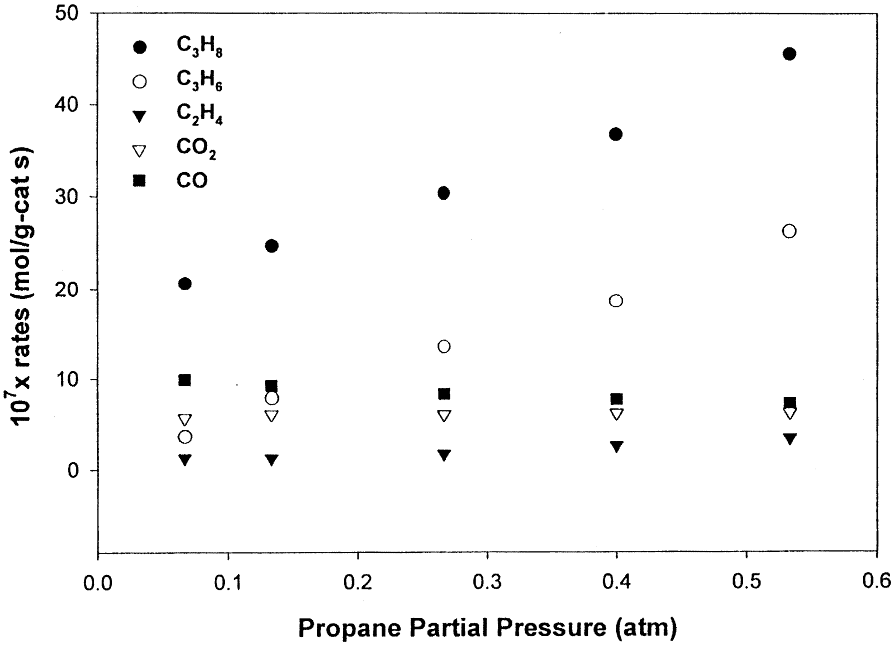

Figure 7. Rates of consumption of C_3H_8 and production of C_3H_6, C_2H_4, CO_2 and CO as functions of P_{C_3} at $P_O = 0.07$ atm and $T = 450\,°C$ over Cr-Mo.

[26]. The low surface oxygen character of molybdenum oxide is assumed to be imparted to Cr-Mo. Therefore, apart from lower reducibility, the higher selectivity to propylene by Cr-Mo may be associated with a decrease in the amounts of adsorbed oxygen as suggested by the TPR results. The oxygen species are shown to reduce the selectivity to olefins in the oxidative dehydrogenation reactions [24]. However, other factors could be more important, since the addition of bismuth and tungsten, unlike molybdenum, has shown a decrease in the selectivity at equal conversions. Perhaps molybdenum is more effective in controlling the agglomeration of chromium oxides that isolate the Cr sites, thereby decreasing the surface-adsorbed oxygen and reducibility of lattice oxygen. These characteristics have been shown to be important in optimizing a catalyst's performance [13]. In addition, the relative difference in atomic sizes between chromium and the metals could be important in determining the availability of the surface-adsorbed oxygen species [29].

Furthermore, the presence of cesium might significantly increase the surface basicity of the catalyst, since cesium is a strong basic metal. On the other hand, addition of weaker basic metal oxides such as those of La, Ho and Li results in lower selectivity to propylene. Their performances (conversion/selectivity) are Cr-La (16.4%/47.7%), Cr-Ho (15.4%/48.6%) and Cr-Li (10.1%/13.6%) under the same reaction conditions. Perhaps higher basicity is required to improve the selectivity. In addition, the lower selectivity exhibited by Cr-La and Cr-Ho could be as a result of higher surface oxygen. The rare earth oxides have been shown to possess a large amount of surface-adsorbed oxygen [12]. The presence of Li appears to induce more severe changes in the properties of the catalyst thereby reducing both the degrees of conversion and selectivity to propylene under the same conditions as the other catalysts were tested. The amount of lithium added might have degraded the catalyst [31]. It has been reported that positive effects of alkali metal dopants occur only within a certain ratio range [30–32]. There are different factors that could be responsible for the better performance of Cr-Mo. As shown by TPR studies, the decrease in surface reducibility is important in improving the selectivity to propylene at equal conversions. Cr-Mo with lower reducibility has shown higher selectivity to propylene compared with Cr- that is more susceptible to reduction. This comparison may be limited since the TPR traces of only a few samples were obtained.

The effect of feed composition on the reaction was further investigated on the Cr-Mo catalyst. The compositions were varied by changing the partial pressures of both propane and oxygen in a manner similar to figures 4 and 5. Figure 7 shows the effect of P_{C_3} on the rates. The trends of the rates are similar to the case of Cr-. The rate of propylene production is higher on Cr-Mo than on Cr- in the pressure range, but the trend is the same. It is interesting to observe the difference in the rates of CO_2 and CO between Cr- and Cr-Mo. On Cr- the rate of CO_2 (8.9×10^{-7} mol/g-cat/s) is higher than that of CO (6.7×10^{-7} mol/g-cat/s) at low P_{C_3}, while the values are 10.5×10^{-7} mol/g-cat/s for CO_2 and 1.5×10^{-7} mol/g-cat/s for CO at $P_{C_3} = 0.53$ atm (see figure 4). As shown in figure 7, Cr-Mo exhibits lower CO_2 (5.7×10^{-7} mol/g-cat/s) than CO (9.9×10^{-7} mol/g-cat/s) at low P_{C_3}, while at 0.53 atm the values are 6.3×10^{-7} mol/g-cat/s (CO_2) and 7.3×10^{-7} mol/g-cat/s

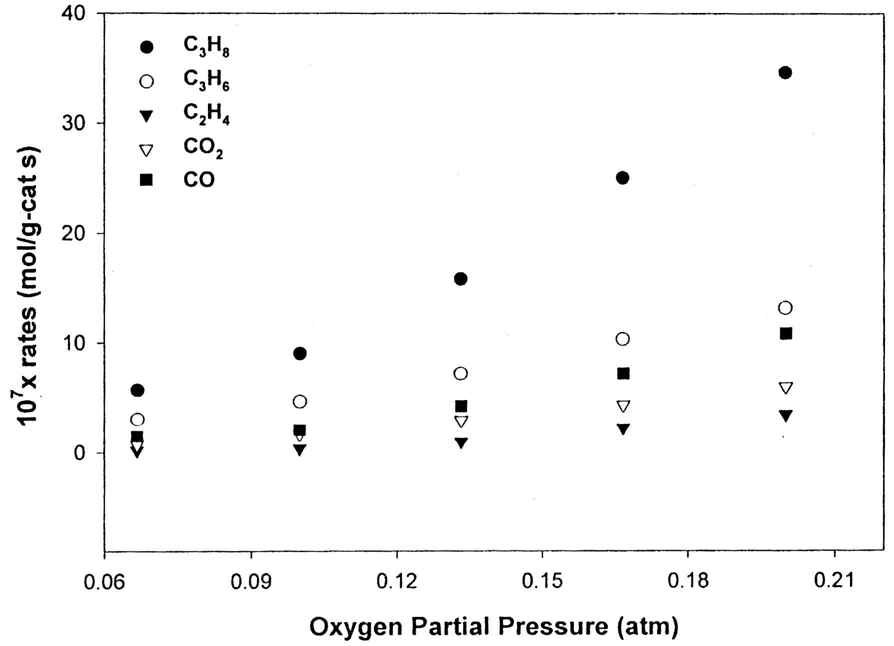

Figure 8. Rates of consumption of C_3H_8 and production of C_3H_6, C_2H_4, CO_2 and CO as functions of P_O at $P_{C_3} = 0.27$ atm and $T = 450$ °C over Cr-Mo.

(CO). This indicates a change in the role of the lattice oxygen species or the surface properties. This is reflected by the TPR result where the reducibility of the catalyst decreases by addition of molybdenum. Perhaps the more reactive oxygen species on Cr- leads to higher CO_2 than CO. The addition of the metal appears also to suppress the amount of surface-adsorbed oxygen. This is in agreement with the reported low amounts of surface-adsorbed oxygen in molybdenum oxide [28]. Figure 8 shows the effect of P_O on the activity of Cr-Mo. There is a higher rate of production of propylene than in figure 5. On Cr- the increase in rate of CO_2 (1.6×10^{-7} to 11.9×10^{-7} mol/g-cat/s) and CO (0.5×10^{-7} to 6.8×10^{-7} mol/g-cat/s) is different from the case of Cr-Mo where the values are 0.8×10^{-7} to 6.0×10^{-7} mol/g-cat/s (CO_2) and 1.5×10^{-7} to 10.8×10^{-7} mol/g-cat/s (CO) in the range $P_O = 0.07$–0.2 atm. This maintains the swap in the amount of CO_x produced by the two catalysts. It further shows the change in the role of the lattice oxygen, which apparently led to lower reducibility and hence the superior performance of Cr-Mo over Cr-.

3.4. Cr-Mo catalysts

The better performance of Cr-Mo compared to Cr- is not unexpected. Recent literature has shown that molybdate-based catalysts are active for the reaction [6,30,33–35]. Stern and Grasselli have reported POD on metal molybdates and showed that Ni–Co–Mo held some promise as catalysts for the reaction [6]. In another report, molybdate was shown to be active and promoted by the addition of potassium within a certain range of K/Mo ratios [30]. Other molybdenum-based catalysts such as V–Nb–Mo/TiO_2 [33], $KMnMoO_4$ [34] and K_2MoO_7 [35] have also been shown to activate alkanes in oxidative dehydrogenation reactions. In a study of the effect of addition of transition metals to V–Mg–O, it was concluded that the role of Mo ions was in increasing the amount of active oxygen in the oxidative dehydrogenation reactions [36].

Therefore, in order to shed more light on the Cr–Mo interactions and their effects on reducibility and performance of the catalyst, we study further the effect of addition of different amounts of molybdenum on the catalytic behavior of the Cr- catalysts. Table 4 shows the degrees of conversion of propane and product distributions for the reaction on the catalysts. The major products are propylene, ethylene and CO_x. At low temperature (300 °C), Cr- exhibits high conversion of propane (7.4%) compared with Mo-. The conversion is drastically decreased to negligible values by addition of molybdenum. Mo- also shows no activity under this condition. At higher temperature (350 °C), the degree of conversion of propane increases, but still there are significant differences in the conversions and product distributions for different ratios of Cr/Mo. For the catalyst of Cr/Mo ratio greater than two, the conversions are similar with an average value of 9%. But for ratios less than two, the conversions decrease to lower values. The lower selectivity shown, for example, by CrMo(4:1) over CrMo(1:4) is reflected by the XPS data. The lower BE (Mo $3d_{5/2}$ and Cr $2p_{3/2}$) of the former indicates a corresponding increase in surface basicity and hence the increase in selectivity. At this temperature, there is higher selectivity to CO_x perhaps due to electrophilic attack on C_3H_6 caused by surface-adsorbed oxygen or highly reducible lattice oxygen

Table 4
Performance of Cr-Mo catalysts (feed flow rate of 75 cm^3/min: 20 cm^3/min propane, 10 cm^3/min oxygen and the balance helium)

Catalyst	Conversion		Selectivity (%)				
	C_3H_8 (%)	SSA[a] × 10^2	C_3H_6	C_2H_4	CH_4	CO_2	CO
$T = 300\,°C$							
Cr-	7.4	6.5	26.8	3.3	2.4	52.6	14.9
CrMo(4 : 1)	0.7	0.7	64.2	0.0	0.0	0.0	35.8
CrMo(4 : 2)	0.5	0.5	53.7	0.0	0.0	0.0	46.3
CrMo(4 : 3)	0.2	0.3	0.0	0.0	0.0	0.0	100.0
Mo-	0.2	0.4	0.0	0.0	0.0	0.0	100.0
$T = 350\,°C$							
Cr-	8.9	7.8	31.7	3.1	2.2	48.0	14.9
CrMo(4 : 1)	10.1	10.1	51.2	2.9	0.0	27.4	18.3
CrMo(4 : 2)	8.2	8.8	46.7	2.9	0.0	28.2	22.1
CrMo(4 : 3)	5.9	7.6	57.8	0.0	0.0	22.6	19.6
CrMo(3 : 4)	7.2	11.6	61.4	0.0	0.0	17.8	19.9
CrMo(2 : 4)	3.7	6.4	76.8	0.0	0.0	10.3	12.9
CrMo(1 : 4)	5.0	10.9	67.6	0.0	0.0	15.0	17.4
Mo-	6.9	13.3	61.0	0.0	0.0	18.5	20.5

[a] Surface specific activity (SSA) is propane conversion per unit surface area of the catalyst.

[24]. Cr- exhibits the highest amount of CO_x probably due to its higher reducibility.

Addition of a small amount of molybdenum (Cr/Mo = 4) shows an increase of selectivity to propylene from 32 to 51% at comparable propane conversion. Further increase of Mo ions (to Cr/Mo = 2) still shows higher selectivity to propylene than Cr-. For instance, at an equal degree of conversion per unit surface area (of about 8%) for Cr- and CrMo(4:3), Cr-Mo exhibits selectivity to propylene of about twice that of Cr-. Furthermore, comparing CrMo(4:1) and CrMo(3:4), improvement in selectivity of about 10% for CrMo(3:4) over CrMo(4:1) at about same degree of propane conversion per unit area could be observed. This is perhaps due to isolation of chromium sites, agglomeration of which may increase the lattice oxygen reducibility and/or electrophilic surface-adsorbed oxygen [21]. The decrease in reducibility due to the presence of molybdenum is reflected by the values of T_M. Further, the XPS result indicates an increase in surface basicity with decrease in Cr/Mo ratio. Mo-, however, exhibits higher selectivity to CO_x. The superiority of Cr-Mo over Cr- is maintained at 420 °C, as shown in figure 9. However, the difference in selectivity to

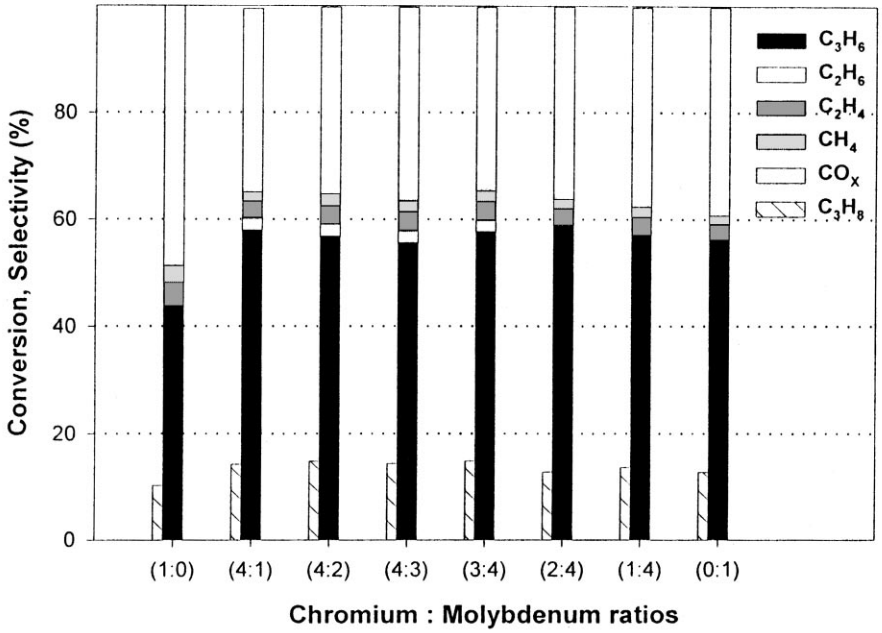

Figure 9. Propane conversions and selectivities to propylene at 420 °C over Cr-Mo oxide/γ-Al_2O_3.

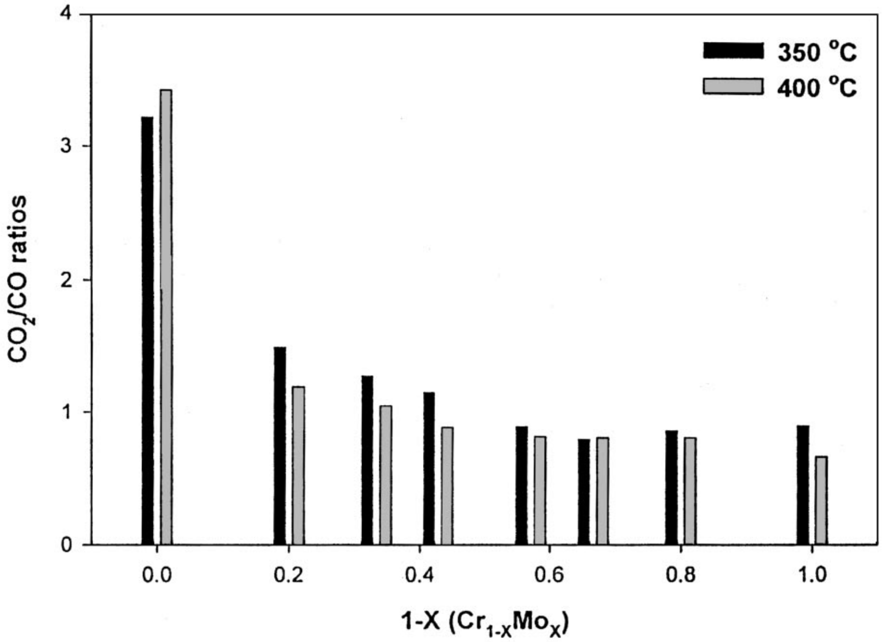

Figure 10. CO_2/CO ratios for different Cr/Mo ratios in the catalysts.

propylene is not as important at this temperature, but the amount of CO_x produced is lower on Cr-Mo. It is interesting to observe the increase in both conversion and selectivity to propylene with addition of molybdenum to chromium. In addition, a selectivity to C_2H_6 of about 2.0% is shown by some Cr/Mo ratios. The selectivity to CO_x is 48.5% on Cr-, 39.0% on Mo- and an average of 35.5% on Cr-Mo. This shows that the interaction between chromium and molybdenum is important in reducing the over-oxidation products.

The difference in reducibilities and performance of the catalysts may be observed from the variation of CO_2/CO ratio, as shown in figure 10. The ratio is about three on Cr- at 350 °C. It decreases with Mo addition to a value of less than one on Mo-. This further indicates the differences in the oxygen species associated with Cr- and Cr-Mo catalysts. Comparing the selectivities to CO and CO_2, and considering the reducibilities in figures 1 and 2, the ratio may be used as a measure of the reducibility of the catalysts. Similar variations in CO_2/CO are observed at 400 °C. The variation of Cr/Mo ratios shows the effect of addition of molybdenum on the performance of the catalyst.

The supported Cr-Mo oxide catalyst exhibits a propylene yield of 10.8% at 450 °C. This is an above average performance based on the yields reported for the same reaction using other catalysts. For instance, the following propylene yields have been reported in the literature: 11.2% for $HoVO_4$ at 320 °C [10], 7.2% for V–Mg–O at 500 °C [17], 16.4% for V–Mg–O at 540 °C [19], 30.0% for K–Mo/silica–titania at 550 °C [30], 6.8% for CeO_2 at 500 °C [37], 5.6% for V_2O_5–Sepiolite at 500 °C [38] and 1.8% for 5%V_2O_5/SiO_2 at 450 °C [39]. This shows that the supported chromium–molybdenum mixed oxides are promising as catalysts for the reaction. A more elaborate comparison of the performance of different catalysts for the same reaction has been reported elsewhere [40].

4. Conclusions

This work shows that the alumina-supported chromium oxide-based catalyst system is active for propane oxidative dehydrogenation. The physicochemical and catalytic properties of the catalysts showed differences due to doping of M (where M is Ni, Co, Mo, W, Ho, La, Li, Cs or Bi). The doping indicated no strong effect on the specific surface area of the support. The catalytic property varied with the basic character of the dopants. Chromium–molybdenum oxide/γ-Al_2O_3 is the most promising among the samples tested. A study of the effect of addition of molybdenum on chromium has shown that it has a strong influence on reducibility and surface structure of the catalyst and hence its performance. The dispersion of chromium is affected strongly by the relative amount of molybdenum as indicated by the XPS study. The specific surface area is also affected by Cr/Mo ratios. An increase in the amounts of molybdenum increased the sintering of alumina as suggested by lower BET surface areas. Cr-Mo is less reducible than Cr- as shown by both the effects of feed compositions and TPR studies. The lower reducibility of the catalyst leads to lower selectivity to CO_x with a corresponding increase in selectivity to propylene. Cr-Mo of appropriate Cr/Mo ratios shows better performance than either of the two metal oxides singly. However, the differences in performance in terms of selectivity to propylene decrease at high temperature, but still Cr-Mo shows generally lower amounts of over-oxidation products.

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