Activities of γ-Al_2O_3-supported metal oxide catalysts in propane oxidative dehydrogenation

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The activities of metal oxide catalysts in propane oxidative dehydrogenation to propene have been studied. The catalysts are M/γ-Al_2O_3 (where M is an oxide of Cr, Mn, Zr, Ni, Ba, Y, Dy, Tb, Yb, Ce, Tm, Ho or Pr). Both transition metal oxides (TMO) and rare-earth metal oxides (REO) are found to catalyze the reaction at 350–450 °C, 1 atm and a feed rate of 75 cm^3/min of a mixture of C_3H_8, O_2 and He in a molar ratio of 4 : 1 : 10. Among the catalysts, Cr–Al–O is found to exhibit the best performance. The selectivity to propene is 41.1% at 350 °C while it is 54.1% at 450 °C. Dy–Al–O has the highest C_3H_6 selectivity among the REO. At 450 °C, the other catalysts show C_3H_6 selectivity ranging from 16.2 to 37.7%. In general TMO show higher C_3H_6 selectivity than REO, which, however, show higher C_2H_4 selectivity. An attempt is made to correlate propane conversion and selectivity to C_3H_6 with metal–oxygen bond strength in the catalysts. For the TMO a linear correlation is found between the standard aqueous reduction potential of the metal cation of the respective catalyst and its selectivity to propane at 11% conversion. No such correlation has been found in the case of REO. Analyses of the product distributions suggest that for TMO propane activation the redox mechanism seems to prevail while the REO activate it by adsorbed oxygen.

KEY WORDS: oxidative dehydrogenation; propane; propene; metal oxide catalysts.

1. Introduction

Chemical conversion of light alkanes such as methane, ethane, propane and butane has been the subject of considerable research efforts in the last 10–15 years. This is in an attempt to replace short-chain olefins with alkanes as chemical building blocks in the petrochemical industries. This work was particularly motivated by the increase in olefin prices in the mid-1990s [1]. In addition, the transformation of alkanes to alkenes and other products is one of the most challenging problems of catalytic chemistry [2]. These considerations therefore provide the economic and academic justification for the study of the conversion of propane into more valuable products such as propene oxide, acrolein and acrylonitrile. A simpler approach, however, would be the understanding of the oxidative dehydrogenation reaction of propane to propene, which in turn could be extended to the production of more desirable products.

Catalytic oxidative dehydrogenation has two fundamental problems: (i) it is difficult to activate the inert alkanes and (ii) the corresponding olefins produced are generally less stable than the alkanes [3]. The latter problem results in overoxidation to undesired CO_X. Designing a catalytic system with the ability to suppress the overoxidation and thus improve the selectivities to the target olefins is a key challenge. Supported transition metal oxides are usually used to activate the alkanes and dioxygen. The catalyst is believed to play more important roles in activating the dioxygen [4] and the nature of the activated oxygen species directly influences the rate and selectivity of the reaction. In turn, the character of the metal cation of the metal oxide catalyst strongly determines the nature of the oxygen species.

There are some promising catalysts reported in the literature [5,6] but no industrial process yet for alkane conversion to valuable products. The exception is the production of maleic anhydride and acetic acid from *n*-butane. Unfortunately, the butane success could not be transferred directly to, for instance, ethane and propane. It is quite important to study the fundamental relationships between the nature of the catalyst's constituent parts and the rate and selectivity of the reaction for each alkane. On the basis of the nature of the oxygen species involved, two types of mechanisms for oxidative dehydrogenation are considered [7]. One type is the Mars–van Krevelen (redox) mechanism where oxygen of the metal oxides abstracts hydrogen from the hydrocarbon thereby forming an OH group. The OH group is removed by dehydration. The catalyst is reoxidized by oxygen in the gas phase. In the other case, the hydrogen is abstracted by the surface adsorbed oxygen species to form OH. The OH is removed as in the previous case. Oxygen is supplied from the gas phase to restore the surface oxygen.

Therefore, in order to improve the performance of promising catalysts, and to design new ones, it is important to study the relationships between the nature of the catalyst constituent parts and the metal–oxygen bond

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strength. The bond strength and/or surface adsorbed oxygen species to a large extent determine the degree of conversion and selectivity of the reaction. It would be interesting to shed more light on the roles of the metal cations of the metal oxide catalysts in selectivities to desired products of the reaction. Among the properties of the metals cations correlated with the activity of the catalysts are: reduction potential [8], electronegativity [4,9] and heat of formation of the corresponding oxides [10]. This approach was shown to be useful in explaining the factors that determine selectivity. However, there is yet no unified hypothesis on the structure–activity relationship [11]. For instance, there have been attempts to correlate the difference in selectivity in oxidation of propene with reducibility among the different catalysts. The general conclusion is that the higher the reducibility of the catalyst, the higher the conversion and the lower the selectivity [12]. This conclusion was limited by the observation of large differences in the catalytic activity for catalysts of similar reducibilities. This was attributed to the difference in the active site density in these catalysts.

Against this background, this paper focuses on propane oxidative dehydrogenation (POD) on a series of alumina-supported metal oxide catalysts with a view to investigating the influences of the metallic characteristics on the reaction. In a previous study, we reported the performances of 10% M–Al–O (where M is V, Cr, Mn, Zr or Ba) in the reaction [13]. In this study, 5 wt% loadings of both transition metal and rare-earth metal oxides have been prepared and tested.

2. Experimental

2.1. Catalyst preparation

Alumina-supported M oxides (where M is Ba, Cr, Zr, Mn, Ni, Dy, Tm, Tb, Ho, Ce, Yb, Pr or Y) were prepared by the impregnation method. In each case a predetermined amount of the precursor was added gradually with stirring to a crystallizing dish containing a pre determined amount of γ-Al_2O_3 (50–200 m^2/g, Riedel De Haen AG) as a support to make 5 wt% active component on the support. For instance, 38.5 g of $Cr(NO_3)_3$ was added to 100 g of γ-Al_2O_3 to obtain 5 wt% chromium oxide on the support. The same support was used in all cases. The content was continuously stirred while the excess deionized water was being evaporated. A thick paste was obtained which was dried in an oven at 100 °C overnight. The catalysts were calcined under air at specified temperatures: table 1 gives the catalyst precursors and calcination temperatures. Different calcination temperatures were used because the precursors convert to the respective oxides at different temperatures [14,15]. M–Al–O is used to represent the metal oxide supported on alumina.

Table 1
Alumina-supported metal oxide catalyst precursors and calcination temperature (calcination time = 3 h)

Metal oxide on Al_2O_3	Precursor (manufacturer)	Calcination temperature (°C)
Pr	$Pr(NO_3)_3 \cdot 6H_2O$ (Aldrich chem)	700
Ce	$Ce(NO_3)_2$ (RDH Germany)	500
Ho	$Ho(NO_3)_3 \cdot 5H_2O$ (Aldrich chem)	700
Tb	$Tb(NO_3)_2 \cdot 6H_2O$ (Aldrich chem)	750
Tm	$Tm(NO_3)_2 \cdot 6H_2O$ (Aldrich chem)	500
Cr	$Cr(NO_3)_3 \cdot 9H_2O$ (RDH Germany)	500
Ni	$NiCl_2 \cdot 6H_2O$ (HW')	600
V	NH_4VO_3 (RDH Germany)	600
Mn	$MnCl_3$ (Aldrich chem)	600
Yb	$(CH_3COO)_3Yb$ (Merck)	800
Ba	$(CH_3COO)_2Ba\ H_2O$ (Merck)	800
Zr	$Zr(NO_3)_3$ (BDH, AnalaR)	600
Dy	$(CH_3COO)_3Dy$ (Merck)	600
Y	$Y(NO_3)_2$ (BDH, AnalaR)	500

The catalysts were tested in a fixed-bed, quartz laboratory reactor, operated at atmospheric pressure and temperature range 350–450 °C. The feed was 26.7% propane, 6.6% oxygen and the balance helium. Negligible conversion was observed when the reaction was tested under this condition over quartz granules of the same sizes as the catalysts. The detailed experimental set-up and the method of analysis are reported elsewhere [13].

2.2. Catalyst characterization

The BET surface areas were measured with a Micromeritics ASAP 2010 N_2 physisorption apparatus. Powder X-ray diffraction (XRD) patterns were recorded at room temperature using CuKα 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.

3. Results and discussion

The supported transition metal (Cr, Mn, Zr and Ni), Ba and rare-earth metal (Dy, Tb, Yb, Ce, Tm, Ho, Pr and Y) oxides have been prepared and tested. These metals were chosen in order to determine the influence of some of their properties on the degrees of conversion and selectivities to propene for the reaction. In addition, we put emphasis on the metals that have not been reported for POD. BET surface area, pore diameters and pore volumes for the catalysts are given in table 2. There are no significant differences in the values of the BET surface area and the other properties of the catalysts. Figures 1 and 2 show typical XRD patterns of the catalysts.

Figure 1 shows the patterns for oxides of (1) V, (2) Cr, (3) Mn, (4) Zr, (5) Ba and (6) Ni while figure 2 shows

Table 2
Some physical properties of some of the catalysts

Sample	Total (BET) surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)
Cr–Al–O	183.1	0.302	66.0
Mn–Al–O	113.0	0.203	71.8
Ni–Al–O	161.3	0.235	60.4
Zr–Al–O	108.1	0.180	66.6
Ba–Al–O	123.4	0.229	74.0
Ce–Al–O	140.1	0.230	66.6
Pr–Al–O	118.0	0.221	75.0
Tb–Al–O	146.0	0.249	68.4
Ho–Al–O	147.7	0.234	63.4
Y–Al–O	131.5	–	–
Tm–Al–O	140.5	–	–
Dy–Al–O	131.4	0.190	59.0

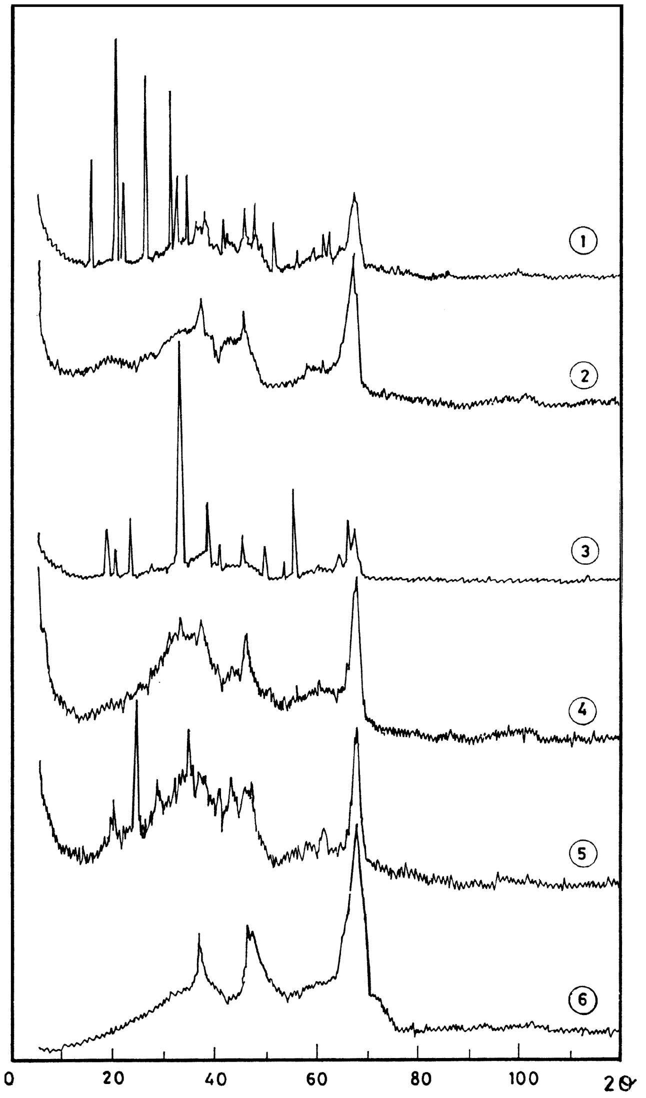

Figure 1. XRD patterns of γ-Al_2O_3-supported metal oxides: V (1), Cr (2), Mn (3), Zr (4), Ba (5) and Ni (6).

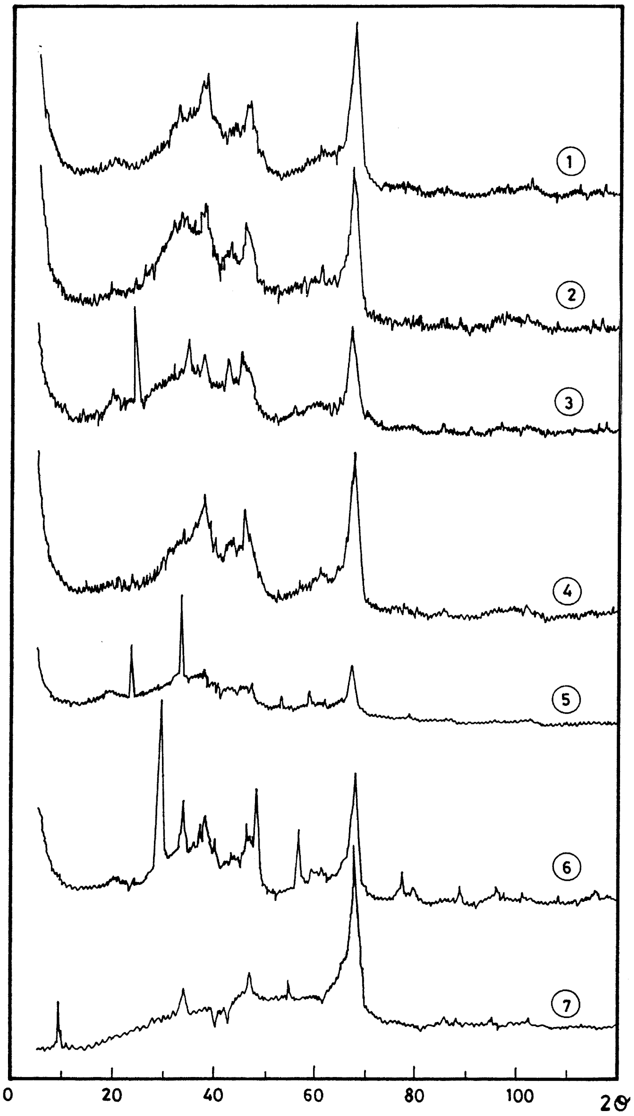

Figure 2. XRD patterns of γ-Al_2O_3-supported rare-earth metal oxides: Ho (1), Dy (2), Yb (3), Tb (4), Tm (5), Ce (6) and Pr (7).

those of (1) Ho, (2) Dy, (3) Yb, (4) Tb, (5) Tm, (6) Ce and (7) Pr. The dominant reflections at 2θ angles of 65–68° are attributable to γ-Al_2O_3. The γ-Al_2O_3 is a high-surface-area material having small crystalline size and therefore broad peaks. Peaks around 2θ angles of 45° and 36° may also be of γ-Al_2O_3. As seen from the figures, both crystalline and amorphous (micro-crystalline) phases of the metal oxides may be present in the samples. There are reflections that could be associated with the oxides. For instance in figure 1(2), typical reflections of α-Cr_2O_3 at 2θ angles of 24.7°, 34°, 43°, etc., could be observed [16]. In figure 2(6), the 2θ angles at 28°, 33°, 27.5°, 57° and 59° are associated with CeO_2.

The major products of the reaction are propene, ethene and CO_X for both transition metal oxides (TMO) and rare-earth metal oxides (REO). The changes in conversion with temperature for the catalysts are

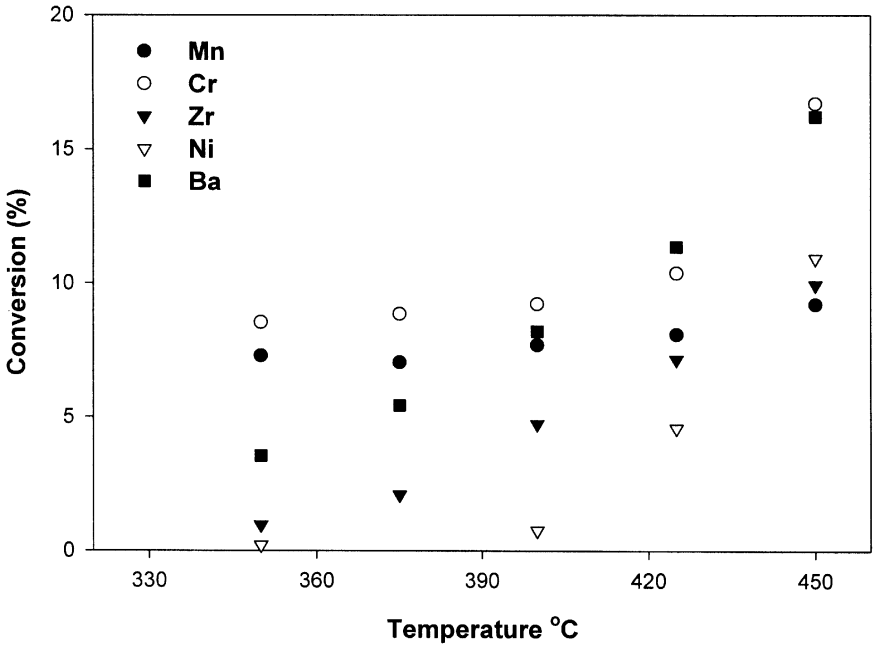

Figure 3. Propane conversion as a function of temperature over alumina-supported metal oxides.

depicted in figures 3 and 4. All the catalysts exhibited increases in the degree conversion with increase in temperature. At low temperature (350 °C), Cr–Al–O shows the highest conversion of propane of 9% while Zr–Al–O shows the least (1.0%). At 450 °C, Cr–Al–O maintains a high degree of conversion of 16.7% while Ce–Al–O has the lowest of 8.2%. The conversions for the others are Mn–Al–O (9.2%), Zr–Al–O (9.9%), Tb–Al–O (11.4%), Tm–Al–O (13.8%), Ho–Al–O (14.6%), Ba–Al–O (16.2%) and Yb–Al–O (16.7%). The differences in conversions indicate the influence of the metallic properties on the rate-determining hydrogen abstraction by the catalysts.

The degrees of conversion of Ce–Al–O, Tb–Al–O and Dy–Al–O seem to show little or no increase with temperature at high temperatures. This could be due to diffusion effects. It could also be due to complete consumption of oxygen, thus a low amount of available lattice oxygen for rate-determining abstraction of hydrogen from propane [8)] At 425 °C and higher temperatures, there was complete consumption of oxygen during the reaction. This may limit the interpretation

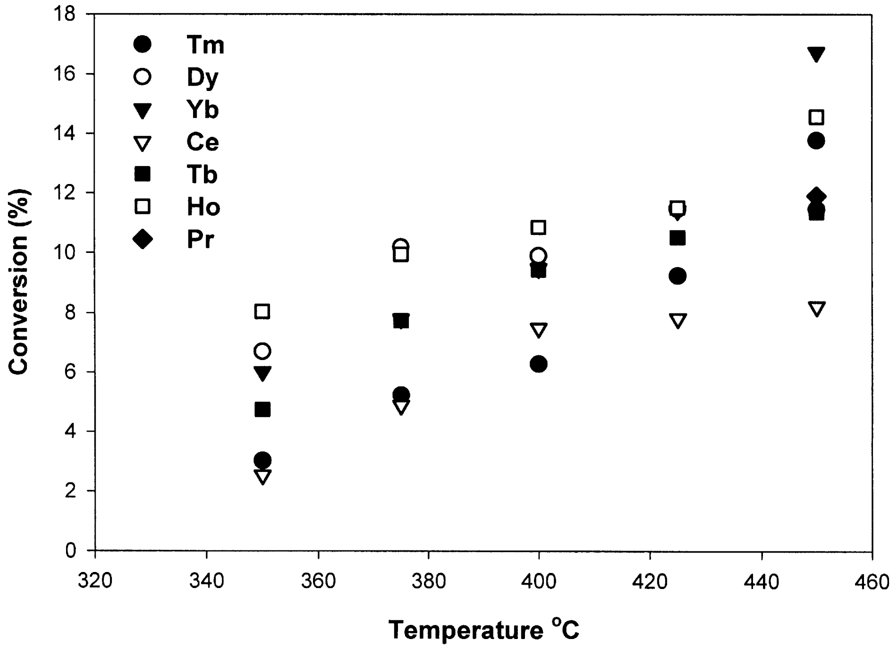

Figure 4. Propane conversion as a function of temperature over alumina-supported rare-earth metal oxides.

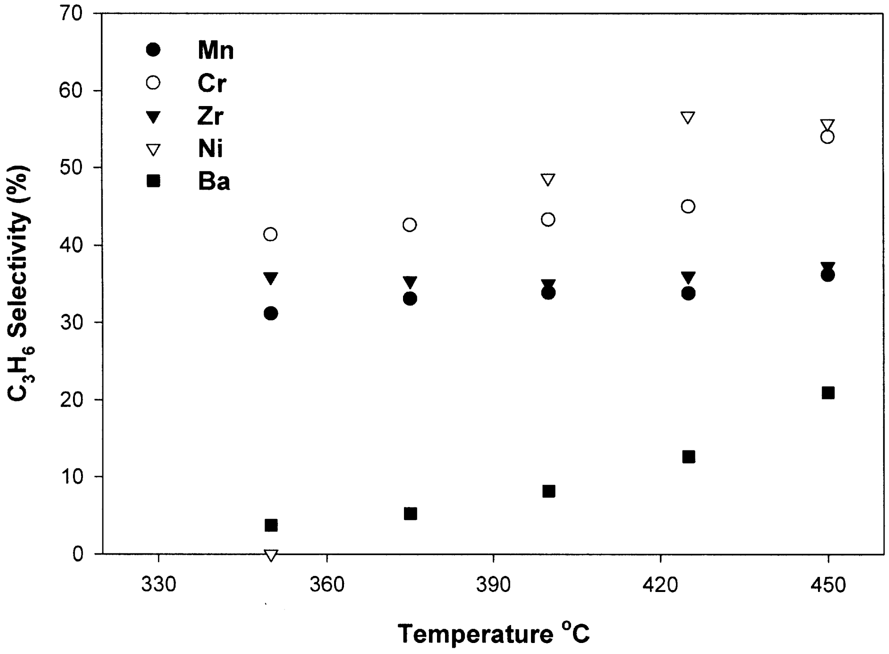

Figure 5. Propene selectivities as a function of temperature over alumina-supported metal oxides.

of the performance of the catalysts. The relatively small increase in propane conversions is shown by some of the REO only, while the TMO show a continuous increase in conversion with increase in temperature. This behavior may not, however, be strictly associated with the behavior of the REO, as other REO (Tm–Al–O, Yb–Al–O and Ho–Al–O) exhibit similar trends to the TMO. The REO behavior observed here is in agreement with the non-redox character as reported earlier [7,17].

The selectivities of the catalysts to propene are shown in figures 5 and 6. At 350 °C, Cr–Al–O shows the highest value of 41.4% while the lowest is shown by Ni–Al–O. At 450 °C, Cr–Al–O still maintains the highest selectivity of 54.1%, while the lowest is Yb–Al–O with 7.6%. It may be observed that Ba–Al–O, Yb–Al–O, Tm–Al–O and Cr–Al–O show continuous increase in propene selectivities with increase in temperature. This is probably due to a decrease of surface-adsorbed electrophilic oxygen with decrease in the oxygen supply at

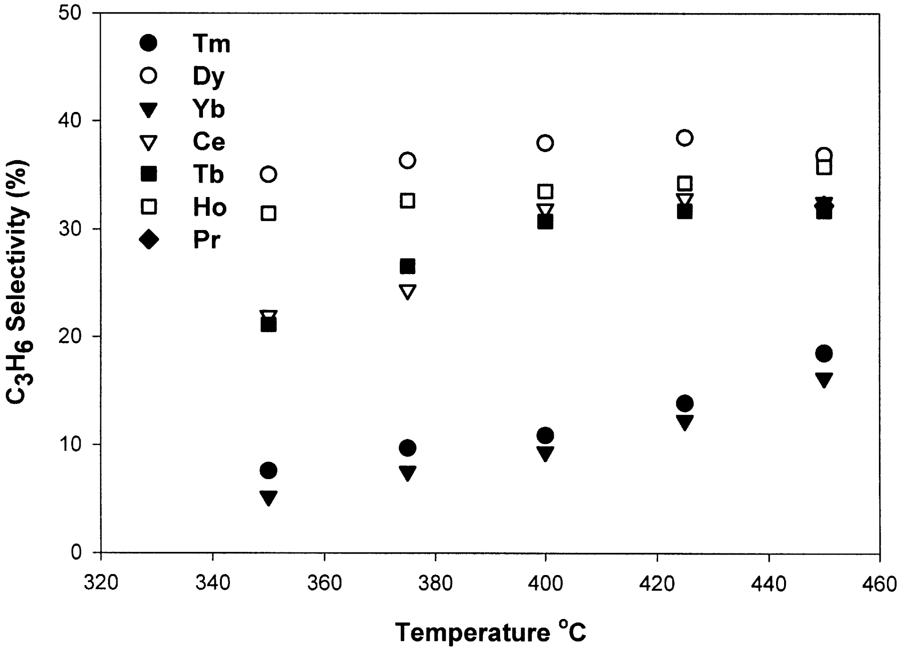

Figure 6. Propene selectivities as a function of temperature over alumina-supported rare-earth metal oxides.

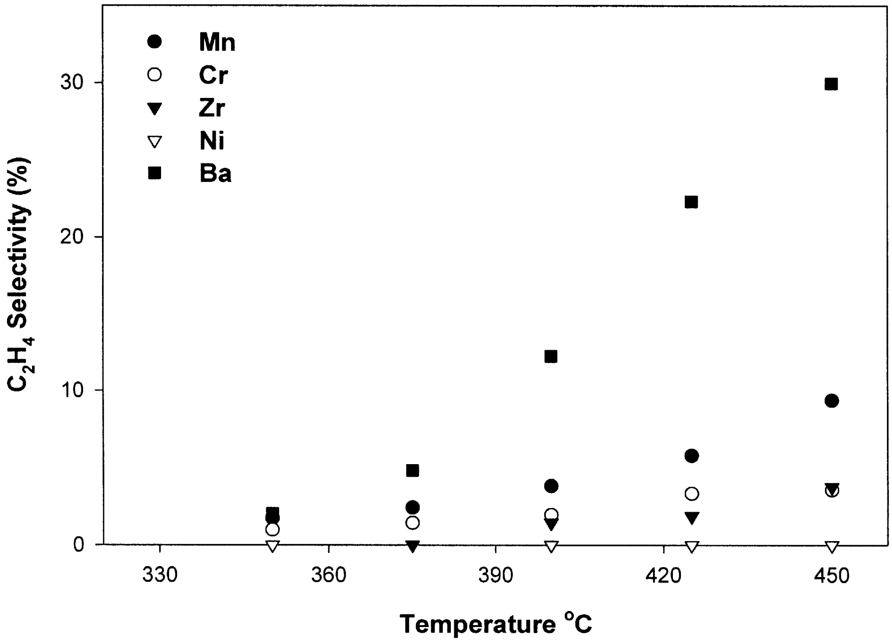

Figure 7. Ethene selectivities as a function of temperature over alumina-supported metal oxides.

high temperature [4]. This is especially so since there was complete consumption of oxygen at high temperatures during the reaction. Dy–Al–O shows a maximum of 38.5% at 425 °C then decreases to 36.9% at 450 °C. The selectivities to propene on Tb–Al–O and Ce–Al–O increase with increase in temperature but level off at 400 °C. The selectivities on Mn–Al–O, Ho–Al–O and Zr–Al–O show little or no change with temperature under the conditions of the experiment. The changes in the selectivities of C_3H_6 and CO_X on the catalysts indicate the effect of the metal properties on the selectivity. For instance, there is high selectivity to C_2H_4 for Mn–Al–O compared with other TMO as clearly shown in figure 7. It may be observed that Cr–Al–O holds the highest promise in terms of degree of conversion and selectivity to olefins among the catalysts investigated. Alumina-supported chromium oxide catalyst has been widely employed in dehydrogenation reactions and recently it was reported to be active in the oxidative dehydrogenation of isobutane [18].

The increase in selectivity to propene with increase in propane conversion is unusual for the reaction. Generally, oxidative dehydrogenation reactions on oxide catalysts exhibit a decrease in selectivities to olefins with increase in alkane conversion [7,19], although some studies reported contrary observations [20,21]. The difference is perhaps due to the fact that the conversion was varied by varying the reaction temperature. The observation here could be explained based on the reducing atmosphere on the surface of the catalysts due to low oxygen supply (hydrocarbon/oxygen ratio of 4). The catalysts' surfaces might have been reduced and the degrees of reduction increase with increase in temperature. On all the catalysts, oxygen was totally consumed at 425 °C and above. This implies that the tendency for the formation of C–O bonds, responsible for reducing the selectivities to olefins, was reduced thereby enhancing the selectivity to olefins. Additionally, the observation might be because of a decrease in the surface-adsorbed electrophilic oxygen at higher temperatures due to low supply of oxygen. The adsorbed oxygen was reported to enhance the selectivity to CO_X in the reaction [9].

The selectivities to C_2H_4 are shown in figures 7 and 8 for all the catalysts. At 350 °C the catalysts exhibit low average ethene selectivities with a maximum of 2% for TMO and 5% for REO. Cr–Al–O and other TMO maintained low values in the reaction temperature range. This partly suggests that the reaction is not by the adsorbed oxygen on the catalysts surfaces. The surface oxygen has been associated with electrophilic attack on the propyl species or propene molecule thereby producing C_2H_4 and CH_4 in POD over REO-based catalysts, where CH_4, C_2H_4 and CO_2 were the predominant products [17]. Similar behavior is observed for the REO catalysts tested in this work, as shown in figure 8. The REO produce more C_2H_4 than the TMO. They show generally higher amounts especially at 450 °C. The behavior of REO observed here suggests that surface-adsorbed oxygen might be involved in the activation of the propane and/or in the selectivity-determining step of the reaction [17]. The selectivities to CO_X are shown in figures 9–12. It is observed that Cr–Al–O exhibits the lowest average selectivity to CO_2 while Mn–Al–O shows the highest. The selectivity to CO shows different trends, with Cr–Al–O showing much higher values than Mn–Al–O. Perhaps this is due to differences in the properties of the metals.

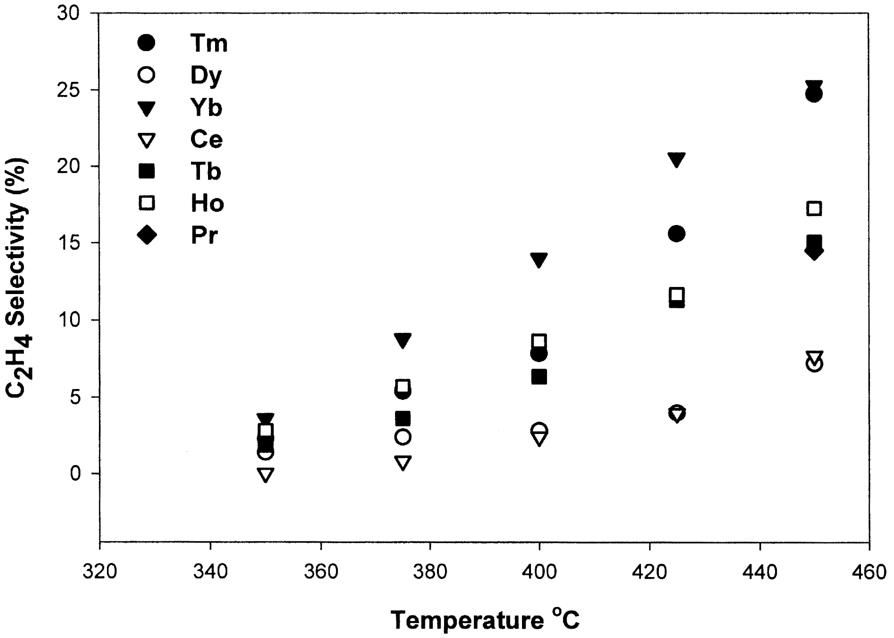

Figure 8. Ethene selectivities as a function of temperature over alumina-supported rare-earth metal oxides.

3.1. TMO product distributions

Among the TMO, Cr–Al–O exhibits the highest C_3H_6 yield as indicated by selectivity in figure 5. Almost equal amounts of C_2H_4 and CH_4 were produced. This may suggest that they are formed from splitting of the same propane molecules. Their respective amounts and that of the propene both increase with increase in temperature. It is observed that the amount of CO_X decreases with increase in temperature. This could be due to the reducing environment because of the low oxygen supply. The product distributions for Cr–Al–O and other TMO can be observed from figures 5, 7, 9 and 10. For Mn–Al–O, CO_2 is a dominant product. The C_3H_6 average selectivity is about 30%. Ba–Al–O is included among the TMO for convenience. It is found to be essentially a combustion catalyst under the conditions of the reaction. Only a small amount of propene is produced. In addition, there is a large difference between the amounts of C_2H_4 and CH_4, which shows a marked deviation from the behavior exhibited by both the TMO and REO.

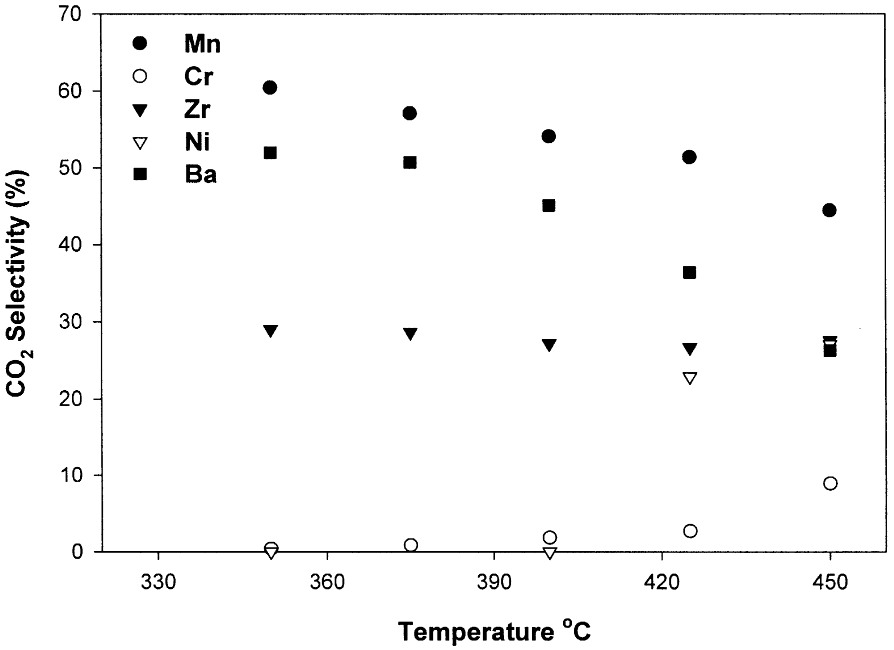

Figure 9. CO_2 selectivities as a function of temperature over alumina-supported metal oxides.

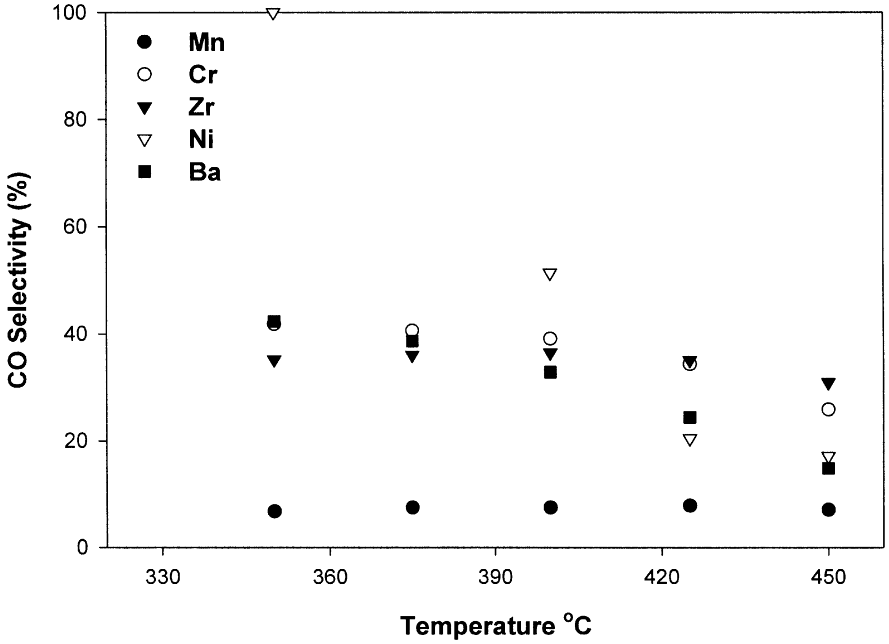

Figure 10. CO selectivities as a function of temperature over alumina-supported metal oxides.

3.2. REO product distributions

Among the REO, Dy–Al–O exhibits the best performance in term of selectivity (37%) to propene. It also shows lower production of C_2H_4 and CH_4. Next in performance is Ho–Al–O as observed in figure 6. It has an average C_3H_6 selectivity of 33% and a CO_X selectivity of 40% at 450 °C. At the same temperature, Ce–Al–O and Tb–Al–O exhibit about equal selectivities to propene of 32.5 and 31.7% respectively. Yb–Al–O and Tm–Al–O are mainly combustion catalysts under the reaction conditions. They show CO_X as the dominant products.

The behaviors of REO, TMO and barium oxide clearly indicate a strong relationship between the character of the metal cations in the catalyst and the performance of the catalyst in the reaction. Proper understanding of this relationship will serve as a guide for designing new catalytic systems and improving the existing ones for oxidative dehydrogenations.

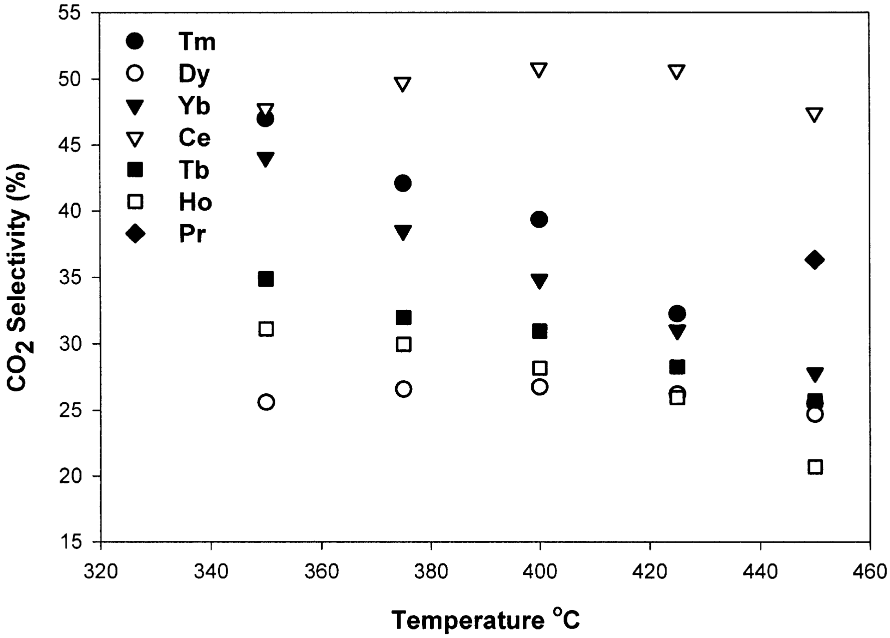

Figure 11. CO_2 selectivities as a function of temperature over alumina-supported rare-earth metal oxides.

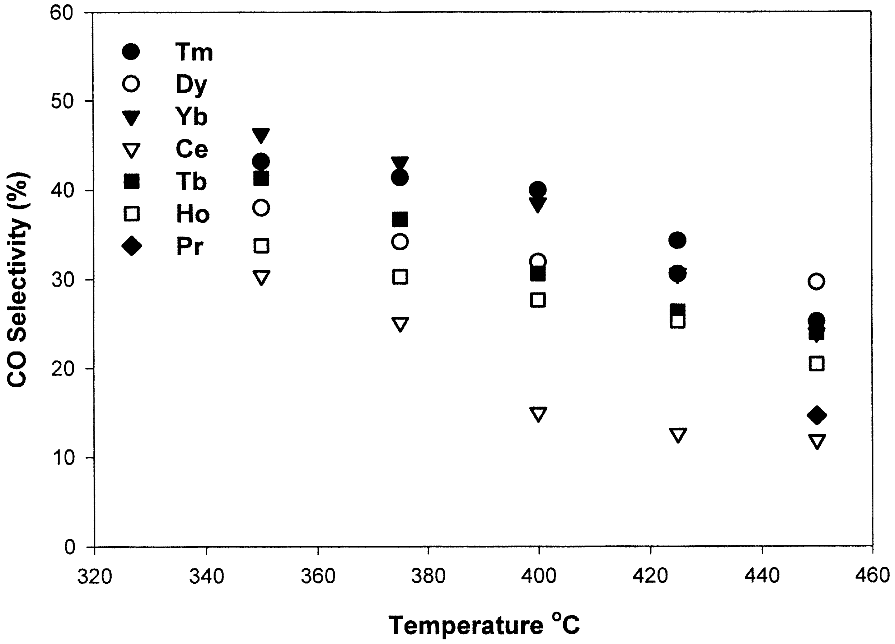

Figure 12. CO selectivities as a function of temperature over alumina-supported rare-earth metal oxides.

3.3. *Reactivities of lattice oxygen*

As shown in table 2, the variation in catalyst BET surface area may not have significant effects on the performances of the catalysts [22]. The different degrees of conversion and selectivities of the catalysts are assumed to be associated with intrinsic properties of the lattice oxygen in the catalysts. The reactivities of the lattice oxygen of the metal oxides could be estimated from the properties of the catalyst cations such as reduction potential, ionization potential and electronegativity of the metal. The oxide standard energies of formation could also give a simple indication of reactivity. As a first approximation, these properties could be used as indices for the metal–oxygen bond strength, which may in turn suggest the activity of the catalyst [8–12]. This simple approach was shown to be useful in CH_4 partial oxidation to formaldehyde tested on metal oxide catalysts. The conversions and selectivities have been shown to correlate with the electronegativities of the counter-metals in the oxides [9]. It has been reported that the reduction potential of the metal cations in metal orthovanadate is linearly correlated with the reducibility of the catalysts as indicated by temperature-programmed reduction (TPR) [23]. In a recent report, standard energies of formation of oxides were shown to correlate with the acidity of metal pyrophophate catalysts [10]. It was concluded that the energy of formation of the metal could be used to determine the character of lattice oxygen in a catalyst.

The use of of these properties is particularly simple and useful since it provides a basic indication of the nature of M–O bonds toward preliminary screening of catalysts as suitable candidates for further investigations. The M–O bond suggests the susceptibility of hydrogen removal by the catalyst. It also suggests the rate of removal of OH or H_2O from the catalyst surface and the tendency to attack the electron-rich centers of both propene and propyl species. The hydrogen removal determines both rate- and selectivity-determining steps in this reaction [8]. At a fixed degree of conversion, the reducibility of the catalyst determines its ability to abstract another hydrogen that leads to the production of propene.

In this study, selectivities to propene at 11% propane conversion for the catalysts are plotted against the aqueous reduction potential (RP) of the corresponding metal cations. The RP indicates the nature of the metal–oxygen bond in the catalysts. Figure 13 shows the selectivity to propene against the RP. In order to facilitate the interpretation of the relationship between the RP and selectivity, the result of the reaction on three more metals is included. Detailed results of the reaction on these additional metals are given in table 3. There is an upward trend, depicting an increase in selectivity with increase in the reduction potential. This simple trend suggests a correlation of the behavior of the metals with the selectivity to propene in the case of TMO. It indicates that the higher the reduction potential the lower the selectivity to CO_X within the range of potentials used in this work. The results obtained here, at 5% loading of the active component on the support, are in agreement with our previous study of 10% M–Al–O (where M is V, Cr, Mn, Zr or Ba) [13]. Although the catalysts with higher loadings exhibit generally higher activities, the correlation of the selectivities with RP is maintained. There is no correlation between the selectivities and RP in the case of REO catalysts, as shown in figure 13.

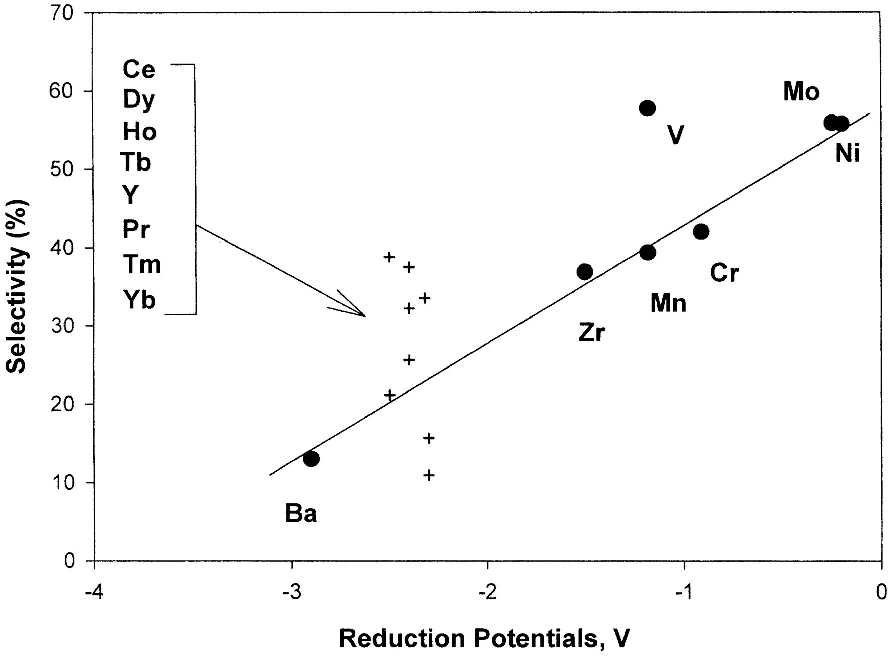

Figure 13. Selectivities to propene at 11% propane conversion as a function of reduction potential of the counter-metal cation in the catalysts.

The aqueous RP of a cation indicates the ease of removal of *n* electrons from a metal to form aquated cations. The RP may be used to infer the metal–oxygen bond strength in a metal oxide. The selectivity to propene is determined by the nature of the surface reaction of the propyl radical produced after the rate-determining abstraction of the first hydrogen from propane. Dehydrogenation products are obtained if primary C–H bonds are further broken and oxygen is not inserted. Otherwise, oxygenates or CO_X may be produced at the expense of propene. The lower the value of RP, the stronger is the attraction of oxygen to the metal. The strong attraction of the electrons from the oxygen makes the oxygen more electrophilic. Therefore, the susceptibility of the oxygen to attack an electron-rich center such as the C=C bonds increases with decrease in the RP of the cation in the metal oxide. This leads to combustion products. On the other hand, when the metal has high RP (i.e. less attraction to the oxygen) the oxygen in the metal oxide has less of a tendency to attack electron-rich species. In addition, it is easier to desorb electron-rich propene from the surface [24]. This explains the observation of higher selectivity to propene on the catalyst whose cation has higher RP.

Table 3
Oxidative dehydrogenation propane on supported vanadium and molybdenum oxides at 350–500 °C and feed flow of 75 cc/min

Catalyst name	Temp. (°C)	Conv. (%)	Selectivity (%)				Ref.
		C_3H_8	C_3H_6	C_2H_4	CO_2	CO	
V–Al–O*	350	12.5	57.7	0.4	15.0	26.6	[8]
	375	13.0	59.8	0.5	14.8	24.4	
	400	14.8	63.2	0.9	14.0	20.9	
	425	17.1	65.7	1.5	13.5	17.3	
	450	25.6	66.1	3.4	13.4	11.9	
Mo–Al–O	350	9.3	56.7	0.0	19.3	24.0	This work
	400	12.0	55.7	2.8	17.0	22.9	
	500	15.1	58.3	4.8	15.6	18.6	

Since no such correlation was observed for the REO catalysts, it could be inferred that the alkanes are activated via different mechanisms. Perhaps the surface-adsorbed oxygen species is involved in the reaction, which makes the selectivities less dependent on the RP. Thus the RP may serve as a simple criterion for determining the reactivity of the lattice oxygen in the case of TMO.

4. Conclusion

It is shown that γ-Al_2O_3-supported transition metals (Cr, Mn, Zr and Ni), Ba and rare-earth metals (Y, Dy, Tb, Yb, Ce, Tm, Ho and Pr) are reactive in propane oxidative dehydrogenation under the conditions employed here. Cr–Al–O is found to exhibit the best performance. The C_3H_6 selectivity is 41.4% (yield = 3.5%) at 350 °C while it is 54.1% (yield = 9.0%) at 450 °C. It is significant to observe that Cr–Al–O shows some promise as a catalyst for the reaction. The high selectivity to CO_X is perhaps as a result of loosely bound oxygen on the surface of the catalyst. Further studies are needed to improve its performance. Dy–Al–O has the highest C_3H_6 selectivity among the REO. Generally, the TMO show higher C_3H_6 selectivity than REO, which, however, show higher C_2H_4 selectivity. There is a linear correlation between the selectivity to propene at 11% propane conversion and the aqueous reduction potential of the metal cations in the case of TMO. No such correlation is established in the case of REO. This perhaps suggests different mechanisms for the reaction on the two groups of catalysts. This work has tentatively shown that the standard aqueous reduction potential of metal cations could be used as a measure of the reactivities of lattice oxygen in transition metal oxide catalysts.

References

[1] M. Vaarkamp and T. Ushikubo, Appl. Catal. A: General 174 (1998) 99.

[2] O.V. Krylov, Kinetic. Catal. 39 (1998) 472.

[3] F. Cavani and F. Trifiro, in: *3rd World Congress on Oxidation Catalysis*, eds. R.K. Grasselli, S.T. Oyama, A.M. Gaffney and J.E. Lyons, 21–26 September 1997, San Diego, CA, p. 19.

[4] Y. Moro-oka, Catal. Today 45 (1998) 3.

[5] D.L. Stern and R.K. Grasselli, J. Catal. 167 (1997) 550.

[6] F. Cavani and F. Trifiro, Catal. Today 24 (1995) 307.

[7] M. Bearns and O. Buyevskaya, Catal. Today 45 (1998) 13.

[8] H.H. Kung, Ind. Eng. Chem. Prod. Res. Dev. 25 (1986), 171.

[9] K. Otsuka and M. Hatano, J. Catal. 108 (1987) 252.

[10] Y. Takita, K. Sano, K. Kurosaki, N. Kawata, H. Nishiguchi, M. Ito and T. Ishihara, Appl. Catal. A 167 (1998) 49.

[11] S.T. Oyama, A.N. Desikan and W. Zang, ACS Symp. Ser. 523 (1992) 16.

[12] W.M.H. Sachtler and N.D. De Boer, in: *Proc. 3rd Int. Cong. Catal.*, Amsterdam, 1964, Vol. 1, p. 252.

[13] S.M. Al-Zahrani, B.Y. Jibril and A.E. Abasaeed, Ind. Eng. Chem. Res. 39 (2000) 4070.

[14] G.A.M. Hussein, S.A. Mansour and M.I. Zaki, Thermochim. Acta 150 (1989) 153.

[15] G.A.M. Hussein, private communications.

[16] F. Cavani, M. Koutyrev, F. Trifiro, A. Bartolini, D. Ghisletti, R. Iezzi, A. Santucci and G. Del Piero, J. Catal. 158 (1996) 236.

[17] W. Zang, X. Zhou, D. Tang, H. Wan and K. Tsai, Catal. Lett. 23 (1994) 103.

[18] B. Grzybowska, J. Sloczynski, R. Grabowski, K. Wcislo, A. Kozlowska, J. Stoch and J. Zielinski, J. Catal. 178 (1998) 687.

[19] A. Dejoz, J.M. Lopez Nieto, F. Marquez and M.I. Vazquez, Appl. Catal. A 180 (1999) 83.

[20] S.L.T. Andersson, Appl. Catal. A 112 (1994) 209.

[21] J.E. Miller, N.B. Jackson, L. Evans, A.G. Sault and M.M. Gonzales, Catal. Lett. 58 (1999) 147.

[22] E.A. Mamedov and S.N. Shaikh, Arabian J. Sci. Eng. 24, 1C (1999) 27.

[23] O.S. Owen and H.H. Kung, J. Mol. Catal. 79 (1993) 265.

[24] B. Grzybowska, J. Sloczynski, R. Grabowski, K. Samson, I. Gressel, K. Wcislo, L. Gengembre and Y. Barbaux, Appl. Catal. A 230 (2002) 1.