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Isobutane oxydehydrogenation on Al_2O_3-supported transition and rare-earth metal oxides

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Abstract

The Oxidative dehydrogenation of isobutane to isobutene was studied on transition (Cr, Mn, V, Ni and Zr), rare-earth and other (Ho, Sm, Pr, Ce, TI, Yb and Tb) metal oxides supported on Al_2O_3 with metals loading varying from 2.5 to 10%. The reaction was carried out at atmospheric pressure and temperatures of 250–500 °C. A 4:1 ratio of isobutane to oxygen at a total flow rate of 75 cm^3/min was used. The tested metal oxides exhibited different activities and selectivities at different reaction temperatures. The catalysts are classified into two groups based on their activity over the reaction temperature range. Cr catalyst showed the best performance among the catalysts active below 400 °C with 62% selectivity towards isobutene at 10% conversion. For the second group (active above 400 °C) Ni showed the highest activity at 500 °C (32% conversion) followed by Zr and Tb (both of 19.2% conversion). The BET surface areas of the catalysts were between 108 and 183 m^2/g. Aqueous reduction potential of the metal cation was also used to explain the selectivity trend of these metal oxides. The obtained relation suggested that metals with low reduction potential are generally selective towards the production of olefins.

Keywords: Oxidative dehydrogenation; Isobutane; Isobutene; Transition metal; Rare-earth metal; Alumina oxide; Reduction potential

1. Introduction

In the last few years there has been a pronounced tendency in petrochemical industry to utilize and upgrade cheaper alkanes instead of using more expensive olefins. The commercial production of isobutene using classical dehydrogenation reactions has increased during recent years due to its utilization as gasoline octane enhancers (i.e., methyl *tert*-butyl ether MTBE). These dehydrogenation processes require much energy and suffer from rapid deactivation of the catalysts. Oxidative dehydrogenation (ODH) of alkanes, on the other hand, represents an important and promising alternative for producing more valuable olefins.

Many studies have been carried out to develop active and selective catalysts for oxidative dehydrogenation of isobutane to isobutene [1–10]. Zhang et al. [2] developed a complex selective catalyst, Y_2O_3–CeF_3, with a relatively high conversion (22%) and reasonable selectivity towards isobutene (59%) at 540 °C. Takita et al. [3,4] evaluated the performance of metal pyrophosphates and reported $Ni_2P_2O_7$ as the most selective catalyst (82% selectivity at 10.8% conversion at 550 °C). In a recent study on catalytic performance of a group of metal pyrophosphates catalysts in oxidative dehydrogenation of isobutane, $V_4(P_2O_7)_3$ was reported to be the most active catalyst (33.5% conversion at 500 °C) [10]. Dawson-type hetropolyoxoanions, $K_xP_2W_{12}MO_{62-y}$ (where M is Fe, Mn, Co, or Cu), were found to be selective for oxidative dehydrogenation of isobutane to isobutene at 427 °C in a fixed-bed reactor [5]. Chromium oxide catalysts on different supports (Al_2O_3, SiO_2, TiO_2 and $La_2(CO_3)_3$) were proved to be active and selective at much lower temperatures (reaction temperature less than 300 °C) than the previously reported catalysts [6–9]. Calcination conditions, type of Al_2O_3 support, and loading percent of chromium catalysts were found to have significant effects on the performance of chromium catalysts in ODH of isobutene as reported in our previous contribution [14].

The main objective of this work is to extend the previous work by examining the performance of some rare-earth

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and transition metal oxides supported on Al_2O_3 for ODH of isobutane to isobutene. The activities of these catalysts were evaluated over a wide range of reaction temperature (250–500 °C). The used catalysts were characterized by using XRD, FT-IR and BET techniques.

2. Experimental

The rare-earth metal oxides supported on Al_2O_3 were prepared from the following high-purity precursors: cerium(IV) ammonium nitrate hydrate, holmium nitrate, terbium nitrate, thallium nitrate, presidium nitrate, ytterbium acetate hydrate and samarium nitrate. The following precursors were used for the preparation of the transition metal oxides supported on Al_2O_3: chromium nitrate, manganese nitrate hydrate, nickel chloride hydrate, vanadium nitrate and zirconium nitrate. The support is an activated, neutral, γ-Al_2O_3 of 96% purity. To prepare the catalysts, a predetermined amount of the metal precursor was dissolved in 200 ml of distilled water at room temperature, and then a specified amount of γ-Al_2O_3 (to give the desired loading percent of metal on the support) was added slowly while stirring at room temperature. The formed paste was then dried overnight in an oven at 110 °C and then calcined in the presence of air at temperature listed in Table 1.

The details of experimental setup and the reaction procedure were reported elsewhere [10]. A fixed-bed quartz reactor operated at atmospheric pressure was used for the reaction. The feed gas contains 26.5% isobutane, 6.2% oxygen and the balance is helium. The isobutene:oxygen ratio was set to 4:1 in all of the experiments in this work. This ratio was checked previously in our lab [10,15] and lies on the optimum regime for the ODH of isobutane which is in agreement with other researchers for such a reaction [3,6,9]. One gram of the 2–40-mesh size catalysts in all runs was used at W/F of 0.01333 g/cm^3 min. An Omega electronic mass flow controller is used to control the gas flow, while an Omega temperature controller monitored the furnace temperature. Before the reaction, all tested catalysts were pretreated in a flow of He and O_2 at 400 °C for 1 h with an O_2 concentration of 66.67%, followed by treatment with He alone for 30 min. The activity and selectivity of the tested metal oxide catalysts supported on Al_2O_3 were measured in a temperature range 250–500 °C.

The product gases were passed through a heat-traced line to GC (HP6890) for online analysis. An HP-Plot capillary column connected to an FID detector separates the following hydrocarbons: C_4H_{10}, C_4H_8, C_3H_6, C_3H_8, C_2H_6 and CH_4. Molecular sieve (MS) and hayesep-R packed columns connected to a TCD detector separate O_2, CO and CO_2. Carbon balance of the product gases ranged in 98 ± 2%. Duplicate runs of each experiment were performed and the values reported in the paper are an average values which varied by less than 2–3%.

The BET surface area, pore volume, and average pore radius of the various catalysts were determined by a Quantachrome Autosorb Automated Gas Adsorption system that uses nitrogen adsorption technique. X-ray diffraction was performed on a Philips PW diffractometer with Cu Kα radiation. The diffractometer was operated in a scanning mode with a step size of 0.04° and accounting time of 1 s. The infrared spectra of the prepared catalysts were collected using a Portage-460 Nicolet FT-IR Instrument before and after the reaction.

3. Results and discussions

3.1. Characteristics and composition of Al_2O_3-supported catalysts

The BET surface area, pore volume and average pore radius of the calcined samples of all metal oxides used in this work are shown in Table 1. As seen in this table, the catalysts BET surface areas, pore volumes and pore radii varied in the range 108–183 m^2/g, 0.18–0.302 cm^3/g and 30.2–37.5 Å, respectively. Fig. 1 shows FT-IR spectra for fresh, calcined and used catalysts of Al_2O_3-supported 10% Ni, 10% Cr and 10% Ho catalysts. For each set, the spectrum on the top belongs to the catalyst after reaction, and the middle to the calcined catalyst sample (before the re-

Table 1
Characteristics of the Al_2O_3-supported catalysts

Catalyst	Calcination		BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore radius (Å)
	Temperature (°C)	Time (h)			
10% Cr/γ-Al_2O_3	700	3	183.1	0.302	33.0
10% Ni/γ-Al_2O_3	600	2	161.3	0.235	30.2
10% Ho/γ-Al_2O_3	700	3	147.7	0.234	31.7
10% Tb/γ-Al_2O_3	750	2	146.0	0.249	34.2
10% Ce/γ-Al_2O_3	500	2	140.1	0.230	33.3
2.5% Sm/γ-Al_2O_3	700	2	125.5	0.222	35.4
5% Pr/γ-Al_2O_3	800	2	118.0	0.221	37.5
10% Mn/γ-Al_2O_3	600	2	113.0	0.203	35.9
10% Zr/γ-Al_2O_3	600	2	109.1	0.170	32.2
10% V/γ-Al_2O_3	600	2	108.1	0.180	33.3

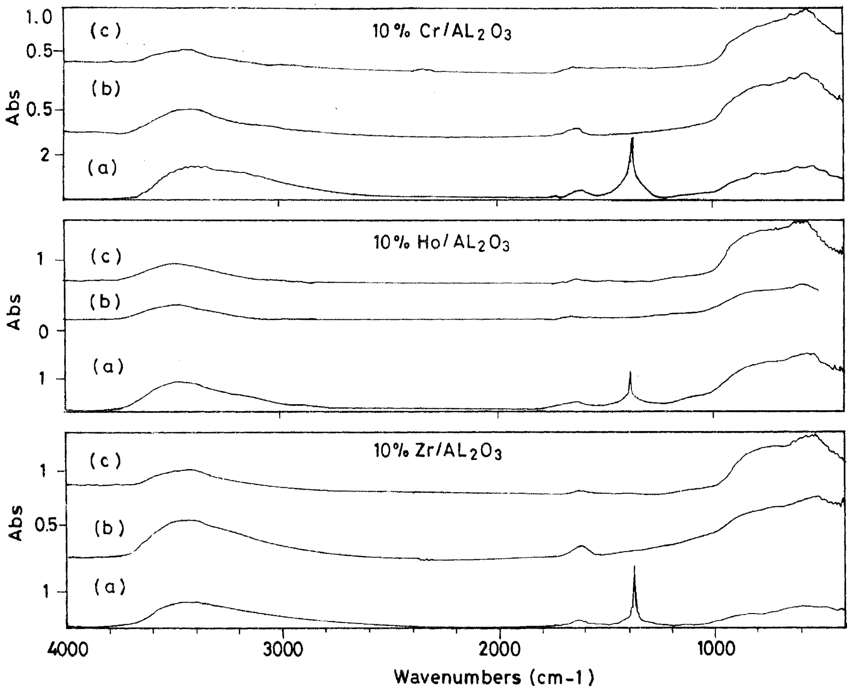

Fig. 1. FT-IR spectra for (a) fresh, (b) calcined and (c) used catalysts of Al_2O_3-supported 10% Ni, 10% Cr and 10% Ho catalysts.

action), while the spectrum underneath belongs to the fresh catalyst (un-calcined). For all used catalysts, the peaks detected in the range 2500–3500 cm^{-1} are OH peaks. Most likely these peaks are adsorbed O–H in the stretching vibrational mode. The metal oxide pattern appeared in the range 900–1200 cm^{-1} as shown in all spectra. The metal precursor (nitrates and acetates) disappeared after calcination as seen in the figures. Such trends were also observed for all other systems.

The X-ray diffraction patterns of the used catalysts in this work are relatively well defined and confirm the formation of metal oxides phase on each catalyst surface as shown in Fig. 2. The XRD patterns before and after the reaction indicate that both transition metals and rare-earth metals did not suffer any structural modifications after the reaction and they are in the crystalline phase.

3.2. *Transition metal oxides*

Catalysts from the transition metal oxides group supported on Al_2O_3 were tested. The ratio of the metal to support was kept at 1:10 by weight for all catalysts. The effect of reaction temperature on isobutane conversion and isobutene selectivity for these catalysts is shown in Fig. 3a and b, respectively, while its effect on oxygen conversion and CO_x ($CO + CO_2$) selectivity is shown in Fig. 3c and d, respectively.

The experimental results showed that the Cr, V and Mn catalyzed the reaction at temperatures below 300 °C, while Ni and Zr were active at high temperatures (>400 °C). The isobutane conversion remained unchanged for Cr, V and Mn catalysts above 400 °C as could be observed from Fig. 3a. The complete depletion of oxygen (100% conversion), as seen in Fig. 3c, limited the investigation of these catalysts to 400 °C. Carbon deposition on the catalyst surface was clearly observed under such conditions. As seen in Fig. 3a, Cr catalyst showed little changes with reaction temperature (an average of 10.5% conversion for temperature range of 250–400 °C). On average, V showed slightly better performance than Mn; however they both showed the lowest activity in the transition metal oxides group. Fig. 3b displays the variations in isobutene selectivity with reaction temperatures. The Cr catalyst gave the best selectivity in the temperature range of 250–400 °C, which was accompanied by low CO_x formation as seen in Fig. 3d. The drop in isobutene selectivity of Cr, Mn and V catalyst above 400 °C is attributed to cracking behavior of these catalysts due to complete depletion of oxygen. Hydrocarbons, propane, methane and ethylene were produced under such cracking conditions. At low reaction temperatures the isobutene selectivity of V catalyst was very low (25%), which improved significantly to 44% at 350 °C and remained almost unchanged up to 400 °C. The isobutene selectivity of Mn catalyst was, on average, 41% over reaction temperatures 250–400 °C.

On the other hand, Ni and Zr catalysts are essentially inactive (conversion $<1\%$, therefore not shown in the figure) at temperature lower than 400 °C. As seen in Fig. 3a, Ni gave the highest isobutane conversion (32%) at 500 °C. Its degree of conversion showed steady increase with the reaction temperature. As seen in Fig. 3b, the isobutene selectivity of Ni catalyst showed a slight increase from 30 to 34% when the temperature increased from 450 to 475 °C followed by a remarkable increase to reach 50% at 500 °C. Zr gave a

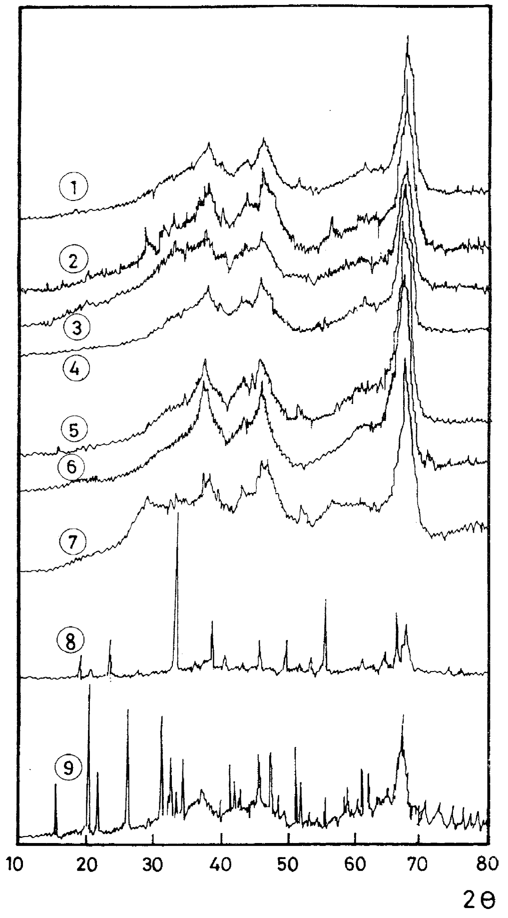

Fig. 2. X-ray diffraction patterns of Al_2O_3-supported catalyst: (1) Sm_2O_3, (2) Pr_2O_3, (3) Ti_2O_3, (4) Tb_2O_3, (5) Ho_2O_3, (6) NiO, (7) Ce_2O_3, (8) Mn_2O_3, (9) V_2O_5.

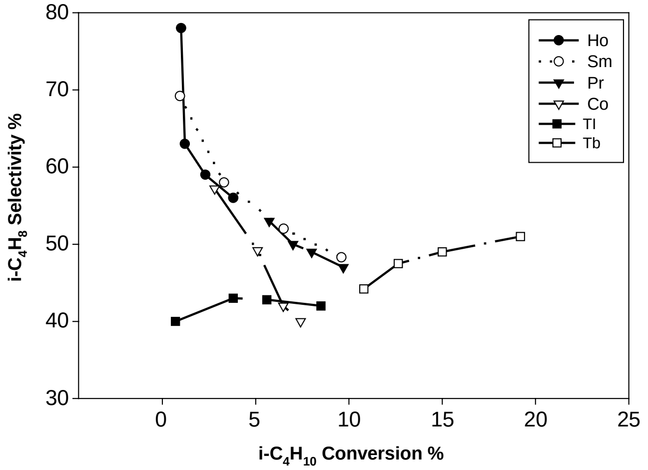

Fig. 4. The variation of isobutene selectivity with isobutane conversion for the transition metal oxides supported on γ-Al_2O_3.

conversion of 19% with relatively good selectivity of 50% at 500 °C. Increasing the reaction temperature activated the Zr further, as could be observed from both conversion and selectivity. For the two systems (Ni and Zr), the oxygen conversion reaches 100% at 500 °C. Experiments were limited to 500 °C to avoid homogenous gas phase reaction under such reaction conditions [10].

For a general comparison between the results obtained for the transition metal oxides reported above, the variations of the selectivity of isobutene with isobutane conversion at different reaction temperatures are illustrated in Fig. 4. Cr showed the highest selectivity in the conversion range of 6–12%, in which a decrease in selectivity with conversion

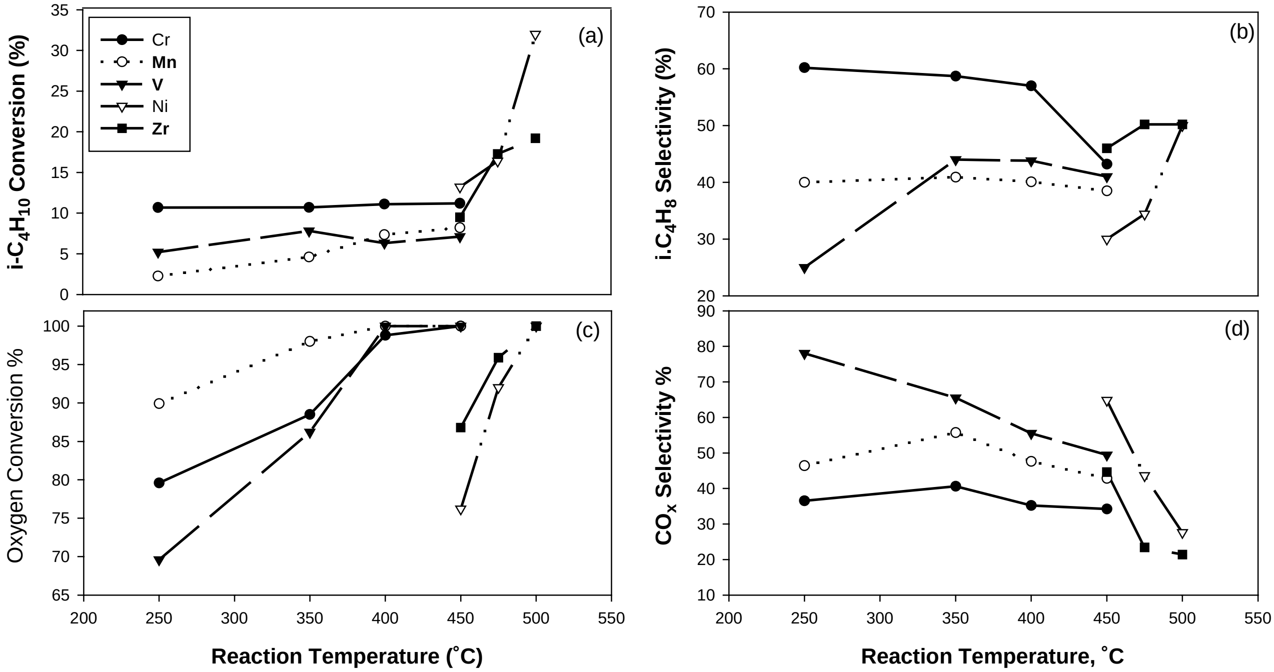

Fig. 3. The effect of reaction temperature on (a) isobutane conversion, (b) isobutene selectivity, (c) O_2 conversion and (d) CO_x selectivity for the transition metal oxides supported on γ-Al_2O_3.

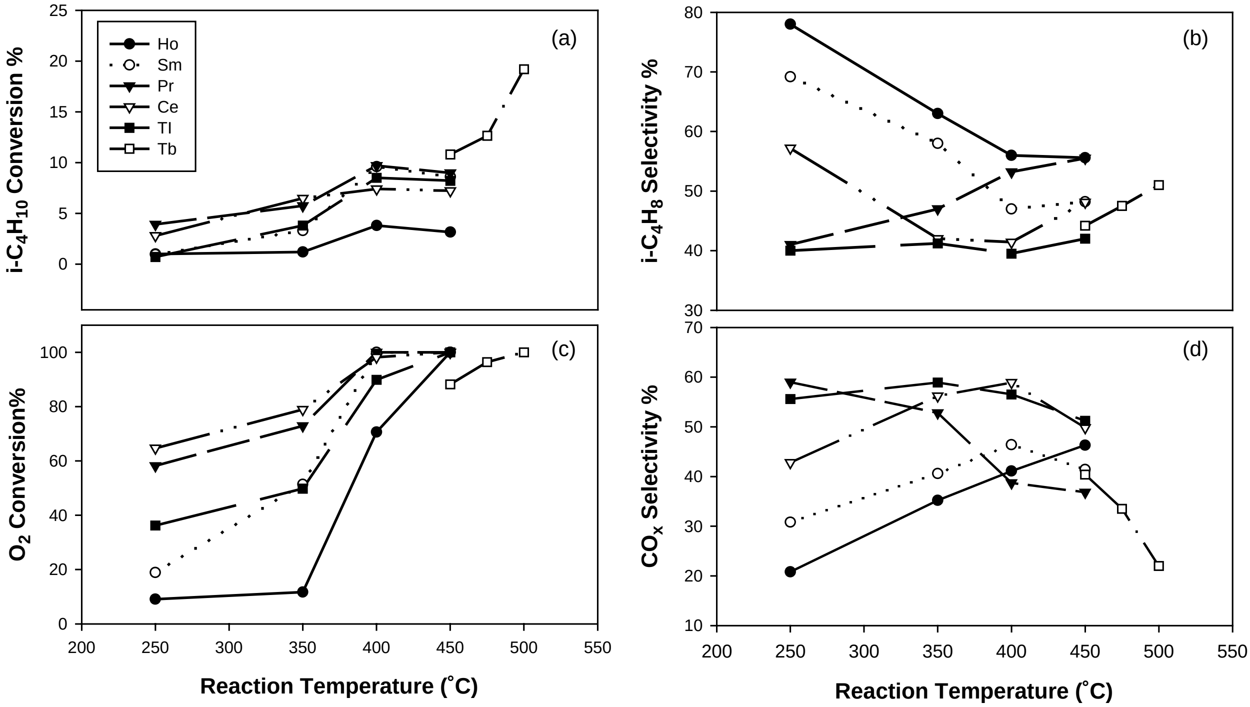

Fig. 5. The effect of reaction temperature on (a) isobutane conversion, (b) isobutene selectivity, (c) O_2 conversion and (d) CO_x selectivity for the rare-earth metal oxides supported on γ-Al_2O_3.

was obtained. This agrees well with the previously reported results on the chromium oxide systems [9]. In the higher conversion range, above 10%, Zr also showed good selectivity (48% on the average), which slightly increased as the conversion increased. In the case of Ni, almost linear increase in selectivity was obtained as the conversion increased to reach a maximum of 50% selectivity at 32% conversion. The isobutene selectivity of V catalyst decreased sharply as the conversion increased. No considerable change in selectivity with conversion was observed for Mn catalyst, especially in the conversion range of 4–8%.

3.3. Rare-earth and some other metal oxides

The tested γ-Al_2O_3-supported rare-earth and other metal oxides catalysts (denoted by their metals only) were 10% Ho, 2.5% Sm, 5% Pr, 5% Ce, 5% TI and 5% Tb. Fig. 5a and b display the effect of reaction temperature on isobutane conversion and isobutene selectivity for these catalysts, while Fig. 5c and d show the O_2 conversion and CO_x selectivity, respectively. It was also observed that some of these catalysts (Ho, Pr, TI, Sm and Ce) catalyzed the reaction in the low temperature range (less than 400 °C), while Tb became active above 400 °C.

As seen in Fig. 5a, at 400 °C, Pr and Sm catalysts showed the same conversion (9.6%), followed by TI and Ce (8.5 and 7.4%, respectively). Ho catalyst showed the lowest activity at this temperature (3.8%) with the highest selectivity towards isobutene (56%) as seen in Fig. 5b. The highest conversion for the rare-earth metal oxides was obtained with the Tb catalyst (19.2% at 500 °C).

Fig. 6 shows the variation of isobutene selectivity with isobutane conversion for the rare-earth metal oxides at different reaction temperatures. As seen in the figure, only Tb showed increase in selectivity as conversion increased. TI showed a slight increase of selectivity as conversion increased in the low conversion range (0.7–3.8%), beyond which the selectivity declined. All other metal oxides (Ho, Sm, Pr and Ce) showed sharp drops in selectivity as conversion increased.

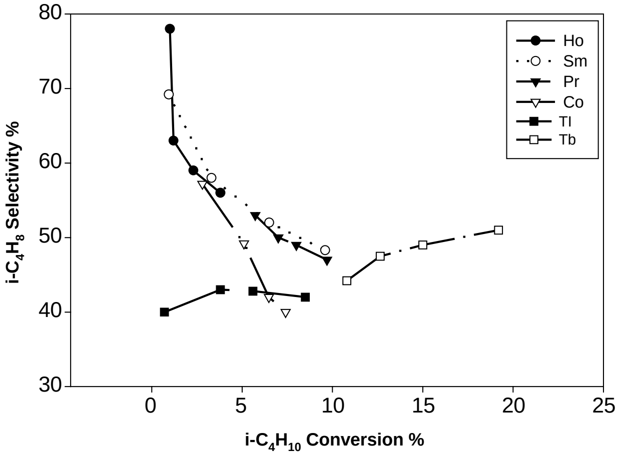

Fig. 6. The variation of isobutene selectivity with isobutane conversion for the rare-earth metal oxides supported on γ-Al_2O_3.

Table 2
The activity and selectivity of the catalysts of group A at reaction temperature of 350 °C

Catalyst	Conversion (i-C_4H_{10}) (%)	Yield (i-C_4H_8) (%)	Selectivity (%)					
			i-C_4H_8	C_3H_6	i-C_4 + C_3	C_2H_4 + C_2H_6	CH_4	CO_2 + CO
10% Ho	1.2	0.8	63.8	0	63.8	0	0	36.2
2.5% Sm	3.3	2.0	59.0	2.0	61.0	0	0	39.0
10% Cr	10.1	5.8	57.0	3.3	60.3	0	0	39.7
5% Pr	6.2	3.3	53.0	7.1	60.1	0	1.2	38.7
10% V	6.3	3.2	50.0	0.7	50.7	0	0	49.3
5% TI	3.8	1.6	43.0	3.9	46.9	0	0.7	52.4
5% Ce	6.5	2.7	42.0	7.1	49.1	0	0	50.9
10% Mn	4.6	1.9	40.9	1.9	42.8	0	0	57.2

The catalytic performance of the tested metal oxides (transition and rare-earth) that we briefly presented in the previous sections suggested that the catalysts may be classified according to their respective degree of conversion and selectivity as low (group A, <400 °C) and high (group B, >400 °C) reaction temperature catalysts. This classification makes it easier to explain their catalytic performance specifically their selectivity to the desired products. Table 2 shows the catalytic activity and selectivity of group A catalysts at 350 °C, while Table 3 shows the activity and selectivity of group B catalysts at 500 °C. The results illustrated in Tables 2 and 3 show that the main products of this reaction are isobutene, propene, methane and carbon oxides. Only traces of ethane and ethylene were produced under the reaction conditions. The reported isobutene yield is a direct mathematical product of its selectivity with the corresponding isobutane conversion.

As seen in Table 2, Ho, Sm and Cr gave the highest isobutene selectivity. On the other hand, Mn, TI and Ce are highly selective towards carbon oxides (above 50%). Ho and Sm have the least isobutane conversion among the catalysts of group A (1.2 and 3.3% conversion). Cr showed the highest yield of 5.8%. It was also observed that Ce and Pr achieved the highest selectivity towards propene (7.1%) and only in the case of Pr and TI small amounts of methane were produced. Neither ethane nor ethylene was detected for all catalysts within this group.

In Table 3 the activity and selectivity at 500 °C of group B catalysts are shown. As seen in this table, similar selectivity (about 50%) towards isobutene is obtained for the three catalysts with Ni producing more CO_x (27% selectivity). The selectivity towards ethane plus ethylene and methane are within the same range for all tested catalysts. The highest yield is obtained for Ni (16%) with relatively good selectivity (65%) towards the desired products (isobutene plus propene). The Ni activity as seen in Table 3 is much higher than the rest of the catalysts (almost double the activity of the other metal oxides of group B).

The results in Tables 2 and 3 show that the selectivity towards the desired products, isobutene plus propene, is higher for the catalysts of group B than that of group A. It has also been observed that more CO_x is produced with group A catalysts compared to group B catalysts. CO_x selectivity of group A is almost double that of group B. This result indicates that low reaction temperature favors the surface alkyl (adsorbed isobutene, propene or ethylene) to further react with the lattice oxygen to produce carbon oxides. The above speculations may explain the results of catalysts of group A that showed very low selectivity towards propene (7% at maximum) and zero selectivity towards ethylene. Cracking behavior (reaction in the absence of O_2) of catalysts of group B was also studied. Fig. 7 shows a comparison between ODH and cracking activities of the Ni system. Total flow rate of 75 cm^3/min of reaction gases was used, while the isobutane flow rate was kept constant at 20 cm^3/min. Cracking activity (isobutane conversion) at 500 °C is only 19% of the ODH activity as seen in Fig. 6. No cracking occurred at 450 °C. The main cracking products are propylene, ethylene, ethane and methane.

It has been postulated that the activity and selectivity of any metal oxide in selective oxidative dehydrogenation reaction are related to the rate of reduction of the oxide [1,11]. The theory is based on the fact that an oxide that is too difficult to be reduced is too inactive while the one that is too easily reduced is active but non-selective. The formation of olefins from oxidative dehydrogenation reactions

Table 3
The activity and selectivity of the catalysts of group B at reaction temperature of 500 °C

Catalyst	Conversion (i-C_4H_{10}) (%)	Yield (i-C_4H_8) (%)	Selectivity (%)					
			i-C_4H_8	C_3H_6	C_4 + C_3	C_2H_4 + C_2H_6	CH_4	CO_2 + CO
10% Tb	19.2	9.7	50.7	20.7	71.4	0.74	6.5	21.4
10% Zr	19.2	9.6	50.1	20.7	70.8	0.70	7.0	21.5
10% Ni	32.0	16.0	49.6	15.2	64.8	0.68	7.7	26.8

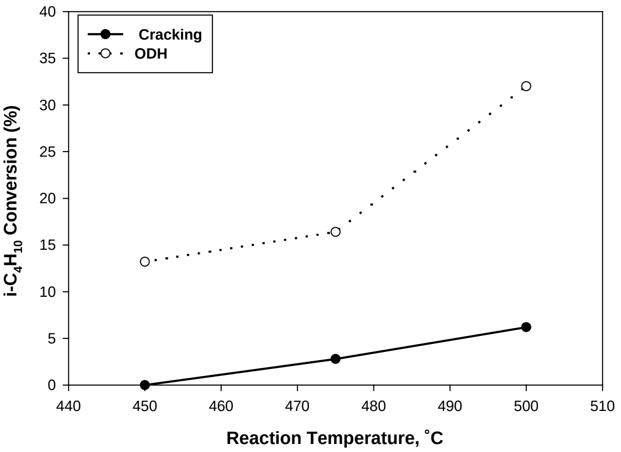

Fig. 7. The ODH and cracking behavior of 10% Ni/γ-Al_2O_3 at reaction temperatures 450, 475 and 500 °C. Total flow rate of reaction gases is 75 cm^3/min, where i-C_4H_{10}:O_2:He ratio is 4:1:10 for ODH reaction, and i-C_4H_{10}:He is 4:11 for cracking reaction.

was assumed to depend on the order of the strength of C–H bonds present in the molecule [12]. After the rupture of the first C–H bond, a surface alkyl species is formed. The stability of the produced alkyl species is considered to be the selectivity-determining step in this reaction. The formation of C–O bond (the undesired product in such reactions) is mainly dependent on further reaction of the surface alkyl with the lattice oxygen. Therefore, the ease of removal of an oxygen atom from the lattice to form C–O bond with the surface intermediate is an important factor in determining the selectivity trend of the metal oxide.

One way to view the possibility of removing the lattice oxygen is to look at the reduction potential of the cations at the active site. The aqueous reduction potential of a cation (transition and rare-earth metals) indicates the ease of removal of oxygen from the metal oxide. This concept was tested for the supported metal oxides series used in this work as seen in Fig. 8, which shows the selectivity to isobutene for group A catalysts at 7% conversion of isobutane against the reduction potential of transition and rare-earth metal cations. This interpretation assumes that lattice oxygen is the species that reacts with surface intermediate (adsorbed isobutene) to form CO_x. This assumption is supported by earlier findings on pulse reaction of butane without oxygen on Mg, Zn, Ni, Fe, and Cu orthovanadates [13], in which a similar correlation between selectivity for dehydrogenation and cation reducibility was observed. The general trend in Fig. 8 shows that as the reduction potential of metal cation increases the selectivity towards isobutene decreases. This indicates that the higher the reduction potential is the more easily reduced is the cation, which results in the decrease in the isobutene selectivity by favoring further conversion to CO_x. This finding agrees well with earlier conclusions of selective oxidative dehydrogenation of butane [12,13].

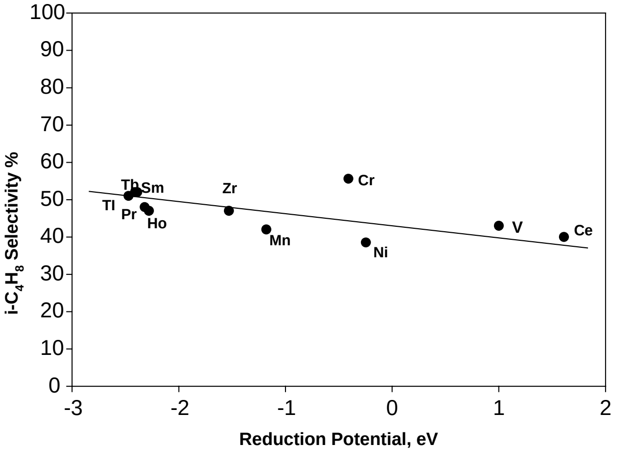

Fig. 8. Dependency of selectivity for isobutene on the reduction potential of cations at isobutane conversion of 7%.

4. Conclusions

Alumina-supported transition (Cr, Mn, V, Ni and Zr) and rare-earth and other (Ho, Sm, Pr, Ce, TI and Tb) metal oxides were tested for oxidative dehydrogenation of isobutane. The activity and selectivity of these catalysts were reported in a wide range of reaction temperature (from 250 to 500 °C). Along with isobutene, significant quantities of propene were produced especially at high isobutane conversion. The other main byproducts from the reaction were carbon oxides (almost half the product gases at low conversion) and methane. The catalysts have been classified into two groups (active below and above 400 °C). Among those active above 400 °C, Ni showed the highest activity (32% conversion with reasonable selectivity towards isobutene plus propene of about 65%) and Tb showed the highest selectivity towards isobutene (about 51% selectivity). Cr showed the highest yield of 6% among catalysts active at low reaction temperatures with less dependency of isobutene selectivity on isobutane conversion. In group A, Mn and TI showed very high selectivity towards carbon oxides (above 50%). In general, group B catalysts were highly selective towards olefins (isobutene and propene) and group A catalysts favored CO_x. The selectivity of these metal oxides was correlated with the metal cations reduction potential. The correlation indicated that metals with low reduction potential favored the olefins (isobutene and propene) with low selectivity for CO_x.

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