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NOTE

Oxidative Dehydrogenation of Isobutane over Supported Chromium Oxide on Lanthanum Carbonate

Isobutylene is an important feed stock for the petrochemical, polymer, and chemical industries (1, 2). As large amounts of isobutane are readily available from natural gas and refinery processes, dehydrogenation will significantly contribute to the supply of isobutylene. Catalytic dehydrogenation of isobutane proceeds at temperatures between 510 and 575°C, consuming energy at the rate of 2185 kJ/kg isobutylene produced (3). Although many improvements in catalyst design and process technology have been achieved, the catalytic dehydrogenation technologies still suffer from a number of limitations including high energy input, side reactions, and catalyst deactivation. Oxidative dehydrogenation is recognized as a promising alternative, provided that highly selective catalysts are developed.

There have been a number of studies on oxidative dehydrogenation of isobutane to isobutylene. Takita *et al.* reported (4) the use of pyrophosphates of Ni, Zr, Cr, Co, Mn, Sn, and Cu as catalysts for this reaction. Of the catalysts tested, $Ni_2P_2O_7$ was the most selective catalyst. At 550°C, 82% selectivity was obtained at 10.8% isobutane conversion in a fixed-bed reactor using a mixture of 75 mol% isobutane, 5 mol% oxygen, and 20 mol% nitrogen as the feed gas.

Huff and Schmidt (5) have studied the oxidative dehydrogenation of isobutane over monoliths at very short residence times (<5 ms) and reported selectivities $>80\%$ of total olefins (40% isobutane, 40% propylene) at 60% isobutane conversion in an atmospheric pressure reactor operating at 800–900°C.

Calvani *et al.* have reported the use of Dawson-type heteropolyoxoanions, $K_xP_2W_{12}MO_{62-y}$ ($M =$ Fe, Mn, Co, Cu), as catalysts. In a fixed-bed reactor at 427°C and with a feed of 26 mol% isobutane, 13% O_2, 12% water, and the balance helium, selectivities between 55 and 65% were obtained at isobutane conversions of 11–17% (6).

Supported chromium oxide is known to possess activity for the selective oxidation of hydrocarbons. Chromium supported on silica has been found to be effective for the oxidation of methane to methanol (7). The catalyst comprises surface oxide chromates in which the chromium is chemically bound to the oxygen of the catalyst support. Active carbon doped with chromium oxide and other redox-active transition metals have been reported to exhibit high activity and selectivity for the oxidative dehydrogenation of ethylbenzene to styrene (8). The selective oxidation of methanol over a chromia catalyst supported on various oxides has been studied by Kim and Wachs (9). A very high selectivity to acetone was obtained on supported chromia/alumina catalysts. Chromia/magnesia was active for total oxidation, and TiO_2 and SiO_2 were found to be preferred supports for the formation of acetaldehyde. The dehydrogenation of isobutane in the presence of carbon dioxide over a supported chromium–manganese/silica catalyst has been studied recently by Mirzabekova and Mamedov (10). Over this catalyst, the reaction of isobutane with carbon dioxide proceeds mainly through the dehydrogenation pathway with subsequent oxidation of hydrogen. A selectivity for isobutylene near 70% was obtained at 650°C. Grabowski *et al.* (11) have studied the oxidative dehydrogenation of isobutane over various supported chromium oxide catalysts at temperatures between 200 and 400°C and reported selectivities up to 73% isobutylene obtained at 5% isobutane conversion.

This paper presents the catalytic oxidative dehydrogenation of isobutane to isobutylene over supported chromium oxide on lanthanum carbonate. It extends the authors previous studies into this reaction over supported transition metal oxide catalysts (12, 13).

The carbonate precursor was prepared by the dropwise addition of a solution of a mixture of $La(NO_3)_3 \cdot 6H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$, in the appropriate mole ratios, to a stirred solution of NH_4HCO_3 (24 g/liter). The resultant hydrogel was separated by centrifugation and washed with water and then with acetone. The product was first dried at room temperature in an air stream and then at 110°C in air for 4 h. The final catalyst was obtained by calcination at 300°C in air for 2 h. Under the above precipitation conditions, chromium was precipitated as $(NH_4)Cr(OH)_2CO_3$. The infrared spectrum featured the C−O stretching and bending modes in the 1300–1500 cm^{-1} range indicative of carbonate, together with bands characteristic of OH and NH_4^+ species. When the precipitate was aged for 20 h at 100°C, the product had an XRD pattern analogous to sodium dawsonite, $NaAl(OH)_2CO_3$. The surface areas of $La_2(CO_3)_3$ and Cr_2O_3 prepared using the above conditions are 20 and 300 m^2/g, respectively. When $La_2(CO_3)_3$ and Cr_2O_3 are coprecipitated,

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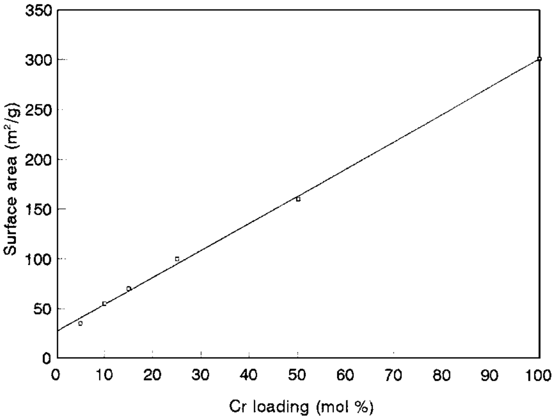

FIG. 1. Catalyst surface area as a function of chromium loading.

the surface area of resulting catalysts varies between 20–300 m^2/g depending on the loading level as shown in Fig. 1.

Although the chromium oxide in the catalyst exists in both III and VI oxidation states, supported chromium oxide is hereafter denoted as $Cr_2O_3/La_2(CO_3)_3$.

The performance of catalysts has been assessed using a pulse mode reactor with ancillary on-line gas chromatography analysis. Gas flow rates were controlled by mass flow controllers and monitored by Porter flow meters. A six-port, two-way air-actuated switching valve, controlled by a Valco DVI unit and fitted with a 100-μl sample loop, allows either pure carrier gas, isobutane, or oxygen to flow through the reactor. A knockout trap immediately downstream of the reactor removed the less volatile hydrocarbon products (if any) and water for off-line analysis. The remaining gas phase product stream underwent on-line analysis using a Varian 3700 gas chromatograph fitted with three columns: (i) a 12-in. VZ-7 column which provided analysis of CO_2 and hydrocarbons from C_1–C_4 and connected to a thermal conductivity detector; (ii) a 12-in. HayeSep N column, also connected to a TCD to separate CO and CO_2, and (iii) a 7-in. VZ-10 column, connected to a FID to separate 1-butylene and isobutylene, if necessary. The catalyst (100 mg) was prepared by a repeated process of pelletizing and grinding to 60–80 mesh size before loading into the middle of the reactor. A silica tube was inserted into the bottom half of the reactor to eliminate possible gas phase reactions. Normally, the catalyst was pretreated *in situ* with He for 1 h at reaction temperature, but other pretreatments with different conditions were possible.

The reaction was carried out at 150 kPa and at temperatures in the range 200–500°C. Pure isobutane was injected into the reactor via a 100-μl sample loop, giving a pulse size of 4.25 μmol.

A catalyst consisting of 25 mol% Cr_2O_3 supported on $La_2(CO_3)_3$ was first selected for testing. This catalyst was previously tested in a fixed-bed reactor. At 230°C a selectivity of 71% at 10% conversion was obtained (12). In the pulse reactor, the selectivity to isobutylene was much higher. For the first two pulses, the selectivity to isobutylene was 90% and then approached 100% for the subsequent pulses. CO_2 is the only by-product at this temperature. The average carbon balance after six pulses was 97%. The results are summarized in Table 1.

The product distribution often depends on the nature of reactant available in the reaction media. Since molecular oxygen in the gas phase is a distinctly different oxidant from the oxygen species on the catalyst surface, its direct reaction with hydrocarbon could be expected to give a different product distribution from that obtained only by surface oxygen species. Thus any differences between redox and cofeed modes of operation must firstly arise from reactions of hydrocarbon with either gas phase oxygen or the oxidized surface. Normally, the redox mode reactor offers higher selectivity. For example, the selective oxidation of *n*-butane to maleic anhydride is carried out in a fixed-bed reactor with a typical selectivity of 60%. Contractor *et al.* (14) found that up to 90% selectivity can be achieved by using a circulating reactor.

The catalytic activity decreased by about 54% over the first six pulses but the selectivity remained unchanged. However, the catalyst activity, expressed as the amount of isobutane reacted per gram of catalyst, and selectivity can be restored by exposure to two pulses of oxygen at the reaction temperature. This experiment is illustrated in Fig. 2. In a redox mode of operation, the regeneration step often requires a higher temperature. The reproducibility of this catalyst activity after exposure to oxygen at the reaction temperature indicates that the surface oxygen exchange on the catalyst is very rapid.

Under the redox mode operation, oxidative dehydrogenation of isobutane proceeded selectively. The average selectivity over six pulses approached 100% at 220°C and then decreased slightly as the temperature was increased. Figure 3 shows the average selectivity after six pulses as

TABLE 1

Pulse Reactor Test for 25 mol% $Cr_2O_3/La_2(CO_3)_3$ at 230°C

Pulse	Isobutylene produced[a] ($\mu mol_{isobutylene}$/g cat.)	Surface oxygen[b] (μmol/g)
1	2.45	1.22
2	2.00	1.00
3	1.56	0.78
4	1.39	0.69
5	1.17	0.58
6	1.13	0.56

Note. At 230°C, after six pulses, isobutylene yield was 0.54 g/kg catalyst.

[a] Calculated using $d_{isobutylene} = 2.39$ kg/m^3 (gas density at 21°C).

[b] Oxygen involved, calculated as O_2.

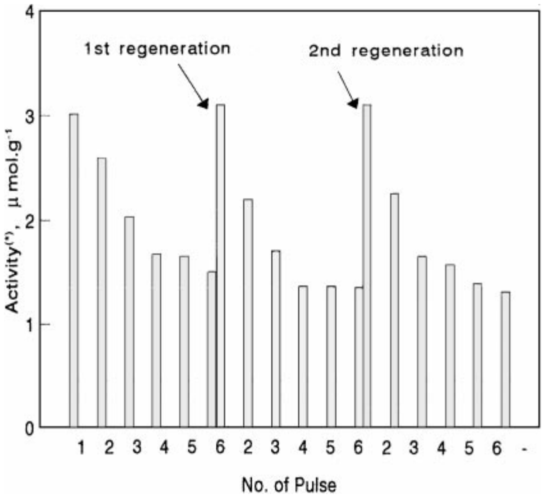

FIG. 2. Pulse reactor test for 25 mol% $Cr_2O_3/La_2(CO_3)_3$ at 240°C. *μmol isobutane reacted/g catalyst.

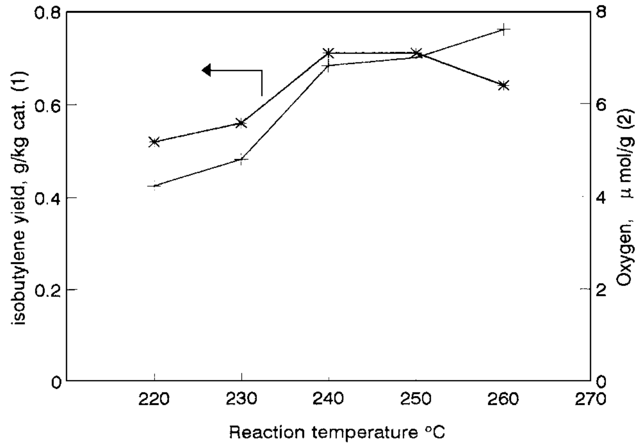

FIG. 4. Performance of 25 mol% $Cr_2O_3/La_2(CO_3)_3$ in pulse reactor at different temperatures. (1) Cumulative yield of isobutylene for six pulses. (2) Surface oxygen involved.

a function of reaction temperature. Within the range of temperatures tested, the contribution of lattice oxygen increased slightly with temperature but the selectivity to isobutylene decreased and the yield of isobutylene was optimized at about 240–250°C. Figure 4 shows the performance of catalyst at different temperatures.

In the range of chromium loading (as Cr_2O_3) between 5 and 50 mol%, the average selectivity after six pulses was virtually unchanged but the cumulative yield of isobutylene for six pulses changed with the loading level (Fig. 5). The optimum performance occurred at chromium oxide loading levels of about 10–15 mol% (i.e., 3.5–5 wt%). At a given pulse size of 4.25 μmol, the isobutane conversion decreased from 21.3% for the first pulse to 9.2% for the sixth pulse. The selectivity was only 82% for the first pulse but reached 96% for the third and 100% for the subsequent pulses. Over six pulses, an average selectivity of 95% at an average conversion of 12.9% per injection was obtained, giving a yield of isobutylene of 0.84 g/kg catalyst. In identical tests using $La_2(CO_3)_3$ and bulk Cr_2O_3 as catalyst, no activity was observed at 240°C.

The reactivity of supported chromium oxide catalyst is influenced by the environment of the active species, i.e., their symmetry, coordination, and surface aggregation, which depend in many cases on the concentration of chromium on the catalyst surface. In the supported chromium oxide catalysts, the formation of surface chromium species is influenced by the surface coverage. In a study of supported chromium oxide on alumina, Vuurman *et al.* (15) reported that, at a loading level of 2 wt%, the chromium was present as hydrated chromate species; at a loading level of 10–40 wt%, dichromate and trichromate species were

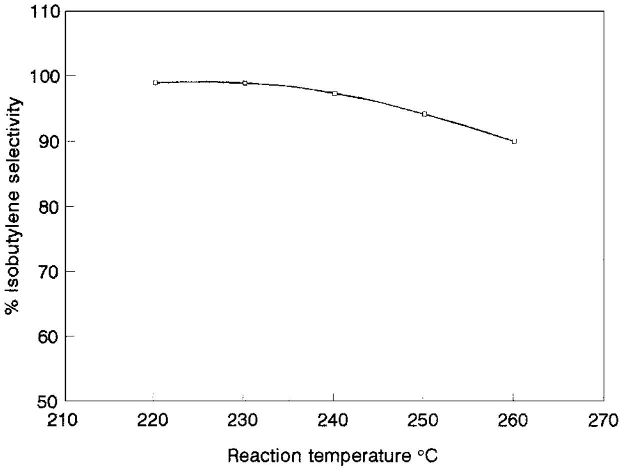

FIG. 3. The catalyst selectivity as a function of reaction temperature.

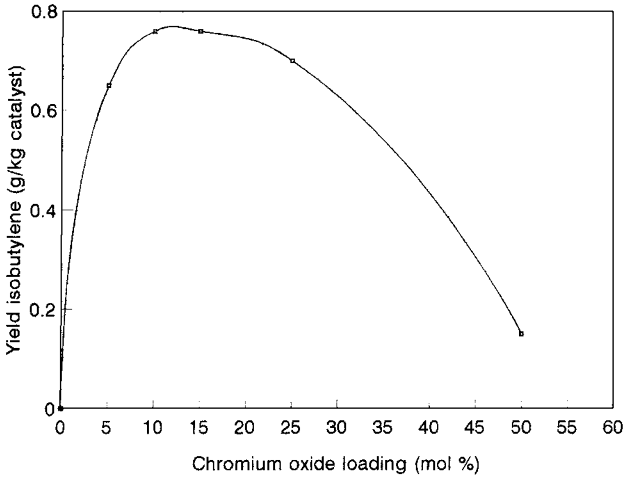

FIG. 5. Cumulative yield of isobutylene at 240°C after six pulses as a function of chromium loading.

formed and at concentrations up to 60 wt% or higher, the catalyst surface was covered by crystalline CrO_3.

The oxidative dehydrogenation of isobutane and the combustion of either isobutane or isobutylene probably take place on the same active center. As the chromium loading level changed, the ratio of active/inactive species varied and resulted in a variation of isobutylene yield but not the selectivity. In the case of supported chromium oxide/lanthanum carbonate, since the surface area of support was only 20 m^2/g, a high concentration of chromium on the surface may have resulted in the formation of inactive crystalline chromium oxide such as Cr_2O_3, which can cover the active sites of the catalyst.

As can be seen in Fig. 5, catalyst containing 10 mol% chromium oxide gives the best yield of isobutylene. Further optimization of this catalyst with respect to improvement of the isobutylene yield has been carried out.

The effect of calcination temperature on the performance of the catalyst has been studied at temperatures between 250 and 450°C and calcination in air for 2 h has been selected as a standard treatment. As can be seen in Fig. 6, a slight improvement in the activity is observed when the catalyst is activated at temperatures lower than 300°C. At a calcination temperature of 350°C, the activity decreases by nearly 30% and at 450°C, the catalyst becomes inactive.

In a study of supported chromium oxide on alumina, Wachs *et al.* (16) found that the chromium oxide is stabilized by the alumina support in the VI oxidation state after calcination in air at temperature >120°C. The formation of the molecular structure of the surface chromium species is as a function of calcination temperature. High calcination temperatures result in the formation of more polymerized species, and isolated species can only be obtained at low temperatures. In the present study, the results from thermal analysis of supported $Cr_2O_3/La_2(CO_3)_3$ catalyst and $La_2(CO_3)_3$ itself have indicated that the decomposition of $La_2(CO_3)_3$ started at about 350°C. This first step of decomposition occurred with a maximum rate at 450°C to form $La_2O_2CO_3$. At temperatures higher than 600°C the formation of $LaCrO_3$ was confirmed by X-ray diffraction.

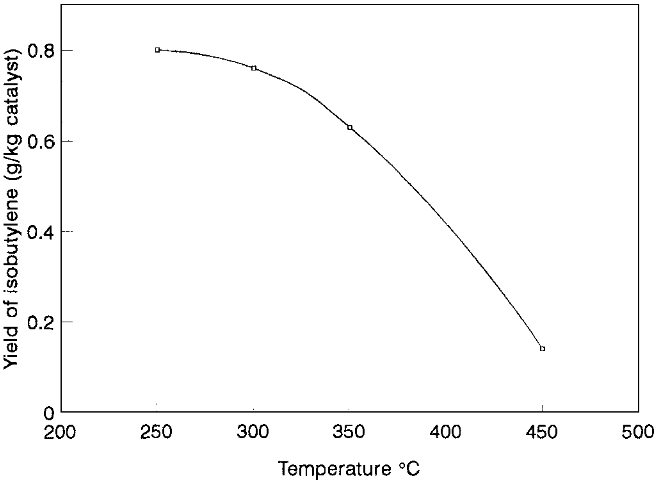

FIG. 6. Effect of calcination temperature on isobutylene cumulative yield after six pulses.

TABLE 2

Effect of Pretreatment on the Performance of Catalyst

Treatment	Oxygen involved[a]	% Selectivity[b]	Isobutylene yield[c]
Air, 300°C	11.5	94	0.79
He, 300°C	6.7	99	0.68
Air, 250°C	12.5	95	0.84
Air, 250°C/He, 300°C	12.4	94	0.80

Note. Catalyst, 10 mol% $Cr_2O_3/La_2(CO_3)_3$.

[a] Oxygen involved in six pulses (as O_2), μmol/g catalyst.

[b] Average selectivity after six pulses.

[c] Cumulative yield for six pulses, g/kg catalyst.

The difference in catalytic behavior observed here is probably due to a combination of the polymerization of chromium species and the alteration of the nature of the support. $La_2(CO_3)_3$ seems to be more effective as a catalyst support than $La_2O_2CO_3$. Again, no change in catalyst selectivity was found.

The effect of pretreatment conditions on the performance of catalysts has been carried out and results for varying treatments are shown in Table 2. Activation of catalyst in He at 300°C resulted in a less reactive catalyst. The catalyst activity was about 40% lower compared to that obtained by air activation. This indicated that the presence of oxygen in the activation step is necessary for maximizing the active phase on the surface. The high selectivity obtained by He pretreatment is attributed to the absence of adsorbed oxygen which can participate in further combustion of isobutylene. In another experiment, after calcination in air at 250°C, the catalyst was then treated with He at 300°C. The selectivity in this case was unchanged. This suggests that adsorbed oxygen, which is formed by an air treatment step, cannot be removed at 300°C. The independence of selectivity on chromium loading levels suggested that as the loading level changed, no other active species which can contribute to any secondary reactions was created. Air calcination prior to a catalytic test may result in adsorbed oxygen being present on the catalyst surface. This may react with isobutylene to give combustion products.

In summary, supported chromium oxide on lanthanum carbonate exhibits high activity and selectivity for oxidative dehydrogenation of isobutane to isobutylene. The temperature at which selective oxidation occurred over this catalyst was found to be significantly lower than that reported in the open literature. In a pulse reactor, selectivities of

>95% were obtained at temperatures below 250°C. Water and carbon dioxide are the only other reaction products observed. There is no detectable coke formation and carbon balances routinely close to better than 98% are obtained. The performance of this catalyst was found to be a function of chromium oxide loading. The optimum yield occurred at chromium oxide loading levels of about 10–15 mol%. The presence of oxygen in the activation step is necessary for maximizing the active phase on the surface. Reoxidation of the reduced catalyst occurred rapidly at reaction temperature. This feature makes the catalyst possibly suitable for redox mode operations.

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