Catalytic Performance of Chromium Oxide Supported on Al2O3 in Oxidative Dehydrogenation of Isobutane to Isobutene

4 AUTHORS:

Saeed al-zahrani
King Saud University
138 PUBLICATIONS **1,133** CITATIONS

SEE PROFILE

Nimir O. Elbashir
Texas A&M University at Qatar
54 PUBLICATIONS **395** CITATIONS

SEE PROFILE

A. E. Abasaeed
King Saud University
135 PUBLICATIONS **700** CITATIONS

SEE PROFILE

Mazhar Abdulwahed
Damascus University
6 PUBLICATIONS **72** CITATIONS

SEE PROFILE

Catalytic Performance of Chromium Oxide Supported on Al₂O₃ in Oxidative Dehydrogenation of Isobutane to Isobutene

S. M. Al-Zahrani,*,† N. O. Elbashir,† A. E. Abasaeed,† and M. Abdulwahed‡

Chemical Engineering Department, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia, and SABIC Industrial Complex for Research & Technology, P.O. Box 42503, Riyadh 11551, Saudi Arabia

In this study, the performance of chromium oxide catalysts supported on Al₂O₃ was evaluated. The effects of the percent loading of Cr on Al₂O₃ and the pretreatment conditions on the activity and the selectivity of the catalysts in the oxidative dehydrogenation of i-C₄H₁₀ to i-C₄H₈ were also tested. Different types of Al₂O₃ were tested as supports for chromium oxide, and the activity and selectivity of these samples were correlated with the alumina properties. The obtained results show that the optimum loading of Cr on Al₂O₃ lies between 5 and 15%. Also, it has been observed that the calcination temperature affects the conversion at lower reaction temperatures, whereas its influence on product selectivity is limited by O₂ availability in the reaction mixture. The catalyst samples were characterized by FTIR and XPS measurements. The XPS analysis confirmed the presence of Cr^{6+} and Cr^{3+} on the surface of the catalyst. Cr^{3+} was dominant in the spent catalyst.

1. Introduction

The exothermic oxidative dehydrogenation (ODH) reaction of alkanes is used for the production of lower alkenes from their corresponding paraffins. The ODH reactions can successfully overcome problems associated with dehydrogenation reactions. Dehydrogenation reactions, which are endothermic, require relatively higher reaction temperatures (≥600 °C). At these temperatures, the catalyst deactivates because of coke formation, thus necessitating periodic regeneration of the catalyst which will increase the operating costs.

Recently, ODH of isobutane to isobutene has received considerable attention because of the increasing demand for methyl tertiary butyl ether methacrylates. These products are used as additives for gasoline to enhance the octane number, to reduce oxidant products, and to substitute lead. Catalysts based on chromium oxide have recently been used in selective ODH of isobutane to isobutene because of their favorable performance at relatively low reaction temperatures (less than 300 °C).[1−4] Moriceau et al.[2] reported 60% isobutene selectivity with 10% isobutane conversion at 270 °C for a binary chromium−cerium oxide (Cr−Ce−O) catalyst. Hoang et al.[3] reported good activity and selectivity for a chromium catalyst supported on lanthanum carbonate in the temperature range of 230−250 °C. Recently, Grzybowska and his colleagues[4] studied the effect of Cr^{3+} and Cr^{6+} species on the activity of CrOx/Al₂O₃ in the ODH of isobutane. However, no studies were reported on the effect of preparation techniques and reaction conditions on the activity of chromium catalysts in isobutane ODH.

In the present study, the performance of chromium oxide catalysts supported on Al₂O₃ for the ODH of isobutane to isobutene will be evaluated. The paper will focus on the influence of the percent loading of Cr oxide on Al₂O₃ and the effects of different types of Al₂O₃

supports, preparation methods (particularly calcination conditions), and pretreatment methods on the activity and characteristics of the supported chromium oxide catalysts. Also, the findings of this study will be compared to those of previous studies on chromium oxide catalysts.

2. Experimental Section

The chromium oxide catalysts were prepared from chromium nitrate precursor. A predetermined amount of the precursor was added gradually with stirring to a crystallizing dish containing a predetermined amount of the support to make the specified weight ratio of the chromium on the aluminum oxide. The contents were continuously stirred while excess deonized water was evaporated. A thick paste was obtained that was dried in an oven at 100 °C overnight. The catalyst powder was calcined in air. After calcination, the catalyst was pressed into pellets, crushed, and sieved into 20−40 mesh granules.

The experimental setup and procedure were reported elsewhere.[5] The reactor was operated at atmospheric pressure with a total feed flow of 75 cm³/min (C₄H₁₀: O₂:He ratio of 4:1:10). The reaction temperature range was 200−450 °C. Triplicate runs of each experiment were conducted.

An on-line gas chromatograph (HP6890) was used for analysis of the feed and the product streams. The hydrocarbons, CH₄, C₂H₆, C₂H₄, C₃H₈, C₃H₆, C₄H₈, and C₄H₁₀, were separated by an HP Plot column connected to an FID detector. Also, MS and a hayesep-R column connected to a TCD detector separated O₂, CO, and CO₂. The carbon balance is in the range 98% ± 2%.

3. Results and Discussion

In the following subsections, the effects of the chromium percent loading, support type, calcination temperature, and pretreatment temperature on the performance of the catalysts are presented.

---

* Corresponding author. E-mail szahrani@ksu.edu.sa.
† King Saud University.
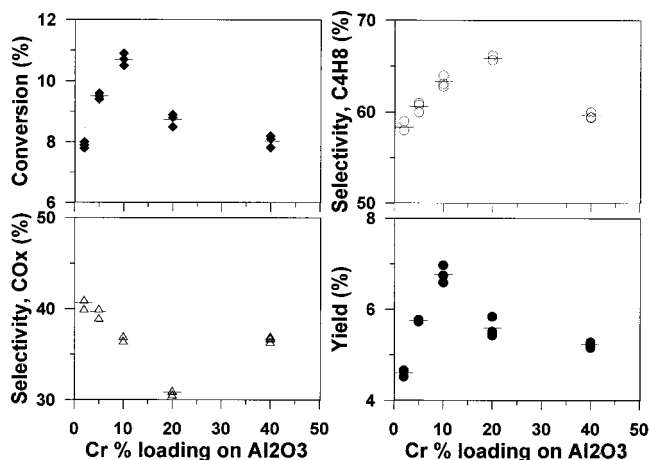‡ SABIC Industrial Complex for Research & Technology.

Figure 1. Effect of percentage Cr loading on Al_2O_3 on the activity and selectivity of the catalyst.

3.1. Percent Loading of Chromium on Al_2O_3.

The percent loading covers the range 2–40% Cr/Al_2O_3. For comparison purposes, unsupported chromium oxide was also tested. All catalysts were calcined at 700 °C for 3 h. Figure 1 shows the effect of Cr percent loading on Al_2O_3 on the activity and selectivity of the catalyst at 250 °C. The reproducibility of the results was good (±2.5–5%) as manifested by the error bars. The i-C_4H_{10} conversion increases steadily with Cr percent loading until it reaches a maximum value of 11% for 10% Cr. This is followed by a sharp decline from 10 to 20% Cr/Al_2O_3 and a gradual decrease from 20% to reach its final value of 8.5% at 40% Cr/Al_2O_3. A similar trend was obtained for the isobutene yield. The selectivity of i-C_4H_8 increases steadily to reach 66% for the 20% Cr/Al_2O_3 and then decreases slightly to 61% for the 40% Cr/Al_2O_3. The opposite behavior was obtained for CO_x (31% selectivity for the 20% Cr-loading). The high selectivity toward CO_x at low loadings can be attributed to secondary reactions. In terms of yield, the behavior shown in Figure 1 indicates that the optimum loading of Cr on Al_2O_3 is about 10%. The effect of Cr loading on Al_2O_3 on the catalyst performance can be related to the bond strength between the lattice oxygen and the catalyst. Pulse techniques and calorimetry revealed that lattice oxygen was bound more strongly in catalysts with lower rather than higher catalyst loadings.[12]

The performance of unsupported chromium oxide catalyst (only 7% conversion and 48% selectivity) was inferior to that of all supported catalysts. This result emphasizes the importance of the support for chromium oxide catalysts. This result is consistent with previously published TPR data for alumina-supported chromium catalysts and unsupported crystalline chromia.[4] More investigations on this behavior were reported elsewhere.[6–8]

3.2. Type of Alumina Support.

Different types of Al_2O_3 supports were studied, including Fluka A. G., Catapal, Puralox 150/100, Puralox 150/170, gamma, and high-surface-area aluminum oxide (HSA). The surface area of these supports and their effects on the activity of a 10% Cr/Al_2O_3 catalyst at a reaction temperature of 250 °C are shown in Table 1. The highest selectivity toward i-C_4H_8 was obtained with the Puralox 150/170 and HSA supports, whereas the gamma, HSA, and Catapal supports gave the highest i-C_4H_{10} conversion. Generally speaking, higher-surface-area supports (e.g., HSA) outperform lower-surface-area supports (e.g.,

Table 1. Properties of Different Types of Al_2O_3 Used as a Support for 10% Cr/Al_2O_3 Catalysts and Their Activities at 250 °C

type[a]	activity of 10% Cr/Al_2O_3		surface area of support (m^2/g)
	conv.[b] (%)	select.[c] (%)	
Puralox 150/100	7.2	45	112
Fluka	9.3	59	150
Puralox 150/170	9.5	68	176
gamma	10.1	62.5	245
Catapal (type A)	9.9	63.5	250
high surface area (HSA)	10	67.9	290

[a] The catalysts were calcined at 700 °C for 3 h and pretreated at 400 °C for 1 h. [b] The reproducibility of the conversion results is within the range of ±1.8–2.6%. [c] The reproducibility of the selectivity results is within the range of ±2–3%.

Table 2. Effect of Calcination Temperature on the Conversion and Selectivity of 10% Cr/γ-Al_2O_3 at Different Reaction Temperatures

calcination temp (°C)	reaction temp (°C)					
	250		350		400	
	conv.[b] (%)	select.[c] (%)	conv.[b] (%)	select.[c] (%)	conv.[b] (%)	select.[c] (%)
700[a]	10.4	64.0	9.4	55.0	9.5	57.0
500[a]	9.6	65.0	8.8	54.0	8.8	52.0
300[a]	9.3	67.0	8.3	51.5	8.3	49.8
original (not calcined)	8.2	71.8	7.5	59.0	7.2	55.5

[a] The samples were pretreated at 400 °C for 1 h. [b] The reproducibility of the conversion results is within the range of ±1.5–2.0%. [c] The reproducibility of the selectivity results is within the range of ±1.8–3.1%

Puralox 150/100). The effect of surface area is more pronounced on selectivity (45–68%) than conversion (7.2–10%). Therefore, not only the alumina support has considerable effects on the performance of chromium catalysts, but also its type.

3.3. Calcination Temperature.

Table 2 shows the effect of calcination temperature on the performance of the supported chromium catalyst. The calcination temperature was varied in the range 300–700 °C, and the calcined samples were tested at the same reaction temperatures (250, 300, and 400 °C). An original, uncalcined sample was also tested. As seen from this table, the conversion increases with the calcination temperature for the same reaction temperature. Compared to calcined catalysts, the original sample showed lower isobutene conversion but higher isobutene selectivity at lower reaction temperatures. The calcination temperature has no significant effect on selectivity at lower reaction temperatures (64–67% at 250 °C). An increase in selectivity was observed with calcination temperature for reaction temperatures of 350 and 400 °C. The drop in conversion and selectivity with reaction temperature for the same calcination temperature can be attributed to depletion of oxygen, which resulted in observable carbon deposits on the surface of the catalysts.

The molecular structure of the surface chromium oxide species can be used to explain the effect of calcination temperature on the performance of the catalyst. A high calcination temperature results in the formation of polymerized species, and isolated species can only be obtained at low temperatures.[3] Chromium oxide was stabilized in the Cr^{6+} oxidation state by the alumina support after calcination in air at 120 °C.[10]
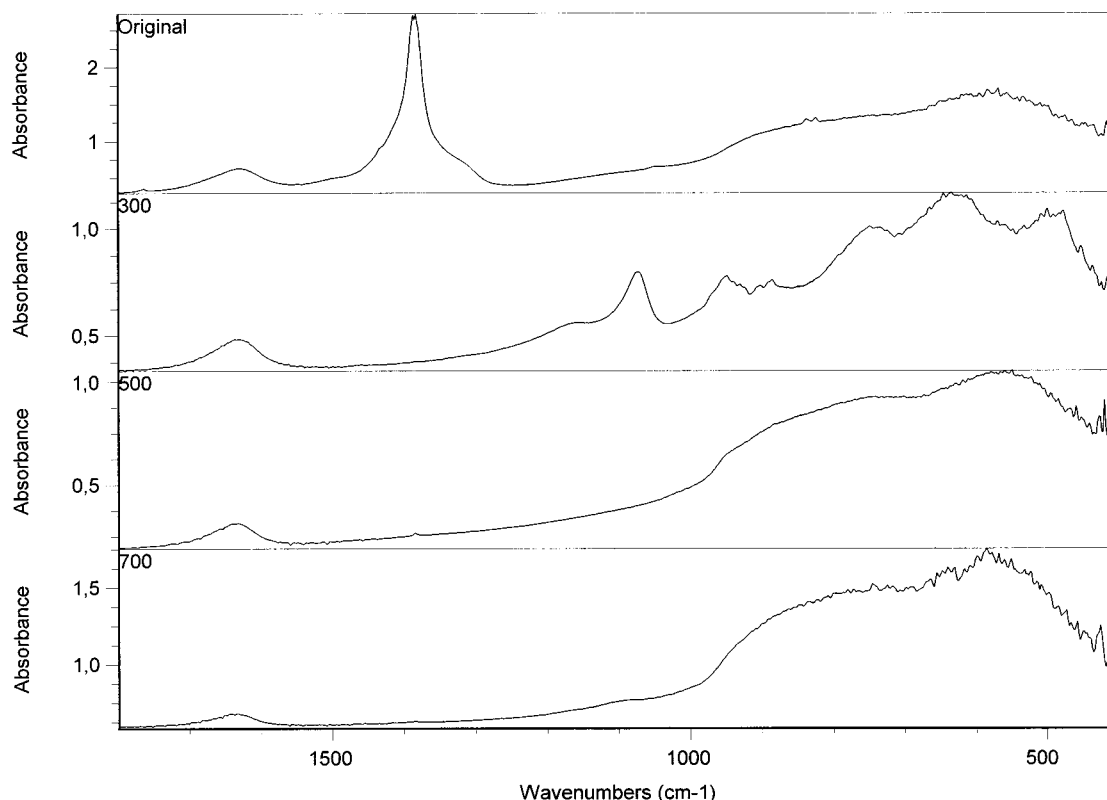
Figure 2. FTIR spectra for the original 10% Cr/Al_2O_3 and the samples calcined at 300, 500, and 700 °C for 3 h.

Figure 2 shows the FTIR spectrum for the original sample and the samples calcined at 300, 500, and 700 °C. As seen in this figure, the nitrate peak observed at 1400 cm^{-1} disappeared after calcination. For the 300 °C calcined sample, broad patterns, attributed to the isolated chromium species formed on the surface, appeared at wavenumbers less than 1250 cm^{-1}. For the 500 and 700 °C calcined samples, these patterns disappeared because of the polymerization process described by Hoang et al.[3] The molecular structure of these chromates was previously detected using Raman spectroscopy.[4,10,11]

The XPS spectra that give an overall view of the elemental distribution at the surface of the fresh, calcined, and spent 10% Cr/Al_2O_3 catalyst samples were obtained. These spectra agree well with the previously reported results[4,9] on the influence of chromium loading on Al_2O_3. Generally speaking, both Cr^{3+} and Cr^{6+} species are present in the catalyst. Their relative amounts vary with the calcination temperature. Cr^{3+} dominates on the surface of the original sample and that calcined at 300 °C, whereas Cr^{6+} dominates on the 500 and 700 °C calcined samples. Figure 3 shows a curve-fitted Cr multiplex spectrum for the calcined catalyst sample at 700 °C. This figure suggests the presence of two distinct chromium species on the surface of the calcined catalyst. These two chromium species have been assigned to Cr^{3+} (peaks B and D) and Cr^{6+} (peaks A and C). These double peaks are related to each other through the spin−orbit interaction. Another interesting result is shown in Figure 4, which gives the Cr multiplex spectrum for the used catalyst sample. The figure shows the presence of Cr^{3+} and Cr^{6+} on the surface. Cr^{3+} dominates, which confirms the transformation of Cr^{6+} into Cr^{3+} during the reaction.

3.4. Pretreatment Temperature. Table 3 shows the effect of the pretreatment temperature on the perfor-
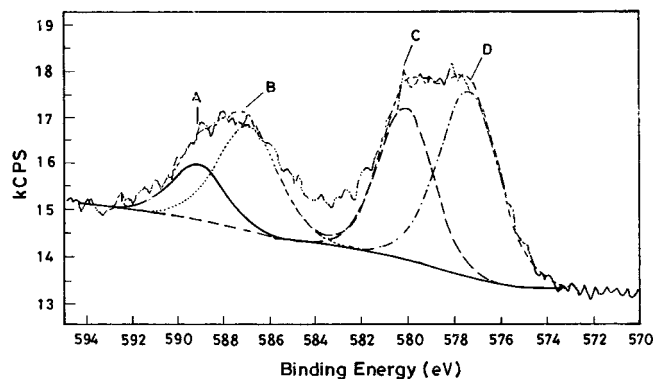

Figure 3. XPS multiplex spectrum showing the Cr 2p region for the calcined 10% Cr/Al_2O_3 (700 °C for 3 h).
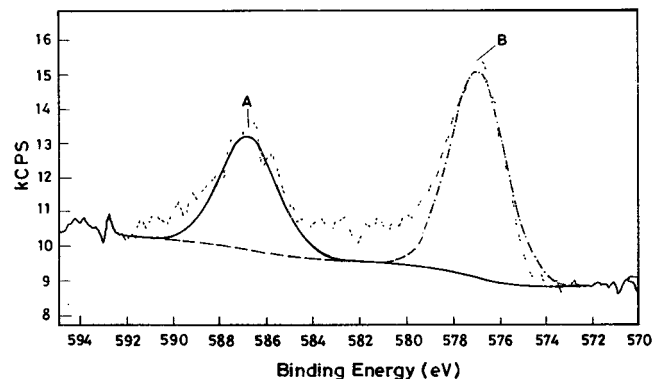

Figure 4. XPS multiplex spectrum showing the Cr 2p region of the spent 10% Cr/Al_2O_3 catalyst calcined at 700 °C for 3 h.

mance activity of 10% Cr/Al_2O_3 tested at a reaction temperature of 350 °C. Different temperatures (300, 400, 450, and 500 °C) were used in the pretreatment stage. The conversion goes through a maximum as the pre-

Table 3. Effect of Pretreatment Temperature on the Activity of 10% Cr/Al$_2$O$_3$ at a Reaction Temperature of 350 °C[a]

pretreat. temp (°C)	i-C$_4$H$_{10}$ conv. (%)	i-C$_4$H$_8$ select. (%)	i-C$_4$H$_8$ yield(%)
300	8.2	57	4.6
400	9.2	53.3	4.9
450	8.7	52	4.5
500	7.1	51.3	3.6

[a] All samples are calcined at 700 °C for 3 h and pretreated in O$_2$ and He environment. The reproducibility of the results is within range of ±1.5−2.5%.

treatment temperature is increased from 300 to 500 °C. A drop in conversion of about 23% was observed when the pretreatment temperature was increased from 400 to 500 °C. However, the selectivity continued to decrease with pretreatment temperature. Based on i-C$_4$H$_8$ yield, the optimum pretreatment temperature is 400 °C.

4. Conclusions

The effects of calcination conditions, pretreatment method, and percent loading of Cr on Al$_2$O$_3$ on the performance of chromium oxide catalysts supported on Al$_2$O$_3$ were investigated. An optimum percent loading of between 5 and 15% has been determined. Increasing the percentage of Cr in the sample to 20% results in a slight increase in the i-C$_4$H$_8$ selectivity but with less conversion and a lower yield. The calcination temperature has more of an effect on the i-C$_4$H$_{10}$ conversion at lower reaction temperatures. It was found that not only aluminum oxide as a support but also its type has a considerable effect on the catalyst performance. XPS analysis reveals the presence of two chromium species (i.e., Cr^{3+} and Cr^{6+}) on the surface of the catalysts; however, Cr^{3+} dominates after the reaction.

Acknowledgment

Literature Cited

(1) Grabowski, R.; Gryzbowska, B.; Sloczynski, J.; Wcislo, K. Oxidative Dehydrogenation of Isobutane on Supported Chromia Catalysts. *Appl. Catal. A: Gen.* **1996**, *144*, 335.

(2) Moriceau, P.; Gryzbowska B.; Barbaux, Y.; Wrobel, G.; Hecquet, G. Oxidative dehydrogenation of isobutane on Cr−Ce−O oxide: 1. Effect of preparation method and of Cr content. *Appl. Catal. A: Gen.* **1998**, *168*, 271.

(3) Hoang, M.; Mathews, J. F.; Pratt, K. Oxidative Dehydrogenation of Isobutane over Supported Chromium Oxide on Lanthanum Carbonate. *J. Catal.* **1997**, *171*, 320.

(4) Grzybowska, B.; Sloczynski, J.; Grabowski R.; Wcislo, K.; Kozlowska, A.; Stoch, J.; Zielinski, J. Chromium Oxide/Alumina Catalysts in Oxidative Dehydrogenation of Isobutane. *J. Catal.* **1998**, *178*, 687 and references therein.

(5) Al-Zahrani, S. M.; Jibril, B. Y.; Abasaeed, A. E. Propane Oxidative Dehydrogenation over Alumina-Supported Metal Oxides. *Ind. Eng. Chem. Res.* **2000**, *39*, 4070-4074.

(6) Kobayashi, M.; Kobayashi, H. Carbon Monoxide Oxidation over Chromium Sesquioxide 1. Nature of Oxygen Adsorbed on Cr$_2$O$_3$. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3009.

(7) Kobayashi, M.; Kanno, T. Surface Oxygen Species Involved in the Oxidation of Carbon Monoxide over Chromium(III) Oxide. *J. Chem. Soc., Faraday Trans.* **1989**, *85*, 579.

(8) Miyamoto, A.; Murakami, Y. Determination of the Number of Active Oxygen Species on the Surface of Cr$_2$O$_3$ Catalysts. *J. Catal.* **1983**, *80*, 106.

(9) Curry-Hyde, H. E.; Baiker, A. Selective Catalytic Reduction of Nitrate Oxide over Amorphous and Crystalline Chromia. 1. Comparative Study of Activities. *Appl. Catal. A: Gen.* **1990**, *65*, 211.

(10) Zaki, M. I.; Fouad, N. E.; Leyrev, J.; Knozinger, H. Physiochemical Investigation of Calcined Chromia Coated Silica and Alumina Catalysts−Characterization of Chromium−Oxygen Species. *Appl. Catal. A: Gen.* **1986**, *21*, 359.

(11) Cavani, F.; Koutyrev, M.; Trifiro, F.; Bartolini, A.; Ghisletti, D.; Iezzi R.; Santucci, A.; Del Peiro, G. Chemical and Physical Characterization of Alumina-Supported Chromia-Based Catalysts and Their Activity in Dehydrogenation of Isobutane. *J. Catal.* **1996**, *158*, 236.

(12) Mamedov, E. A.; Cortes Corberan, V. Oxidative Dehydrogenation of Lower Paraffins on Vanadium-Oxide-Based Catalysts: The Present State of Arts and Outlooks. *Appl. Catal. A: Gen.* **1995**, *127*, 1.