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Distribution of chromium species in catalysts supported on ZrO₂/Al₂O₃ and performance in dehydrogenation

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Abstract

Chromium catalysts (2–3 wt% Cr) supported on Al₂O₃ and ZrO₂/Al₂O₃, prepared with Cr(NO₃)₃ · 9H₂O or K₂CrO₄, were characterized and studied in the isobutane dehydrogenation. Depending on the chromium salt and the support, CrO₃, Cr₂O₃, and K₂CrO₄ species were observed in the calcined samples, and amorphous Cr₂O₃ remained after reduction with H₂. The preparation of ZrO₂/Al₂O₃ support yields zirconia dispersed on the surface of alumina. In the Cr/ZrO₂/Al₂O₃ calcined catalysts, the chromium sites were distributed on the ZrO₂ and Al₂O₃ surfaces. The O₂ chemisorption and the activity and selectivity to isobutene were also affected by the chromium species distribution. The addition of potassium decreased the O₂ chemisorption. In the isobutane dehydrogenation, the turnover number and selectivity to isobutene increased for the catalysts prepared with K₂CrO₄.

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1. Introduction

Chromium catalysts supported on alumina or on silica are used industrially in dehydrogenation and polymerization reactions, respectively [1,2]. Among the applications of Cr/Al₂O₃ catalysts, isobutane dehydrogenation yielding isobutene, intermediary in the production of methyl tertbutyl ether (MTBE), is noteworthy [3–11]. About 25% of the world production of MTBE is obtained by this route [1]. MTBE is added to gasoline to improve the octane number, yielding cleaner burning fuel [12], but the contamination of drinking water and groundwater by MTBE is causing its elimination as a gasoline additive [13]. However, an important amount of isobutene is used to produce butyl rubber, polyisobutylene, and other specialities [14]. Besides, oxidative and nonoxidative isobutane dehydrogenation with chromium catalysts still deserves a interest in the literature as a model reaction [15–17].

The active site for isobutane dehydrogenation is reported to be the mononuclear Cr^{3+} species with two coordinative

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vacancies linked to an $O^{=}$ ion of the support [5], obtained from the reduction of Cr^{5+} species [18–20]. On the contrary, other authors reported that the Cr^{3+} active sites are derived from the Cr^{6+} species [3,6,11]. Cavani et al. [3] suggested that Cr^{3+} species, formed after calcination of the Cr/Al_2O_3 catalyst, are more active sites than Cr^{3+} species obtained from the reduction of Cr^{6+} . Besides, the activity of the Cr^{2+} site has also been reported [5], although Weckhuysen et al. [10] reported that Cr^{3+} sites are more active than the Cr^{2+} sites. The characterization of the Cr^{3+} species in chromium catalysts is carried out by O₂ chemisorption at low temperature [21–24]. Recently, we used O₂ chemisorption in association with the dehydrogenation reaction [25]. We also showed that O₂ chemisorption at low temperature is appropriate for characterizing the amorphous Cr^{3+} species.

Dopants (e.g., potassium) are used in order to increase the activity and selectivity to isobutene. The addition of potassium changes the behavior of chromium catalysts for the isobutane dehydrogenation. Cavani et al. [3] observed an increase in the activity of Cr/Al₂O₃ catalysts with 15.3 wt% CrO₃ and less than 1 wt% K₂O. This result was ascribed to the formation of potassium chromate at the expenses of amorphous Cr³⁺ and α -Cr₂O₃ in the calcined catalysts. The promotion with alkali metals is also reported to increase the selectivity for dehydrogenation reactions due to the reduc-

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tion in the number of acid surface sites [26,27]. The most recent studies report the characterization of the chromium species in the surface of different supports and to relate them with the activity for dehydrogenation [3,4,6,25]. De Rossi and co-workers [4,5,7,28] studied the dehydrogenation reaction with chromium catalysts over different supports and with the addition of potassium. Comparing the supports Al₂O₃, SiO₂, and ZrO₂, the influence on the activity is attributed to the control of the Cr⁵⁺ concentration, the stabilization of the Cr³⁺ species formed after reduction, and the supply of the oxygen bond to the active site. The dehydrogenation activity was found to be substantially higher for chromium catalysts supported on ZrO2 than on Al2O3 or on SiO₂. The addition of potassium in Cr/ZrO₂ catalysts was reported to reduce the activity, a fact ascribed to the reaction between the O⁼ surface sites of the support in the vicinity of the amorphous Cr³⁺ species with potassium ions, reducing the number of active sites [5]. However, despite presenting larger thermal stability and smaller acidity [3], the zirconia presents smaller specific surface, typically about 50 m^2/g , than the usual supports, as Al_2O_3 and SiO_2 (100–600 m²/g). Many efforts have been made to produce ZrO₂ supports with higher surface area [29,30].

The preparation and characterization of ZrO₂/Al₂O₃ systems have been studied [31-33]. Damyanova et al. [31] reported that the monolayer of zirconia over alumina is formed in the range 13-17 wt% ZrO₂. ZrO₂/Al₂O₃ supports have been prepared and characterized in our laboratory. Souza et al. [34–36] prepared Pt/ZrO₂/Al₂O₃ catalysts with 1– 20 wt% ZrO₂ and observed that surface coverage of zirconia on alumina increased to 10 wt% of ZrO₂, falling above this concentration, due to the nucleation of zirconia crystallites. The introduction of ZrO₂ in the Al₂O₃ surface occurs due to the formation of Zr-O-Al bonds the strength of which decreases with the ZrO₂ content. The stronger Lewis acid sites decrease relative to the weak ones when increasing the ZrO₂ content. The lower acidic character of ZrO₂ increases the activity to dehydration and dehydrogenation reactions due to the reduction of cracking and coking side reactions [5,31,32].

To our knowledge, there are no studies concerning the isobutane dehydrogenation on Cr/ZrO₂/Al₂O₃ catalysts in the literature. In a previous work, Cr/Al₂O₃ and Cr/SiO₂ catalysts, prepared with different chromium salts, were characterized and submitted to isobutane dehydrogenation [25]. The Cr/SiO₂ catalysts showed a decrease of both activity and selectivity due to the interaction between potassium and the $O^{=}$ groups in the neighborhood of the Cr^{3+} active site. However, the potassium chromate catalyst supported on Al₂O₃ showed an increase of the activity and selectivity to isobutene [25]. In the present work, chromium catalysts supported on ZrO₂/Al₂O₃ were prepared with Cr(NO₃)₃ · 9H₂O and K₂CrO₄ seeking to conjugate the properties of the zirconia in a support of higher area. Finally, the catalysts were submitted to the isobutane dehydrogenation, correlating the chromium species with the activity and selectivity.

2. Experimental

2.1. Sample preparation

The catalysts were prepared in a rotatory evaporator by wet impregnation of aqueous solutions (15 ml/g support) of $Cr(NO_3)_3 \cdot 9H_2O$ (Acros) or K_2CrO_4 (Acros) in γ -Al₂O₃ (Engelhard), ZrO₂, and ZrO₂/Al₂O₃. The ZrO₂/Al₂O₃ support was also prepared in a rotatory evaporator by wet impregnation of an aqueous solution (15 ml/g γ -Al₂O₃) of the zirconium acetate hydroxide $(Zr(C_2H_3O_2)_{1,4} \cdot (OH)_{2,6})$ Aldrich) and γ -Al₂O₃, followed by calcination under dry air flow at 823 K for 1 h. The ZrO₂ was prepared by calcination of the zirconium acetate hydroxide in a furnace at 1123 K for 4 h with dry air flow (30 cm³/min). The catalysts prepared with this support were used as reference materials for the characterization analyses. After impregnation, the catalysts were dried at 393 K for 18 h and calcined at 773 K for 1 h; the resulting chromium contents were in the range 2–3 wt% Cr and potassium in the range 3–4 wt% K for the samples prepared with potassium chromate. Physical mixtures of CrO₃, Cr₂O₃, and K₂CrO₄ (3 wt% Cr) with Al₂O₃ were also prepared by careful grinding both components in an agate mortar. The samples were designated as CrXY, where X represents the precursor salt (N, nitrate, or C, chromate) and Y represents the support (Zr, ZrO₂; Al, Al₂O₃; and ZrAl, ZrO_2/Al_2O_3).

2.2. Characterization

The elemental analysis of zirconium in the ZrO_2/Al_2O_3 support was performed by X-ray fluorescence (FRX) and the determination of chromium and potassium in the catalysts was accomplished by atomic absorption spectroscopy (AAS).

The specific surface areas, pore volume (PV), and average pore diameter (PD), calculated as $4V/S_{BET}$, were measured with a Micromeritcs Model ASAP 2000 equipment, using N₂ at 77 K. The samples were outgassed for 18 h at 573 K before the measurement of N₂ adsorption.

The decomposition behavior of the $Zr(C_2H_3O_2)_{1.4}$ (OH)_{2.6} and the ZrO_2/Al_2O_3 support was accomplished by DTA/TGA analysis using a Rigaku Thermal Analysis Station TAS100 equipment. The samples (4 mg approx) were heated from room temperature to 900 K (rate 10 K/min) under 17% O_2/N_2 (60 cm³/min) mixture flow. Alumina was used as a reference material.

X-ray diffraction (XRD) measurements were carried out with the calcined samples and supports, employing a Rigaku Miniflex diffractometer (voltage, 30 kV, and current, 15 mA), equipped with a copper tube ($\lambda = 1.5417$ Å) and a graphite monochromator, operated in the step-scan mode 0.05° 2 θ per step and counting for 2 s per step.

Temperature-programmed reduction (TPR) of H_2 was performed in a Pyrex U-tube reactor with an on-line thermal conductivity detector (TCD). The catalysts (0.5 g) were dried at 773 K for 1 h with argon flow (AGA, 99.99%) and reduced from 298 to 1023 K (10 K/min) with 1.6% H_2/Ar flow (30 cm³/min). The TCD, connected to a PC computer, allowed study of the reduction profiles of H_2 with the temperature.

Diffuse reflectance spectroscopy (DRS) analyses were done on a Varian Cary 5 UV-VIS-NIR spectrophotometer equipped with a Praying Mantis diffuse reflection device from Harrick. Spectra were taken in the calcined catalysts, in the range of 800–200 nm, in order to observe the distinct Cr^{6+}/Cr^{3+} species distribution. CrO_3 , K_2CrO_4 , and α - Cr_2O_3 physical mixtures with alumina (3 wt% Cr) were used as references.

X-ray photoelectron spectroscopy (XPS) of the ZrO_2/Al_2O_3 support was carried out in a PHI Model 1257 spectrometer using Mg-K_a radiation (1253.6 eV). The pressure in the analysis chamber was kept at 10^{-9} Torr. A hemispheric analyzer PHI Model 10-360 was used to select the energy of the electrons (46.95 eV). The binding energies of O 1s, Al 2p, and Zr 3d were referenced to the C 1s peak, established at 284.6 eV [37]. The XPS intensity ratios between Zr 3d and Al 2p and between O 1s and (Zr 3d + Al 2p) were determined by multiplying the relative area by the sensitivity factors in order to obtain the normalized intensity of the related bands.

The chemisorption analysis of O_2 in the chromium catalysts was carried out in a Micromeritcs ASAP 2000-C equipment at 193 K, after reduction of the samples with pure H_2 at 773 K for 1 h. The chemisorption temperature was kept by using a mixture of isopropilic alcohol with liquid N_2 . A detailed description of this analysis was reported in a previous paper [25].

2.3. Activity measurements

The isobutane dehydrogenation was carried out at 773 K in a flow apparatus with a mixture of 5% isobutane in nitrogen (AGA). Each catalyst (0.5 g) was placed in a Pyrex U-tube reactor, dried with pure N₂ at 473 K for 30 min, and reduced at 773 K with pure H₂ for 1 h prior to the reaction tests. A Varian 3400 chromatograph with flame ionization detector and a KCl/Al₂O₃ column (Chrompack—50 m and 0.53 mm) was used in order to test the gas composition after reaction. The experimental conditions were adjusted to reach isobutane conversions lower than 10%, in order to calculate reaction rates assuming differential conditions.

3. Results and discussion

3.1. Characterization of the supports

Table 1 presents the results of the BET analysis of the supports, the pore volume, and average pore diameter. The ZrO₂ presented the lowest surface area (10 m²/g), compatible with that reported by other authors [5,34]. The addition

Table 1 Textural characteristics of the supports

Support	$S_{\rm BET}~({\rm m}^2/{\rm g})$	$PV (cm^3/g)$	PD (Å)
γ -Al ₂ O ₃	212	0.46	118
ZrO_2/Al_2O_3	214	0.46	80

of ZrO_2 over the Al_2O_3 support caused no reduction in the surface area of the ZrO_2/Al_2O_3 support in comparison with the alumina. The ZrO_2/Al_2O_3 support presented 6.8 wt% ZrO_2 from the X-ray fluorescence (XRF) analysis.

The XRD diffractograms of the supports are presented in Fig. 1. The alumina presented the crystalline γ -Al₂O₃ structure. The ZrO₂, prepared by calcination of the zirconium acetate hydroxide, presented the major peaks ascribed to the monoclinic ZrO₂ (m-ZrO₂), thermally stable phase [38]. However, the diffractogram also showed a peak at $2\theta \approx 30^{\circ}$ attributed to the tetragonal phase (t-ZrO₂) [39]. The residual fraction of the tetragonal phase was calculated as reported by Evans et al. [40], yielding 17% of t-ZrO₂, according to the literature [41]. The crystalline phase of ZrO₂ was not identified in the ZrO₂/Al₂O₃ support, probably due to ZrO₂ content (6.8 wt%). Damyanova et al. [31] observed the formation of crystallites of ZrO₂ with contents around 13–17 wt% ZrO₂ in γ -Al₂O₃.

The decomposition of the zirconium acetate hydroxide with 17 wt% O_2/N_2 mixture was monitored by TGA/DTA analysis and is presented in Fig. 2. The DTA curve showed a single exothermal peak occurring at 624 K. The weight loss, reported in the TGA curve in the temperature range 373–673 K, was about 43%, ascribed to the complete decomposition of the zirconium precursor to ZrO₂ in the used conditions. The TGA/DTA analysis of the ZrO₂/Al₂O₃ support after calcination showed a unique weight loss, about 5 wt%, observed around 373 K and assigned to the loss of physisorbed water. Thus, the calcination at 823 K of the ZrO₂/Al₂O₃ support allowed complete conversion of the zirconium acetate hydroxide to the oxide.

The ZrO₂/Al₂O₃ support was also submitted to XPS analysis. The binding energies (BE) of Zr $3d_{5/2}$ and Al 2pwere observed at 182.2 ± 0.2 and 74.4 ± 0.2 eV, respectively. The BE of the Zr $3d_{5/2}$ is in agreement with the literature for Zr^{4+} in pure zirconia [42]. The zirconia concentration (6.8 wt%) in the ZrO_2/Al_2O_3 support was not sufficient to shift the BE of Zr $3d_{5/2}$, indicating weak interaction between the Zr and the Al atoms. The Zr/Al atomic ratio obtained by XPS (0.35) was greater than the Zr/Al bulk ratio (0.03), suggesting that the zirconium oxide was preferentially dispersed in the surface of the alumina. These values are in agreement with the study of Damyanova et al. [31], that reported the formation of a monolayer of ZrO₂ over the Al₂O₃ support. The O/(Al + Zr) atomic ratio obtained by XPS was 2.03, greater than the O/(Al + Zr) bulk ratio, 1.51, showing the contribution of the surface hydroxyls of alumina in the XPS analysis.



Fig. 1. XRD diffractograms of the catalysts and supports (*, K_2CrO_4, and $\blacklozenge, \alpha\text{-}Cr_2O_3).$

3.2. Characterization of the catalysts

Chromium and potassium contents, obtained by atomic absorption spectroscopy, are presented in Table 2, as well as the crystalline phases of the catalysts, obtained by XRD



Fig. 2. TDA/TGA analysis of the zirconium acetate.

Table 2 Chemical analysis and XRD results of the catalysts

Catalyst	Precursor salt	Cr (wt%)	K (wt%)	Crystalline phase
CrNAl	Nitrate	2.7	_	γ -Al ₂ O ₃
CrNZr		2.1	-	ZrO_2, α - Cr_2O_3
CrNZrAl		2.1	-	γ -Al ₂ O ₃
CrCAl	Chromate	2.1	2.9	γ -Al ₂ O ₃
CrCZr		2.1	4.2	ZrO ₂ , K ₂ CrO ₄
CrCZrAl		2.2	3.6	γ -Al ₂ O ₃ , K ₂ CrO ₄

analyses. The XRD diffractograms of the calcined catalysts are presented in Fig. 1. The commercial software JADE v. 5.0 (Materials Data, Inc.) and the data bank ICDD PDF2 were used in order to obtain the assignment of the crystalline Cr₂O₃ and K₂CrO₄ species in the catalysts. The results show that the support and the precursor salt have influence in the formation of the chromium crystalline phases. The catalysts prepared with γ -Al₂O₃ and chromium nitrate (CrNAl) or potassium chromate (CrCAl) presented only diffraction peaks ascribed to the support, as shown in Fig. 1A. On the other hand, both samples prepared with ZrO₂ presented chromium crystalline phases. The CrNZr catalyst, prepared with chromium nitrate, presented characteristic peaks of α - Cr_2O_3 , at $2\theta \approx 33.6$ and 36.3° , only detected after processing of the diffractogram by the JADE v. 5.0 software, and indicated in Fig. 1B. The CrCZr catalyst, prepared with potassium chromate, showed peaks at $2\theta \approx 29.9$ and 39.5° , ascribed to orthorhombic K₂CrO₄. The CrNZrAl catalyst presented only the peaks ascribed to γ -Al₂O₃, as observed in the catalysts supported on alumina (Fig. 1C). However, the CrCZrAl catalyst, prepared with potassium chromate, presented characteristic peaks of orthorhombic K₂CrO₄. It suggests that a fraction of the chromium species is supported directly on ZrO₂ in the ZrO₂/Al₂O₃ support. The formation of small ZrO_2 islands or crystallites on ZrO_2/Al_2O_3 support, even below the loading of 10 wt% Zr, is noted in the literature [36]. Thus, for the chromium content, these results are in agreement with the literature [43,44] that suggests the for-



Fig. 3. Diffuse reflectance spectra of the catalysts.

mation of a crystalline α -Cr₂O₃ phase starting from 6 wt% Cr on alumina using a support with textural characteristics similar to those studied in this work. The formation of the crystalline α -Cr₂O₃ phase is reported to begin at 0.17 wt% Cr on zirconia [4]. This species was hardly visible in the diffractogram of the CrNZr catalyst, and was only detected with the JADE v. 5.0 software.

Diffuse reflectance spectra of the catalysts prepared with chromium nitrate and potassium chromate, obtained between 200 and 800 nm, are reported in Figs. 3A and B, respectively. The wavelengths corresponding to the maximum of intensity, obtained by Gaussian decomposition of the spectra, are shown in Table 3. The attributions of the chromium species in the catalysts were compared with the spectra of the compounds α -Cr₂O₃, CrO₃, and K₂CrO₄ in physical mixture (3 wt% Cr) with Al₂O₃ and are in agreement with the literature [3,10,45–47]. The band at 600 nm, ascribed to the d–d transition of Cr³⁺ ions in octahedral symmetry (⁴A_{2g} \rightarrow ⁴T_{2g}), was used to characterize the Cr³⁺ species in the catalysts [3,4,46].

The catalysts prepared with chromium nitrate on Al₂O₃, ZrO₂, and ZrO₂/Al₂O₃ (CrNAl, CrNZr, and CrNZrAl) presented two distinct bands at about 280 and 360 nm, in the charge transfer region, ascribed to tetrahedral chromate transitions ${}^{1}A_{1} \rightarrow {}^{1}T_{2}$ (1t₁ \rightarrow 7t₂ and 6t₂ \rightarrow 2e) and ${}^{1}A_{1} \rightarrow$

Table 3	
DRS of the catalysts and standards	

Sample	ple Wavelength (nm)				Attribution	
CrNAl	283	367	429		Cr ⁶⁺	
CrNZr	282	360	438	594	Cr^{6+}/Cr^{3+}	
CrNZrAl	291	367	427		Cr ⁶⁺	
CrCAl	279	363	431		Cr ⁶⁺	
CrCZr	282	369	427		Cr ⁶⁺	
CrCZrAl	298	362	425		Cr ⁶⁺	
CrO ₃	278	363			CrO ₃	
K ₂ CrO ₄	261	365	435		CrO_4^{2-}	
α -Cr ₂ O ₃	272	355	467	610	Cr_2O_3	



Fig. 4. TPR profiles of the catalysts.

 ${}^{1}T_{2}$ (1t₁ \rightarrow 2e), respectively [3,4,10,45,46]. These catalysts presented also a shoulder at about 430 nm, which can be related to Cr⁶⁺ transition ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$ (1t₁ \rightarrow 2e). This band is ascribed in the literature to a chromate structure, under dehydration conditions, anchored to sites of the support [3,45,48].

The catalyst prepared with chromium nitrate on zirconia (CrNZr) presented, besides the bands at 280, 360, and 440 nm, a broad band in the d–d region, around 600 nm. The bands at 440 and 600 nm are ascribed to transitions of Cr^{3+} in the Cr₂O₃ form [3,4,45]. Indeed, this catalyst presented crystalline α -Cr₂O₃ species by XRD analysis. The catalysts prepared with potassium chromate are presented in Fig. 3B. As observed for the catalysts prepared with chromium nitrate, two bands at 280 and 360 nm and a shoulder at about 430 nm, ascribed to chromate form, were observed in the catalysts.

Fig. 4 presents the profiles of consumption of H₂ in the TPR. The consumption of H₂ was not observed in the supports, as well as in the bulk α -Cr₂O₃, as reported by Zaki et al. [49]. All the catalysts, except the CrCZr, presented reduction peaks around 700 K, corresponding to the reduction from CrO₃ to Cr₂O₃, in agreement with the literature [6,8,50–52]. In fact, a physical mixture of CrO₃ (3 wt% Cr) with Al₂O₃ presented only a single reduction peak at 714 K, with consumption of H₂ associated to the complete reduc-

Table 4 TPR results of the catalysts

Catalyst	H ₂ consur	CrO ₃	Cr ^{6+a}		
	654–754 K	799–898 K	Total	(%)	(%)
CrNAl	23.1	_	23.1	80	80
CrNZr	5.3	15.3	20.6	18	71
CrNZrAl	27.0	_	27.0	93	93
CrCAl	20.8	_	20.8	72	72
CrCZr	_	28.0	28.0	0	97
CrCZrAl	23.9	1.9	25.8	83	89

^a Total Cr^{6+} (%) amount: $CrO_3 + CrO_4^{2-}$.

tion of CrO₃ to Cr³⁺. For Cr/Al₂O₃ catalysts, Grzybowska et al. [8] and Mentasty et al. [52] observed consumption of H_2 in temperatures between 623 and 723 K. In the CrNZr catalyst the peak of reduction of the CrO3 supported on ZrO2 was verified at 656 K, while in the CrNZrAl and Cr-CZrAl catalysts, the peaks were observed at 654 and 688 K, respectively. Thus, it is possible that those reductions are referring to CrO₃ supported on the zirconia in the ZrO₂/Al₂O₃ system, once the XPS results showed the distribution of the ZrO₂ preferentially over the surface of that support. In the CrCZrAl catalyst a reduction peak at 735 K also appeared, but in smaller intensity than the peak at 688 K, which could be due to the CrO₃ supported directly on alumina. The catalysts prepared with potassium chromate on ZrO₂ and ZrO₂/Al₂O₃ (CrCZr and CrCZrAl) also presented a reduction peak around 800 K, ascribed to the reduction of the fraction of K₂CrO₄ present, in agreement with the results of XRD. In this work, the physical mixtures of K_2CrO_4 (3 wt%) Cr) diluted in Al₂O₃ presented only a single reduction peak around 850 K. Cavani et al. [3] observed that the presence of potassium stabilizes the Cr⁶⁺ by the formation of chromate or dichromate species, therefore, reduced in larger temperatures.

The CrCZr catalyst, prepared with K_2CrO_4 , and the CrNZr catalyst, although prepared with $Cr(NO_3)_3 \cdot 9H_2O$, also presented a reduction peak in the region of 800–900 K. These catalysts presented a shoulder in the DR spectrum at about 430 nm, ascribed to chromate species. Sohn et al. [48] observed the formation of the chromate species on zirconia in Cr/ZrO₂ catalysts starting from 1 wt% Cr. Thus, the reduction peak at the highest temperature observed in TPR can be associated to the Cr⁶⁺ with larger interaction with the support, corresponding to the species chromate.

In Table 4 the results of TPR of H_2 are presented and grouped by temperature regions, in agreement with Fig. 2. Thus, the H_2 consumptions of CrO₃ and chromate are represented in the regions of 654–754 and 799–898 K, respectively. Also reported is the percentage of the CrO₃ species, in relation to the total of chromium, considering that its reducibility is complete to Cr³⁺ (28.9 µmol H_2/mg Cr) and it occurs in the range of 654–754 K. The CrNAl, CrCAl, and CrNZrAl catalysts only presented reduction of CrO₃ and the CrCZrAl catalysts presented predominance of CrO₃ species, although it also presented consumption of H_2 relative to the



Fig. 5. Schematic representation of chromium particles supported on ZrO_2/Al_2O_3 .

chromate species reduction. On the other hand, the catalysts supported on ZrO_2 (CrNZr and CrCZr), presented mainly the chromate species with consumption of H₂ in the temperature region of 873–898 K.

The total Cr^{6+} amount $(CrO_3 + CrO_4^{=})$ of the calcined precursors, presented in Table 4, was calculated by the total experimental consumptions of H₂ and the stoichiometry of the reaction $2CrO_3 + 3H_2 \rightarrow Cr_2O_3 + 3H_2O$. The procedure is also valid for the catalysts with chromate, admitting the reaction $2K_2CrO_4 + 3H_2 \rightarrow Cr_2O_3 + 2K_2O + 3H_2O$ (also $28.9 \,\mu mol \, H_2/mg \, Cr$). All the catalysts presented consumption of H₂ close to the equivalent value of the reduction of Cr^{6+} (CrO₃ or K₂CrO₄) to Cr₂O₃ (28.9 µmol/mg Cr). Thus, the catalysts presented predominance of Cr⁶⁺. The CrNZr catalyst, although it also had the α -Cr₂O₃ species detected by XRD and DRS, resulted in larger consumption of H_2 in the TPR, probably a function of the formation of chromate, identified by DRS and also by the temperature range of H₂ consumption. The H₂ consumption in the catalysts supported on Al₂O₃ was smaller than the stoichiometric and the absence of α -Cr₂O₃ suggests the presence of the amorphous Cr_2O_3 species, which does not reduce with H₂. Cavani et al. [3] suggested the formation of that species starting from 2 wt% Cr in Cr/Al₂O₃ catalysts and attributed it to its larger activity in the dehydrogenation reaction than the amorphous Cr³⁺ obtained from the reduction of Cr⁶⁺. An increase of H₂ consumption was observed in the catalysts prepared with K_2CrO_4 on ZrO_2 (CrCZr) in contrast with the sample prepared with nitrate (CrNZr). This phenomenon can be ascribed to the stabilization of chromium in the hexavalent state by the presence of potassium [3]. In fact, the CrCZr catalyst does not present α -Cr₂O₃ in its XRD diffractogram, while the CrNZr catalyst does.

The results of the XRD, DRS, and TPR permitted an estimation of the distribution of the chromium species presented in the catalysts. In the samples prepared on alumina (CrNAI and CrCAI) it was predominantly Cr^{6+} , in the form of CrO₃, and about 20% amorphous Cr₂O₃. In the sample prepared with potassium chromate on ZrO₂/Al₂O₃ (CrCZrAI), CrO₃ and K₂CrO₄ were detected, while the TPR profile and the XRD diffractograms suggest that the CrO₃ particles interact with the Al₂O₃ and ZrO₂ surfaces of the ZrO₂/Al₂O₃ support in comparison with the catalysts supported on γ -Al₂O₃ and on ZrO₂. Fig. 5 represents schematically the chromium particles supported on ZrO₂/Al₂O₃. In the CrNZrAI catalyst, prepared with the chromium nitrate precursor, mainly CrO₃ was detected,

Table 5 O₂ chemisorption and isobutane dehydrogenation results

Catalyst	O_2 chemisorption (µmol O_2/g Cr)	<i>S</i> iB= (%)	−(<i>r</i> _{iB}) (mmol iButane/g Cr·h)	TON (l/h)
CrNAl	3520	95.7	49.4	0.12
CrNZrAl	4620	97.6	107.2	0.19
CrCAl	960	99.8	114.6	0.99
CrCZrAl	1150	99.8	56.6	0.41

while in the CrNZr catalyst three chromium species were observed, i.e., Cr_2O_3 , CrO_3 , and K_2CrO_4 .

Table 5 presents the results of O₂ chemisorption and performance in the isobutane dehydrogenation for the catalysts with similar surface area (200 m^2/g), supported on Al₂O₃ and ZrO₂/Al₂O₃. The O₂ chemisorption was not observed in the supports, as well as in the α -Cr₂O₃. The selectivity of the method for O_2 chemisorption on amorphous Cr^{3+} , active site of the dehydrogenation reaction, was established and reported in a previous work [25]. The catalysts supported on ZrO₂ presented the smallest O₂ chemisorption, which can be ascribed to the α -Cr₂O₃ phase, that does not adsorb O₂, and, mainly, to the smaller surface area of the zirconia (10 m²/g). The O₂ chemisorption was affected by the support and chromium precursor. In the samples without chromium nitrate, the order of O₂ chemisorption in relation to the supports was $ZrO_2/Al_2O_3 > Al_2O_3$. The CrNZrAl catalyst presented O₂ chemisorption about 30% larger than the CrNAl catalyst. In the catalysts prepared with potassium chromate, the order of O₂ chemisorption was unaffected in relation to the supports, compared with the chromium nitrate precursor. However, reduction of O2 chemisorption was verified for the catalysts with potassium for both supports. In the catalysts supported on Al₂O₃ and on ZrO₂/Al₂O₃ such reduction was similar, 3.7 and 4 times, respectively. Physical mixtures of CrO3 and K2CrO4 with 3 wt% Cr in Al2O3 adsorbed, after total reduction for Cr³⁺, 2918 and 1594 µmol O_2/g Cr, respectively, with variation of 1.8 times.

The influence of potassium in the chromium species in the Cr/Al₂O₃ and Cr/ZrO₂ catalysts has been described in the literature [3,5]. In the catalysts supported on alumina, the potassium addition stabilizes the chromium in the Cr⁶⁺ state, avoiding the formation of α -Cr₂O₃ [3]. This mechanism increases the number of amorphous mononuclear Cr³⁺ active sites. In the Cr/ZrO_2 catalysts the effect is opposite, decreasing the active species by interaction of the potassium with the $O^{=}$ groups of the support adjacent to the chromium [5]. Thus, the reduction in the chemisorption for the samples with potassium can be attributed to the interaction of the potassium with the groups $O^{=}$ of the support. These studies used catalysts with low potassium content (< 1.5 wt% K) and the distinct behaviors could be observed between the supports. In the present study, the potassium source (K₂CrO₄) resulted in contents of the order 3-4 wt% K and the main observed phenomena was the reduction of O_2 chemisorption for the supports.

3.3. Isobutane dehydrogenation

The catalysts were tested in the dehydrogenation of isobutane at 773 K and the conditions were adjusted for conversion lower than 10%, as shown in Table 5. All the samples were dried with N₂ flow at 473 K and reduced with H₂ flow (30 cm³/min) at 773 K. Some authors [4,5] used the reduction with CO at 623 K. Such procedure results in more Cr^{2+} species than Cr^{3+} in supports as Al₂O₃ and mainly SiO₂ [46,47,53,54]. Recently, Weckhuysen et al. [10,11] showed that Cr^{2+} species.

The supports were submitted to the reaction, but only the ZrO_2/Al_2O_3 presented activity, resulting mainly in cracking products, methane (14%) and propene (44%). The catalysts presented high selectivity to isobutene (Table 5), with the same by-products. The cracking products are attributed to the acidity, in agreement with the literature [5,6,9]. Deactivation was not observed in the period of 4 h for all the catalysts. Such stability can be attributed to the use of diluted mixtures of the reagent and temperature about 200 K smaller than the industrial [3].

In the catalysts without potassium addition, high selectivity to isobutene (S iB⁼) was observed, above 95% (Table 5). This value is in agreement with that reported in the literature [3–9]. Expressed variation of selectivity among the samples for the different supports was not noted. However, in the CrCAl and CrCZrAl catalysts, a small selectivity increase was noted, relative to the nitrate precursor. This effect can be related to the decrease in the acidity in the Al₂O₃ and ZrO₂/Al₂O₃ supports.

Table 5 also presents the results of reaction rate calculated under the hypothesis of differential reactor. For the catalysts prepared with $Cr(NO_3)_3 \cdot 9H_2O$, the activity order was the same as that observed in the O₂ chemisorption: CrNZrAl >CrNAl. Under the same reaction conditions, the reaction rate for the bulk α - Cr_2O_3 was just 9.8 mmol iButane/(g Cr h). The catalyst with potassium chromate on ZrO_2/Al_2O_3 presented reduction in the activity, while on Al_2O_3 the activity increased. The interaction of the potassium with the superficial O⁼ groups of the support [5] reduced the activity of the catalyst supported on ZrO_2/Al_2O_3 . In this support, the chromium sites should be interacting with the zirconia, taking into account the characterization by XRD and TPR analyses and the behavior of the samples supported on ZrO_2 or Al_2O_3 .

The results of turnover frequency (TON), presented in Table 5, were obtained with the results of O₂ chemisorption, taking into account a dissociative stoichiometry, representing an O₂/Cr ratio of 1:2 [55]. Thus, in the catalysts without potassium, the order of activity obtained was CrNZrAl > CrNAl.

Considering the catalysts with potassium in our study, in the samples supported on ZrO_2/Al_2O_3 and on Al_2O_3 , a significant increase of the activity per site was observed in relation to chromium nitrate, due to the stabilization of the chromium in the surface of the support as Cr^{6+} after calcination.

4. Conclusions

The support and the chromium precursor have influence in the distribution of chromium species. CrO_3 , amorphous and crystalline Cr_2O_3 , and K_2CrO_4 were observed by DRS, XRD, and TPR, depending on the support and chromium salt. The preparation of ZrO_2/Al_2O_3 support yields zirconia dispersed on the surface of alumina. In the catalyst supported on ZrO_2/Al_2O_3 , chromium particles supported on zirconia and on alumina were observed.

The amount of the active site for dehydrogenation, amorphous Cr^{3+} , determined by O_2 chemisorption, was also influenced by the support and chromium precursor. The selectivity to isobutene was always high, independent of the support, but it was influenced by the potassium presence. The potassium has an effect on the turnover number and selectivity to isobutene in the isobutane dehydrogenation. A significant increase is observed, due to the stabilization of the chromium in the surface of the support as Cr^{6+} , after calcination, and to the decrease in the acidity.

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