Alkane dehydrogenation over supported chromium oxide catalysts

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Abstract

The dehydrogenation of alkanes over supported chromium oxide catalysts in the absence of oxygen is of high interest for the industrial production of propene and isobutene. In this review, a critical overview is given of the current knowledge nowadays available about chromium-based dehydrogenation catalysts, in particularly the industrially used Cr/Al_2O_3 catalysts. It will be shown that detailed information on the dehydrogenation site can be obtained by using advanced spectroscopic tools. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The catalytic dehydrogenation of alkanes has a considerable industrial impact, because it represents a route to obtain alkenes from feedstocks of low-cost saturated hydrocarbons [1]. In the 1970–1980s, the main interest was devoted to the catalytic dehydrogenation of *n*-butane to butene and butadiene, which are precursor molecules for manufacturing synthetic rubber [2]. Nowadays, however, the dehydrogenation of propane and isobutane has become more important. Propene is used in the polymer industry for the synthesis of high-purity polypropylene, whereas isobutene is needed for the synthesis of MTBE and ETBE, additives to gasoline. The reknown CATO-FIN[®] process leads the world for producing propene and isobutene with an installed capacity of 600 000

and 2 600 000 metric tons per year, respectively. It is estimated that 25% of the worldwide production of MTBE originates from the catalytic dehydrogenation of isobutane. This number is expected to increase in the future because the traditional sources of isobutene, i.e. steam cracking and FCC, are already heavily used, and the availability of isobutene has become a bottleneck in the expansion of the MTBE market.

Alkane dehydrogenation is an endothermic process, and requires relatively high temperatures and low pressures to obtain significant yields of alkenes [3]. Because all equivalent C–H bonds in an alkane molecule have an equal chance of reacting, a dehydrogenation reaction is expected to be rather unselective. Furthermore, the required high temperatures favor thermal cracking reactions to lighter alkanes and coke. As a consequence, suitable catalysts not only have to possess good activity and selectivity, but also must suppress thermal cracking reactions.

Since the pioneering work of Frey and Huppke [4,5], the superior properties of supported chromium

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oxide catalysts in alkane dehydrogenation are well-known, and Cr_2O_3/Al_2O_3 catalysts are widely used as the commercial catalyst of choice. The main result concerning Cr_2O_3/Al_2O_3 catalysts until the late 1960s are summarized in review papers by Poole and McIver [6], and by Kearby [7]. Subsequently, numerous papers have been published in the literature on CrO_x/SiO_2, CrO_x/Al_2O_3 and CrO_x/ZrO_2 catalysts [8–50]. All the newer studies primarily focus on (a) identification of the active sites; (b) influence of preparation and treatment conditions on chromium oxide speciation, and on the catalytic activity/selectivity; and (c) elucidation of the dehydrogenation mechanism.

In this review, a critical overview is given of the current knowledge about chromium-based dehydrogenation catalysts, in particular the industrially used Cr/Al_2O_3 catalysts. In Section 2, the thermodynamical constraints for alkane dehydrogenations and their technological consequences will be introduced. Sections 3 and 4 are devoted to the synthesis and spectroscopic characterization, while Section 5 discusses the factors governing the catalytic activity and selectivity. In Section 6, the spectroscopic and catalytic data of Cr-based catalysts will be combined in an attempt to define structure–activity/selectivity relationships.

2. Thermodynamical constraints for alkane dehydrogenations and their technological consequences

Dehydrogenation reactions, $C_nH_{2n+2} \leftrightarrow C_nH_{2n} + H_2$, are strongly endothermic, and the conversion per pass is limited by thermodynamical equilibrium [51]. Theoretical dehydrogenation equilibria for alkanes to alkenes indicate that longer chains are dehydrogenated at lower temperatures, whereas lighter alkanes require higher dehydrogenation temperatures. This is illustrated in Table 1 for several linear and branched alkanes [3]. The table summarizes the reaction temperatures at which a certain conversion of the alkane towards the corresponding alkene can be obtained. For example, an equilibrium conversion of 50% is reached under atmospheric pressure at around 585°C and 725°C for *n*-hexane (to *n*-hexene) and ethane (to ethene), respectively. In addition, *trans*-2-butene formation requires about the same temperature as 1-butene formation, whereas *cis*-2-butene is formed only at higher temperatures. Conversions can also be increased by using lower pressures or by using diluents with the alkane feed.

Dehydrogenation reactions are rather unselective, because all equivalent C–H bonds have an equal bonding energy, and therefore an equal chance of reacting [3]. When two C–H bonds of neighbouring carbons are split, a double bond is formed and alkanes are converted to alkenes. However, when the two C–H bonds belong to non-neighboring carbon atoms, dehydrocyclization and possibly also aromatization may occur. The latter reaction is especially pronounced for alkanes with carbon chains of at least six carbons. Thermodynamics show that aromatization equilibria overtake dehydrogenation equilibria at higher temperatures. Thus, *n*-hexane is primarily converted to benzene, whereas toluene can be made from *n*-heptane. If the two C–H bonds are part of two different alkane molecules, higher molecular-weight hydrocarbons are formed, and extensive C–H bond breaking and C–C bond formation may lead to hydrogen gas and coke. Thus, to achieve an acceptable activity and selectivity per pass, the catalyst needs to be periodically regenerated by burning the coke deposited on the surface. It is also clear that degradation reactions

Table 1

Dehydrogenation equilibria for several linear and branched alkanes: the reported numbers are the temperatures (°C) required for the given conversions at a total pressure of one atmosphere (after [3])

Conversion (mol%)	Ethene	Propene	1-Butene	*cis*-2-Butene	*trans*-2-Butene	Isobutene	1-Pentene	1-Hexene
10	555	456	460	470	450	405	450	450
30	660	540	545	555	540	490	535	535
50	725	595	600	625	598	540	585	585
70	790	660	670	700	640	590	650	650
90	900	750	753	800	760	680	730	730

result in more hydrogen being produced than alkene, and that a proper choice of feed rate and temperature are needed to achieve an optimum industrial dehydrogenation process that has the required selectivity.

Since the discovery of Cr-based dehydrogenation catalysts by Frey and Huppke [4,5], several industrial companies have done extensive research to develop a commercial dehydrogenation process. The main technological problems, within the constraint to operate as a continuous process; are (1) sufficient heat supply to the reactor; (2) careful temperature control to minimize degradation products and to maximize conversion and (3) catalyst regeneration. Different solutions have been developed, depending on the know-how of the various companies. The best known processes are the CATOFIN® (for alkenes), the CATADIENE® (for dienes), the LINDEBASF® the UOP® and the SNAMPROGETTI-YARSINTEZ® processes. However, it is important to stress here that the LINDE® process has only been used on a demonstration plant, and has never been really commercialized.

In all these industrial processes, the heat obtained from the burning of coke is used in the dehydrogenation step. In the worldwide CATOFIN® process, licensed by UCI-ABB Lummus Global, series of adiabatic fixed bed reactors are in cyclic operation with quickly alternating dehydrogenating and regeneration periods. In contrast, the fluidized bed SNAMPROGETTI-YARSINTEZ® process uses a fluidized bed reactor, and a regenerator interconnected with each other. The latter process is mainly used in Russia, and the industrial plants are of relatively small capacity. Details of these processes and reactor designs can be found in several interesting papers [52–55].

3. Catalyst synthesis

Commercial Cr-based dehydrogenation catalysts are typically composed of chromium oxides dispersed on a porous support including dopants to regulate deactivation and improve selectivity. The Cr loading is mostly around 13 wt% Cr [56], but dehydrogenation activity has been observed in the entire range between 0 and 20 wt% Cr. Although alumina with a surface area of 50–300 m^2/g is the preferred support for industrial applications, other supports such as zirconia, silica and magnesium oxide have also been stu-

died in great detail [7]. Alumina possess the undesired feature of catalyzing degradation reactions, i.e. cracking and coking, leading to catalyst deactivation. To overcome these problems, the responsible acid sites are often poisoned with an alkali ion dopant, mostly potassium, in a concentration up to 2 wt%. In this respect, zirconia has some advantages over alumina, because of its high thermal stability and low surface acidity. Indeed, De Rossi et al. [44,45] have found even higher dehydrogenation activities for Cr/ZrO$_2$ catalysts.

The initial Cr-based dehydrogenation catalyst of Frey and Huppke was prepared by coprecipitation of aluminium and chromium nitrates with ammonium hydroxide, but numerous modified preparation procedures have since been developed [6,7]. Many of these preparation methods, mostly differing in their Cr content and type of alkali metal ion, have appeared in the patent literature. Generally speaking, Cr/Al$_2$O$_3$ catalysts can be prepared by three techniques:

1. Impregnation procedures in which a chromium salt is deposited on an alumina support from a suitable solvent and then decomposed to the chromium oxides. Most frequently, supported chromium oxide catalysts are prepared by an incipient wetness impregnation of a porous high-surface area alumina with an aqueous solution containing chromium (VI) trioxide or chromium (III) nitrate. If an alkali ion, such as potassium, is needed, an aqueous solution containing K$_2$CrO$_4$ is used.
2. Coprecipitation procedures in which chromium and aluminium species are more or less simultaneously precipitated, dried, and calcined.
3. Atomic layer epitaxy procedures in which a chromium salt, such as Cr(acac)$_3$, reacts with the alumina surface from the vapor phase. This alternative preparation method was recently reported by Kytokivi et al. [43].

4. Catalyst characterization

Numerous papers have been published in the literature regarding the characterization of chromium oxides supported on different inorganic oxides, and much research has dealt with the use of a specific spectroscopic technique, such as electron spin reso-

nance (ESR) [26,30], X-ray photoelectron spectroscopy (XPS) ([41–43,49]), diffuse reflectance spectroscopy (DRS) [13,14,24,25,35,36], infrared spectroscopy (IR) [38,44], and Raman spectroscopy (RS) [16–23,31–33]. An overview of this field, and the potential and limitation of each characterization technique has been recently given in another review paper (1). As a consequence, we will limit our discussion here to a detailed discussion of the structure of (a) freshly prepared, (b) catalytically active, and (c) deactivated Cr/Al_2O_3 catalysts.

4.1. Freshly prepared catalysts

The surface composition of calcined Cr/Al_2O_3 catalysts as a function of the Cr oxide loading is summarized in Table 2. The table shows three distinct Cr loading regions, their exact limits are a function of the preparation method, coupled with the surface area of the alumina support. It is important to notice that the reported surface composition in Table 2 refers to fully dehydrated catalysts.

At low Cr oxide loadings, typically lower than 1 wt%, only Cr^{6+} and Cr^{5+} are detected. However, XPS only detects Cr^{6+}, whereas DRS and RS are able to discriminate between chromate and polychromate (dichromate, trichromate, etc.) [1]. However, at these low loadings, monochromate is the dominant species [24]. This species strongly interacts with the alumina support via its most basic hydroxyl groups, and cannot be removed by rinsing the catalyst with cold water [39]. In addition to Cr^{6+}, some Cr^{5+} is detected by EPR. This Cr^{5+} is in square pyramidal coordination, and represents only a small fraction of the surface, typically less than 3% of the total Cr content [30].

At intermediate Cr oxide loadings, typically between 1 wt% and monolayer coverage loading, both $Cr^{6+/5+}$ and Cr^{3+} are detected, and the amount of $Cr^{6+/5+}$ decreases as a percentage of the total Cr content with increasing Cr oxide loading. In addition, the polychromate:chromate ratio increases with increasing Cr loading, indicating that less (reactive) hydroxyl groups are available to stabilize the surface chromium oxide as an anchored chromate species [29]. This results in weakly bonded polychromate species, which are (more) easily removed via rinsing with cold water [39]. Besides $Cr^{6+/5+}$, Cr^{3+} is also detected by XPS, DRS and EPR [1]. These Cr^{3+}-species are present as isolated surface species (δ-signal in EPR) and/or amorphous oxide clusters (β-signal in EPR) of small sizes, which are XRD-invisible.

At much higher Cr oxide loadings, i.e. above monolayer coverage loading, Cr^{3+} is the dominant species, and the fraction of Cr^{6+} is rather low. Two types of Cr^{3+} are observed isolated and clustered Cr^{3+}. The latter can be present as either crystalline α-Cr_2O_3, which is XRD-detectable, and amorphous Cr_2O_3. The remaining fraction of Cr^{6+} is typically around 2 wt%, as shown in Table 3. It is also important to mention here that different research groups have experimentally determined a monolayer coverage of about 4 Cr/nm^2. This corresponds, depending on the surface area of the alumina support, with 6–8 wt%. Although Vuurman et al. [20] report that up to a monolayer almost all the chromium oxide species are stabilized as Cr^{6+}, other research groups have observed both Cr^{3+} and Cr^{6+} at monolayer coverage. For example, Kozlowski [50] reports that only 60% of Cr is stabilized as Cr^{6+} at monolayer coverage. These discrepancies in literature must be attributed to differences in preparation and

Table 2
Surface composition of calcined Cr/Al_2O_3 catalysts as a function of Cr oxide loading as determined by several characterization techniques

Cr oxide loading (wt% Cr)	XPS	DRS	RS	ESR	XRD
0–1	Cr^{6+}	Chromate	Chromate Polychromate	Traces of Cr^{5+}	No Cr oxide phase
1–7	Cr^{6+}; Cr^{3+}	Chromate Polychromate Traces of Cr^{3+}	Chromate Polychromate	Traces of Cr^{5+}; Cr^{3+}	No Cr oxide phase
>7	Cr^{3+}; Cr^{6+}	Chromate Polychromate; Cr^{3+}	Chromate Polychromate; Cr_2O_3	Traces of Cr^{5+}	α-Cr_2O_3

Table 3
Amount of Cr^{6+} in calcined Cr/Al_2O_3 catalysts before and after alkane dehydrogenation

Cr loading (wt%)	Treatment	Cr^{6+} (wt%)	Reference
7.4	Calcined	2.59	50
5.6	Calcined	2.60	39
13.0	Calcined	1.99	43
	Calcined catalyst after 10 dehydrogenation cycles	1.85	

pretreatment conditions. The initial calcination temperature seems in this respect very important because of the low thermal stability of anchored polychromate species, which are readily convertable to Cr^{3+}. Summarizing, different surface species are observed on the surface of freshly prepared catalysts, their relative concentration mainly depending on the overall Cr loading, the alumina surface area, and the calcination treatment.

4.2. Active catalysts

Up to now, most reported characterization studies were done under conditions often far away from real catalytic conditions. This is mainly due to the fact that in situ capabilities have only recently become commercially available. As a consequence, only a limited number of in situ characterization studies are available in the literature. The most promising techniques in this respect are Raman spectroscopy and diffuse reflectance spectroscopy in the UV–Vis region, both techniques are suitable to monitor surface Cr-species during alkane dehydrogenations [32,33,36,37,57–59]. In situ Raman spectroscopy has been used to study the reduction process of surface Cr^{6+} species on a 5 wt% Cr/Al_2O_3 catalyst in the presence of *n*-butane. It was concluded that polychromate was more readily reducible than monochromate [32]. However, above 350°C the in situ Raman spectra became less informative due to coke formation. In situ DRS spectroscopy studies on 0.1–8.0 wt% Cr/Al_2O_3 catalysts show that surface Cr^{6+} species are reduced at high temperature in the presence of *n*-butane or isobutane to mainly pseudo-octahedral Cr^{3+} [57–59]. Thus, surface Cr^{3+} species are formed under reaction conditions at the expense of Cr^{6+}. The in situ DRS cell was coupled with a GC in order to monitor on line the activity and selectivity of the catalysts under study. It was found that there is a – more or less – quantitative

relationship between the amount of pseudo-octahedral Cr^{3+} formed by reduction and the dehydrogenation activity [58,59]. The nature of these surface Cr^{3+} species was further unraveled by infrared spectroscopy measurements of adsorbed probe molecules (CO/NO). De Rossi et al. [45] concluded that isolated Cr^{3+} sites with two coordinative vacancies are formed on 0.16–1.55 wt% Cr/Al_2O_3 catalysts in the presence of *n*-propane. In conclusion, Cr/Al_2O_3 catalysts contain coordinatively unsaturated Cr^{3+} species under reaction conditions.

4.3. Deactivated catalysts

The industrial cycling of Cr/Al_2O_3 catalysts under oxidizing and reducing conditions strongly affects their physicochemical structure, and ultimately leads to catalyst deactivation. First of all, the specific surface area of the catalyst decreases with increasing time-on-stream, increasing reaction temperature and increasing number of catalytic cycles [42]. In addition, the amount of surface Cr^{6+} decreased with increasing number of cycles. Hakuli et al. [42] observed that in a fresh 13 wt% Cr/Al_2O_3 catalyst 15% of the Cr was present as Cr^{6+}, whereas after 25 cycles, the amount of Cr^{6+} as a percentage of the total Cr content was only 12.7. Thus, part of the Cr^{6+} was irreversibly reduced to a lower oxidation state. The same authors also found an almost linear relationship between the initial dehydrogenation activity and the amount of Cr^{6+} as determined by XPS in the spent catalyst [42].

Similar results were obtained by De Rossi et al. [45]. These authors observed that the extent of reduction (as determined from the amount of H_2 or CO consumed by their Cr/Al_2O_3 catalysts) decreases with increasing number of reduction–dehydrogenation–recalcination cycles. This decrease has been attributed to an incomplete reoxidation of reduced Cr^{3+} species. In another systematic study, 0.1–0.8 wt% Cr/Al_2O_3

catalysts have been studied by combined DRS-EPR spectroscopies after successive reduction–reoxidation cycles [24]. Upon reduction with CO, surface Cr^{6+} species were mainly reduced to Cr^{3+}, which could only be partially reoxidized to Cr^{6+}. Thus, Cr^{3+} seems to be stabilized in/on the alumina surface. These phenomena can be explained by the incorporation of Cr^{3+} in the vacant octahedral sites of the spinel surface of alumina. Diffusion into these vacant Al^{3+} sites is facilitated by the similar ionic radii and charge of Cr^{3+} and Al^{3+}. Detailed ^{27}Al MAS NMR measurements suggest that Cr^{3+} occupies sites on alumina in the close vicinity of the octahedral Al^{3+} sites, continuing the spinel structure of the alumina [26]. This suggests that a type of Cr_2O_3–Al_2O_3 spinel is formed during catalytic cycling, which results in the deactivation of the catalyst. However, it is clear that more characterization work has to be done to fully understand this deactivation process.

5. Catalyst activity and selectivity

There is a general consensus in the literature that the activity pattern of Cr-based dehydrogenation catalysts is dependent on the overall Cr loading, the dehydrogenation temperature and the time-on-stream [6,7] The initial dehydrogenation activity increases, independently of the type of alkane, almost linearly with increasing Cr loading. However, at Cr loadings typically higher than 4–10 wt% Cr, the activity gain levels off or even decreases. Furthermore, the overall activity decreases with increasing time-on-stream and with an increasing number of regeneration–dehydrogenation cycles in cyclic operation. This deactivation is attributed to the increased formation of coke. It is also important to notice here that the overall coke formation increases with an increasing number of regeneration–dehydrogenation cycles. This implies that coke formation is not solely responsible for catalyst deactivation. A constant dehydrogenation activity over the total life-span of the catalyst can be achieved by gradually increasing the reaction temperature with increasing time-on-stream.

The selectivity pattern is also a function of the time-on-stream. In the beginning of the reaction, the selectivity towards alkenes is rather low, and CO and CO_2 are mainly formed. After this induction time, the

Table 4
Isobutene dehydrogenation results of a performance test run of the Ibn Zahr CATOFIN® Plant no. 2 in Saudi Arabia, which is considered as one of the largest dehydrogenation unit for MTBE production (after [55])

Test parameter or compound	Performance
Isobutane consumed (metric tons/h)	64
Isobutene produced (metric tons/h)	58
Conversion (%)	55
Selectivity (mol%)	93.6
Isobutene (wt%)	51.4
C_3 and lighter compounds (wt%)	0.1
Normal butane and butene (wt%)	1.8
Butadiene (wt%)	0.1
C_5 and heavier compounds (wt%)	0.1

alkene selectivity increases typically above 90%. Other detectable products are ligther alkanes/alkenes (e.g. methane), benzene, and toluene. As an example, the catalytic test run performances of one of the world's largest dehydrogenation plant for MTBE production with an isobutene production capacity of 452 000 metric tons per year, are given in Table 4 [55]. It is concluded that a selectivity towards isobutene of 93.6% can be obtained at a conversion of 55%, and that the fraction of lighter and heavier hydrocarbons is rather small. The selectivity remains stable, and can be maintained well into the middle of the catalyst-life, and only declines toward the end-of-run, which is typically after one or two years.

There is, however, no agreement about the effect of reducing agents on the initial dehydrogenation activity, and different authors have observed different effects. De Rossi et al. [45] reported that pre-reduction of the Cr/Al_2O_3 catalysts (0.04–2.55 wt% Cr) with carbon monoxide or hydrogen had no influence on the dehydrogenation of propane. In a study of the *n*-hexane aromatization activity of prereduced Cr/Al_2O_3 catalysts (10.5 wt% Cr), Grunert et al. [40,41] also found that the nature of the reducing agent (H_2, CH_4, *n*-hexane or CO) did not influence the activity. On the other hand, Gorriz et al. [37] observed slight differences in the dehydrogenation activity depending on the reducing agent (H_2, propane or CO). These authors concluded from a detailed analysis of the product distribution with a gas chromatograph, that the main differences occurred during the first 10 min on stream. Recently, Hakuli et al. [42] have monitored with FT-IR spectroscopy the very first

stages of the dehydrogenation of butane over Cr/Al_2O_3 catalysts (13 wt% Cr), and provided interesting data on the initial dehydrogenation activity on prereduced surfaces. The authors found that pre-reduction with methane or H_2 had no noticeable effect on the catalytic activity and selectivity. Clearly different results were obtained when the catalyst was reduced with carbon monoxide. The formation of cracking products (C_1–C_3) was increased during the first 60 s on stream and the initial selectivity for butenes was rather low. However, the selectivity for butenes increased with increasing time on stream, and within 2 min a selectivity pattern was observed comparable with that obtained with methane- and hydrogen-pre-reduced catalysts. The effect of the carbon monoxide pre-reduction depended on the reduction temperature, and below 400°C no effect on the catalytic activity and selectivity was observed. The negative effect of CO has been explained in terms of coke formation, and of a deeper reduction of supported chromium oxides with carbon monoxide than with *n*-butane, methane or H_2. Finally, it is important to stress here that industrially used CrO_x/Al_2O_3 catalysts are reduced prior to alkane dehydrogenation (after burning off the coke in the regeneration step). This suggests that reduction of a regenerated catalyst has a beneficial effect for the catalyst used on an industrial scale.

Although the addition of dopants has been considered to promote activity and/or selectivity, its beneficial role is not properly understood. Some authors even observed a decreasing activity upon the addition of dopants [6,7]. Recent work on isobutane dehydrogenation, however, showed that the effect of potassium strongly depends on both the Cr- and K-loading [39]. For a 7.7 wt% Cr/Al_2O_3 catalysts, an increase of dehydrogenation activity was observed at a K_2O loading of 0.8 wt%. On the other hand, the same authors observed that a catalyst containing only 5.3 wt% Cr showed a decrease in activity with increasing K_2O loading [39].

Summarizing, high alkane dehydrogenation activities and selectivities can be reached over Cr/Al_2O_3 catalysts by fine-tuning the operating conditions (reaction temperature, regeneration–dehydrogenation cycles, reactant flow rate, etc.) as well as the catalyst composition (chromium loading, addition of dopants, etc.).

6. Molecular structure–reactivity relationships

The reported characterization results, in combination with the catalytic results, allow a detailed discussion of the nature of the chromium active site for alkane dehydrogenation. The discussion will be focused on (a) the oxidation state, (b) the coordinative requirements, and (c) nuclearity of the active site in Cr/Al_2O_3 catalysts. On this basis, a catalytic mechanism for alkane dehydrogenation is proposed.

6.1. Oxidation state

The oxidation state of the active species has been the subject of debate and controversy for many years. According to several authors the active species in alkane dehydrogenation is Cr^{3+}, while other authors propose both Cr^{2+} and Cr^{3+}, or solely Cr^{2+} as the active species. These discrepancies in literature can be due to differences in catalyst pretreatment and preparation. It is also important to stress here that the catalyst has to reach a well-defined equilibrated surface composition. Nevertheless, the present literature data, more particularly the in situ characterization results, confirm the absence of oxidized surface chromium oxide species, i.e. Cr^{6+} and Cr^{5+}, and the presence of Cr^{3+} in an active Cr/Al_2O_3 catalyst. Furthermore, surface $Cr^{6+/5+}$ species seems to be the precursor for these active Cr^{3+} sites, at least at low Cr loadings. The reduction of the oxidized surface chromium oxide species is responsible for the rather low selectivities towards alkenes in the beginning of the dehydrogenation reaction.

6.2. Coordinative requirements

The catalytic data clearly show that the conversion towards alkenes does not linearly increase with increasing Cr loading for catalysts above monolayer coverage. Some authors have even reported a decrease in catalytic activity at such high Cr loadings. The characterization studies, on the other hand, reveal the presence of crystalline Cr_2O_3-clusters in such catalysts. This suggests that bulk Cr^{3+}-ions, with a perfect and stable octahedrally surrounding, are inactive for alkane dehydrogenations. Thus, surface Cr^{3+}-ions with an incomplete coordination have to be active. Such ions will try to re-establish the very stable

configuration of bulk Cr^{3+}-ions by capturing molecules, such as alkanes, from the gas phase. De Rossi et al. were able to show by infrared spectroscopy that two NO molecules could be adsorbed by a mononuclear surface Cr^{3+}-ion [45]. Thus, coordinatively unsaturated Cr^{3+}-ions are the active centers for alkane dehydrogenations.

6.3. Nuclearity

The almost linear relationship between dehydrogenation activity and Cr loading below monolayer coverage indicates that both isolated and clustered Cr^{3+}-centers can be active. Indeed, the spectroscopic data indicate that three types of Cr^{3+}-ions are present under reaction conditions below monolayer coverage:

1. Cr^{3+}-ions formed by reduction of surface $Cr^{6+/5+}$-ions.
2. Cr^{3+}-ions present as isolated centers stabilized on the alumina surface.
3. Small amorphous Cr^{3+}-clusters which are XRD-invisible.

However, with the present knowledge it is almost impossible to discriminate between the individual contributions of these Cr^{3+}-centers to the overall catalytic activity and selectivity. Nevertheless, there are indications that surface $Cr^{6+/5+}$-ions, forming the dispersed surface phase on the alumina and/or chromia (Cr_2O_3), are the precursors for the Cr^{3+} dehydrogenation centers. The following arguments can be put forward

1. Hakuli et al. [42] have demonstrated that the initial dehydrogenation activity is directly proportional to the initial amount of surface Cr^{6+};
2. Weckhuysen et al. [57–59] have shown by in situ DRS that there exists a semi-quantitative relationship between the catalytic activity and the amount of Cr^{3+} formed by reduction of Cr^{6+};
3. Surface $Cr^{6+/5+}$-species, which are the dominant species at low loadings, give rise to dehydrogenation activity, and the activity increases with increasing amount of Cr.

Thus, it is reasonable to assume that about 90% of the catalytic activity is related to dispersed phase, while the other co-existing phases are crucial for the con-
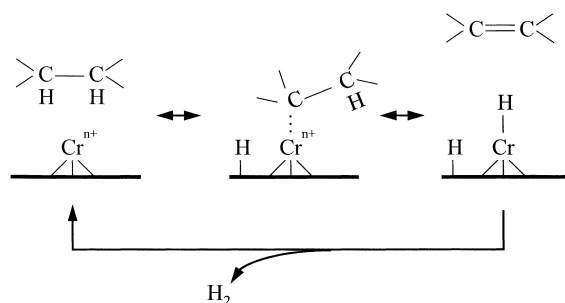

Fig. 1. Possible catalytic mechanism for alkane dehydrogenation over Cr/Al_2O_3 catalysts.

tinuous replenishment of the depleted surface phase during (prolonged) catalytic actions.

A possible catalytic mechanism for alkane dehydrogenation over Cr/Al_2O_3 catalysts is given in Fig. 1. It involves the adsorption of an alkane on a coordinatively unsaturated Cr^{3+}-center, which can be either isolated or clustered. In a second step, the C–H bond of the alkane is broken, and a OH–bond and a Cr–C bond are formed. In the final step, an alkene is formed, which is released from the surface, and the catalytic surface is regenerated by the formation of H_2.

7. Conclusions

The catalytic dehydrogenation of isobutane and propane over Cr/Al_2O_3 catalysts is an important process which is used worldwide in the chemical industries because it represents an inexpensive route to obtain high-purity alkenes from hydrocarbon feedstocks. These catalysts are composed of chromium oxides dispersed on a porous alumina support, and often contain a dopant such as potassium. The dehydrogenation activity almost linearly increases with increasing Cr loading up to monolayer coverage. At higher Cr loadings the activity gain levels off or even decreases. The present characterization results point towards the important role of both isolated and clustered coordinatively unsaturated Cr^{3+}-centers for the activation of alkanes. However, more characterization results have to be done under conditions close to catalytic conditions. This will ultimately lead to – more relevant – structure/composition–activity/selectivity relationships, and the development of an expert system for an industrial dehydrogenation reactor.

Acknowledgements

References

[1] B.M. Weckhuysen, I.E. Wachs, R.A. Schoonheydt, Chem. Rev. 96 (1996) 3327.
[2] S. Carra, L. Forni, Catal. Rev.-Sci. Eng. 5 (1971) 159.
[3] J.E. Germain, Catalytic Conversion of Hydrocarbons, Academic Press, London, 1969.
[4] F.E. Frey, W.F. Huppke, Ind. Eng. Chem. 25 (1933) 54.
[5] F.E. Frey, W.F. Huppke, US Pat. 2 098 959 (1937).
[6] C.P. Poole, D.S. Maciver, Adv. Catal. 17 (1967) 223.
[7] K.K. Kearby, in: P.H. Emmet (Ed.), Catalysis, Fundamental Principles, Chapter 10, vol. 3, Reinhold, New York, p. 453.
[8] Y. Okamoto, M. Fujh, T. Imanaka, S. Teranishi, Bull. Chem. Soc. Jpn. 49 (1967) 859.
[9] J. Masson, J.M. Bonnier, P.H. Duvigneaud, B. Delmon, J. Chem. Soc., Faraday Trans. 73 (1977) 1471.
[10] F.M. Ashmawy, J. Chem. Soc., Faraday Trans. 76 (1980) 2096.
[11] O.D. Sterligov, K.M. Gitis, K.I. Slovetskaya, E.S. Shapiro, A.M. Rubinstein, K.M. Minachev, in: B. Delmon, G.F. Froment (Eds.), Proceedings of the Second International Symposium on Catalyst Deactivation, 1980, p. 363.
[12] Ch. Marcilly, B. Delmon, J. Catal. 24 (1972) 336.
[13] M.I. Zaki, N.E. Fouad, J. Leyer, H. Knozinger, Appl. Catal. 21 (1986) 359.
[14] N.E. Fouad, H. Knozinger, M.I. Zaki, S.A.A. Mansour, Z. Phys. Chem. 171 (1991) 75.
[15] N.E. Fouad, H. Knozinger, M.I. Zaki, Z. Phys. Chem. 186 (1994) 231.
[16] F.D. Hardcastle, I.E. Wachs, J. Mol. Catal. 46 (1988) 173.
[17] D.S. Kim, J.M. Tatibouet, I.E. Wachs, J. Catal. 136 (1992) 209.
[18] M.A. Vuurman, D.J. Stufkens, A. Oskam, J.A. Moulijn, F. Kapteijn, J. Mol. Catal. 60 (1990) 83.
[19] M.A. Vuurman, I.E. Wachs, D.J. Stufkens, A. Oskam, J. Mol. Catal. 80 (1993) 209.
[20] M.A. Vuurman, F.D. Hardcastle, I.E. Wachs, J. Mol. Catal. 84 (1993) 193.
[21] M.A. Vuurman, I.E. Wachs, J. Phys. Chem. 96 (1992) 5008.
[22] D.S. Kim, I.E. Wachs, J. Catal. 142 (1993) 166.
[23] I.E. Wachs, G. Deo, M.A. Vuurman, H. Hu, D.S. Kim, J.M. Jehng, J. Mol. Catal. 82 (1993) 443.
[24] B.M. Weckhuysen, L.M. De Ridder, R.A. Schoonheydt, J. Phys. Chem. 97 (1993) 4756.
[25] B.M. Weckhuysen, A.A. Verberckmoes, A.L. Buttiens, R.A. Schoonheydt, J. Phys. Chem. 98 (1994) 579.
[26] B.M. Weckhuysen, L.M. De Ridder, P.J. Grobet, R.A. Schoonheydt, J. Phys. Chem. 99 (1995) 320.
[27] B.M. Weckhuysen, I.E. Wachs, R.A. Schoonheydt, Stud. Surf. Sci. Catal. 91 (1995) 151.
[28] J.M. Jehng, I.E. Wachs, B.M. Weckhuysen, R.A. Schoonheydt, J. Chem. Soc., Faraday Trans. 91 (1995) 953.
[29] B.M. Weckhuysen, R.A. Schoonheydt, J.M. Jehng, I.E. Wachs, S.J. Cho, R. Ryoo, S. Kijlstra, E. Poels, J. Chem. Soc., Faraday Trans. 91 (1995) 3245.
[30] B.M. Weckhuysen, R.A. Schoonheydt, F.A. Mabbs, D. Collison, J. Chem. Soc., Faraday Trans. 92 (1996) 2431.
[31] B.M. Weckhuysen, I.E. Wachs, J. Chem. Soc., Faraday Trans. 92 (1996) 1969.
[32] B.M. Weckhuysen, I.E. Wachs, J. Phys. Chem. 100 (1996) 14437.
[33] B.M. Weckhuysen, I.E. Wachs, J. Phys. Chem. B 101 (1997) 2793.
[34] B.M. Weckhuysen, B. Schoofs, R.A. Schoonheydt, J. Chem. Soc., Faraday Trans. 93 (1997) 2117.
[35] B.M. Weckhuysen, A.A. Verberckmoes, A. De Baets, R.A. Schoonheydt, J. Catal. 166 (1997) 160.
[36] A. Bensalem, B.M. Weckhuysen, R.A. Schoonheydt, J. Phys. Chem. B 101 (1997) 2824.
[37] O.F. Gorriz, V. Cortes Corberan, J.L.G. Fierro, Ind. Eng. Chem. Res. 31 (1992) 2670.
[38] H.J. Lugo, J.H. Lunsford, J. Catal. 91 (1985) 155.
[39] F. Cavani, M. Koutyrev, F. Trifiro, A. Bartolini, D. Ghisletti, R. Lezzi, A. Santucci, G. Del Piero, J. Catal. 158 (1996) 236.
[40] W. Grunert, W. Saffert, R. Feldhaus, K. Anders, J. Catal. 99 (1986) 149.
[41] W. Grunert, E.S. Shpiro, R. Feldhaus, K. Anders, G.V. Antoshin, K.M. Minachev, J. Catal. 100 (1986) 138.
[42] A. Hakuli, A. Kytokivi, A.O. Krause, T. Suntola, J. Catal. 161 (1996) 393.
[43] A. Kytokovi, J.P. Jacobs, A. Hakuli, J. Merilainen, H.H. Brongersma, J. Catal. 162 (1996) 190.
[44] S. De Rossi, O. Ferraris, S. Fremiotti, E. Garrone, G. Ghiotti, M.C. Campa, V. Indovina, J. Catal. 148 (1994) 36.
[45] S. De Rossi, G. Ferraris, S. Fremiotti, A. Cimino, V. Indovina, Appl. Catal. A 81 (1992) 113.
[46] D. Cordishi, V. Indovina, M. Occhiuzzi, Appl. Surf. Sci. 55 (1992) 233.
[47] A. Rahman, M.H. Mohamed, M. Ahmed, A.M. Aitani, Appl. Catal. A 121 (1995) 203.
[48] S. Kohler, M. Reiche, C. Frobel, M. Baerns, Stud. Surf. Sci. Catal. 91 (1995) 1009.
[49] S.J. Scierka, M. Houalla, A. Proctor, D.M. Hercules, J. Phys. Chem. 99 (1995) 1537.
[50] R. Kozlowski, Bull. Polish Acad. Sci. Chem. 35 (1986) 365.
[51] F. Cavani, F. Trifiro, Catal. Today 34 (1997) 269.
[52] D. Sanfilippo, F. Buonomo, G. Fusco, M. Lupieri, I. Miracca, Chem. Eng. Sci. 47 (1992) 2313.
[53] S.J. Penny, R.G. Clark, D.C. Spence, Can. Chem. News 36 (1984) 19.
[54] K.L. Rock, R.O. Dunn, Energ. Prog. 8 (1988) 191.

[55] A.A. Al-Ghamdi, A.M. Al-Bassam, J.L. Draus, Annual Meeting of the National Petroleum Refiners Association, March 20–22 1994, San Antonio, TX, USA, Paper AM-94-28.

[56] R.G. Craig, J.M. Duffallo, Chem. Eng. Prog. 75 (1979) 62.

[57] B.M. Weckhuysen, A. Bensalem, R.A. Schoonheydt, Book of Abstracts of the 15th Meeting of the North American Catalysis Society, 18–22 May 1997, Chicago, p. 115.

[58] B.M. Weckhuysen, A. Bensalem, R.A. Schoonheydt, J. Chem. Soc., Faraday Trans. 94 (1998) 2011.

[59] B.M. Weckhuysen, A.A. Verberckmoes, J. Debaere, K. Ooms, I. Langhans, R.A. Schoonheydt, submitted.