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The nature of active chromium species in Cr-catalysts for dehydrogenation of propane: New insights by a comprehensive spectroscopic study

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ABSTRACT

Dehydrogenation of propane (DHP) was studied over a series of *x*Cr–SBA-15 and *x*Cr–Al_2O_3 catalysts, prepared by incipient wetness impregnation, to gain a better understanding of the nature and distribution of Cr species and their catalytic function. To this end, the catalysts were characterized by N_2-physisorption, X-ray diffraction (XRD), UV-Raman spectroscopy, scanning transmission electron microscopy–energy dispersive X-ray spectroscopy (STEM–EDXS) and X-ray absorption spectroscopy (XANES and EXAFS). All these characterization techniques indicate that, at $\leqslant 1$ wt% Cr, SBA-15 contains exclusively uniform distribution of chromium as isolated Cr(VI) species in tetrahedral (T_d) coordination, whilst on γ-Al_2O_3 a fraction of oligomers (including dimers) is present along with isolated species. At $\geqslant 5$ wt% Cr, SBA-15 is dominated by crystalline α-Cr_2O_3 particles, besides a fraction of isolated Cr(VI) species in T_d coordination. Remarkably, γ-Al_2O_3 contains mainly oligomers with different degrees of nuclearity and a fraction of isolated species but no Cr_2O_3 particles. Among *x*Cr–SBA-15 catalysts, those containing exclusively isolated Cr species (i.e., $\leqslant 1$ wt% Cr) exhibit higher activity and selectivity with respect to per mole of Cr than the catalyst dominated by crystalline α-Cr_2O_3 particles ($\geqslant 5$ wt% Cr). The intrinsic activity of these isolated Cr species is higher than those observed on γ-Al_2O_3 ($\leqslant 1$ wt% Cr). Interestingly, among *x*Cr–Al_2O_3, the catalysts dominated by oligomeric species show the highest activity, indicating the important role of the species in the reaction. In situ XAS studies evidence that active Cr sites are apparently generated on-site during the reaction and that Cr is typically in (III) oxidation state. Based on ex situ and in situ characterization results and catalytic data, it appears that the activity of the Cr species is different in *x*Cr–SBA-15 and *x*Cr–Al_2O_3. For *x*Cr–SBA-15, isolated Cr(III) sites with coordination number greater than four are more active, selective and stable than Cr sites on the surface of crystalline Cr_2O_3. In contrast, for *x*Cr–Al_2O_3, oligomeric Cr species are more active and selective than the isolated Cr sites.

1. Introduction

Dehydrogenation of propane (DHP) is one of the on-purpose propylene production technologies that has received much attention in the recent past [1,2] due to it's potential to make-up the shortfall of propylene supply left by conventional crackers (e.g., FCC) [3–5]. Propylene is an important building block in a myriad of (petro)chemical applications, for instance in the production of polypropylene [6,7]. Typically, the CrO_x–Al_2O_3 catalyst system is used for industrial processes, for example in the Catofin process (ABB Lummus) that runs at cyclic operation (reaction and regeneration) at ∼850 K [8]. However, major challenges associated with this catalytic system are cracking and coking which influence the product selectivity and catalyst stability, respectively. Thus, the deactivated catalyst must frequently be regenerated without losing dehydrogenation activity, selectivity to propylene and catalyst stability, which makes the process not only complex but also expensive. Therefore, considerable research has been done to gain a deep fundamental knowledge on the structure–reactivity relationships of Cr catalysts in dehydrogenation of alkanes by various characterization techniques [9–18] and to improve catalytic performance.

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Alternatively, oxidative dehydrogenation of propane (ODHP) was also extensively studied to overcome the challenges associated with DHP however without much success in terms of commercial viability [19]. Nonetheless, CO_2 was interestingly reported as an alternative to O_2 or N_2O as an oxidizing agent for ODHP, in which again Cr based catalysts were found to be more active than other metal catalysts [16,20–22]. Especially, Cr supported on silicon (either on SiO_2 or on siliceous mesoporous materials like SBA-15 and MCM-41) have shown higher activity than the regular catalysts, for example on Al_2O_3 [20,21]. Thus, these materials have recently got attention to understand their better catalytic performance either in ODHP or in DHP as compared to other catalysts [15,16,20].

As evidenced from various studies, the distribution of Cr species is strongly dependent on the nature of the support, Cr content and method of activation [23–30]. A variety of Cr species (isolated, dimers, trimers, polymeric species with different nuclearity and large Cr_2O_3 clusters) with different oxidation and coordination states and with different redox properties coexist in the same catalyst. It is known that DHP activity increases with Cr loading and a typical industrial Cr catalyst contains ∼13 wt% Cr at which level heterogeneous distribution of Cr species is virtually unavoidable [23–30]. Thus, it has been a major challenge to gain definitive information on the nature of active Cr sites. As a result, the nature of active Cr species in Cr catalysts during DHP remains elusive and is still a subject of debate [9–18]. For instance, studies on Cr–ZrO_2 catalysts with a Cr content of 0.05 to 0.8 wt% showed that mononuclear Cr(III) species are the active sites [31]. The same conclusion was also reached after considerable studies on Cr–Al_2O_3 and other Cr catalysts [13,32–34]. In contrast, it was concluded that coordinatively unsaturated clustered Cr(III) and/or Cr(II) sites play an important role in the activation of alkanes while crystalline α-Cr_2O_3 are rather inert [9,10,12]. In a different study, La doped Cr–Al_2O_3 and Cr–ZrO_2 catalysts monitored during DHP simultaneously by in situ—EPR and—UV/vis coupled with online GC showed that in both the catalysts the oxidation state of Cr is not higher than (III) however, coordination state of Cr species was not discussed [11]. The structure of Cr species in differently prepared Cr–MCM-41 (Cr content varied between 0.35 and 1.7 wt%) studied by in situ XAS (XANES and EXAFS) showed that aggregated Cr(III) are the active sites for DHP [15,16], which is similar to that concluded on Cr–Al_2O_3 [12]. On the other hand, a study on the oxidative dehydrogenation of ethane (ODHE) with CO_2 over Cr/H-ZSM-5 concludes that a redox cycle between Cr^{+6} and Cr^{+3} is important for a high dehydrogenation rate [22].

In the present work, a series of Cr catalysts with varying Cr content (0.5–10 wt%) was prepared aiming to create a well defined Cr site distribution in the catalysts and thereby to derive the catalytic function of each specific Cr species. To this end, SBA-15 and γ-Al_2O_3 supports were employed. On high surface area mesoporous SBA-15, it was expected that highly dispersed and completely accessible isolated Cr species can be created. The large pores and the weak acidity of SBA-15 should facilitate adequate transport of gaseous reactants and products to and from the active Cr species. This in turn should lead to better catalytic performance and stability than the regular catalysts [20]. The structure and catalytic properties of these Cr species are compared with those supported on γ-Al_2O_3, which is typically used in industrial DHP processes and is also known to contain well defined Cr site distribution depending on the Cr content [26,27,30]. This will allow us to investigate the influence of the molecular structure, which is dependent on the nature of the support as evident from literature, of Cr species on DHP with identical Cr content and in some cases (at $\leqslant$1 wt% Cr) with similar Cr distribution. The nature and distribution of Cr species in the catalysts was thoroughly investigated by various characterization techniques that are complementary to each other. The behavior of Cr species during DHP was monitored by in situ—X-ray absorption spectroscopy (XAS) which is a powerful tool to investigate the oxidation and coordination state of Cr species, however under suitable experimental conditions [36]. Steady-state catalytic activity tests were performed isothermally at 853 K. The correlation of steady-state activity data and characterization results derived from ex situ and in situ spectroscopic studies enabled us to gain new insights into the nature of active Cr species involved in DHP.

Table 1
Chemical composition and textural properties of the catalysts.

Catalyst	Cr[a] (wt%)	V_{total}[b] ($cm^3\ g^{-1}$)	S_{BET}[c] ($m^2\ g^{-1}$)	Pore size[b] (nm)
0.5Cr–SBA-15	0.5	1.11	535	7.7
1Cr–SBA-15	1.0	1.13	532	7.7
5Cr–SBA-15	5.0	1.03	485	7.7
10Cr–SBA-15	10	0.95	445	7.8
0.5Cr–Al_2O_3	0.5	0.39	174	7.7
1Cr–Al_2O_3	1.0	0.35	152	7.1
5Cr–Al_2O_3	5.0	0.34	150	5.7/7.65
10Cr–Al_2O_3	10	0.28	140	5.5

[a] Nominal loading.
[b] BJH method.
[c] BET method.

2. Experimental

2.1. Preparation of catalysts

The parent siliceous SBA-15 was prepared in our laboratory according to the recipe reported elsewhere [37–39]. Briefly, a gel prepared from Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, BASF), the template, 2 M HCl and tetraethylorthosilicate (TEOS, Alfa Aesar, 99%), silicon source, was stirred at 313 K for 24 h. The gel was then transferred into a Teflon bottle and aged in an oven at 373 K for 48 h. The resulting white solid was filtered, washed thoroughly with double deionized water and dried at room temperature for 24 h. The final product was then calcined in flowing air at 823 K for 6 h to remove the template and thereby to produce mesoporous SBA-15. The γ-Al_2O_3 (Puralox from Sasol) was calcined at 773 K for 6 h prior to using it as a catalyst support.

A series of *x*Cr–SBA-15 and *x*Cr–Al_2O_3 catalysts (*x* in the catalyst label represents the nominal Cr content, wt%) were prepared by incipient wetness impregnation. Impregnation solutions were prepared by dissolving appropriate amounts of $Cr(NO_3)_2\ 9H_2O$ (Merck, 98–100%) in double deionized water. The resulting solution was added dropwise to the supports, which have been pre-treated in an oven at 373 K for 16 h. After impregnation, the samples were dried at 383 K for 10 h and subsequently calcined at 823 K for 5 h, with a heating rate of 2 $K\,min^{-1}$. Physical appearances of the catalysts are as follows: 0.5Cr–SBA-15 and 1Cr–SBA-15 are pale yellow while 5Cr–SBA-15 and 10Cr–SBA-15 are dark green which is characteristic of the reference sample α-Cr_2O_3. Interestingly, none of the catalysts in the series of *x*Cr–Al_2O_3 show the latter color and 0.5Cr–Al_2O_3 is the only one that is pale yellow. 1Cr–Al_2O_3 is pale yellow with a shade of pale green. 5Cr–Al_2O_3 and 10Cr–Al_2O_3 are light and dark brownish in color, respectively. The varying colours of the catalysts indicate that Cr speciation is different in them [22]. The composition and textural properties of the catalysts are presented in Table 1.

2.2. Characterization techniques

Nitrogen adsorption and desorption isotherms at 77 K were obtained on a Micromeritics TriStar 3000 instrument. Prior to the experiments, the samples were evacuated at 473 K for 12 h. The total surface area of the samples was determined by the Brunauer–Emmett–Teller (BET) method. The pore size distributions were