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Reduction and Aromatization Activity of Chromia–Alumina Catalysts

I. Reduction and Break-in Behavior of a Potassium-Promoted Chromia–Alumina Catalyst

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The reduction of a potassium-promoted Cr_2O_3/Al_2O_3 catalyst and the transient behavior of its aromatization activity were studied in gradientless and pulse flow reactors and by temperature-programmed reduction. Above 773 K, the oxidized catalyst is reduced in two stages. In the first, very rapid stage, essentially the transition of Cr^{6+} to Cr^{3+}, a considerable retention of hydrogen and carbon from the reducing agent (H_2, CH_4, or *n*-hexane) is observed. Aromatization activity is fully developed after this stage. Delayed recoverage of activity after this rapid reduction step as found in flow and gradientless reactors is due to the poisoning action of H_2O released in the second, slow stage of catalyst reduction, which leads to (a) species not determining aromatization activity.

INTRODUCTION

Cr_2O_3/Al_2O_3 catalysts have been extensively investigated because of their activity in alkane dehydrogenation, dehydrocyclization (*1*), and in oxidation reactions. While interest in these traditional applications has decreased recently, chromium has been successfully used to improve the properties of reforming catalysts (*2*). The development of catalytic systems dispensing with noble metals may direct new attention to the Cr_2O_3/Al_2O_3 system.

The origin of the aromatization (and dehydrogenation) activity of Cr_2O_3/Al_2O_3 catalysts is disputed in the literature. It was attributed to Cr^{2+} ions by Sloveckaya *et al.* (*3*), who demonstrated the existence of these ions by their ability to reduce H_2O (*4*) and Fe^{3+} ions (*5*). These arguments are confirmed by the conclusions of van Reijen *et al.* (*6*), Shelef *et al.* (*7*), and Ashmawy (*8*) on the basis of reduction stoichiometry, ESR investigations (decrease of signals typical of Cr^{3+}) and the analogy to the Cr/SiO_2 system. The reducibility of Cr_2O_3/Al_2O_3 catalysts was found to increase with decreasing chromia content (*5*), with typical conversions of 10–25% at concentrations of 5–1 wt% Cr_2O_3 after 20–30 min reduction at 833 K in H_2 (*3, 5*).

On the other hand, the basic aromatization activity was ascribed to coordinatively unsaturated Cr^{3+} ions by Kazansky (*9*), Bremer *et al.* (*10*), Marcilly and Delmon (*11*), and Segawa *et al.* (*12*), who conceded only transient contributions of other ions (Cr^{2+} (*11*), Cr^{5+} (*12*)).

Some elucidation of the problem might be expected by an investigation of the phenomena observed when Cr_2O_3/Al_2O_3 catalysts, previously regenerated in air, are contacted with alkanes. Thus, in a flow reactor at 805 K, the activity of a catalyst containing 15 wt% Cr_2O_3 and 4 wt% K_2O was recovered in a period of 30–40 min following the violent reduction of the Cr^{6+} in the oxidized catalyst by the alkane (*n*-heptane) (*13, 1*). This "activity formation," essentially a break-in period, the length of which depends on temperature, feed rate, the chromia and alkali content of the cata-

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lyst, was ascribed to the desorption of water formed in the rapid reduction process and poisoning the active sites.

Observations from experiments in pulsed systems range from the complete absence of break-in behavior (*14*) to the existence of such phenomena even in the absence of Cr^{6+} (*15, 16*). Some of the contradictions seem to be due to the lacking or disputable material balance of the reactant pulses and, partially, to large pulse sizes.

In this paper, the dispute on the origin of the aromatization activity of chromia/alumina catalysts is discussed in the light of new experimental material including a reinvestigation of break-in phenomena (Part I) and an XPS investigation of the reduction of these catalysts (Part II).

EXPERIMENTAL

1. Materials. A commercial catalyst manufactured by the VEB Leuna-Werke was used in the investigation of break-in phenomena (20 wt% Cr_2O_3, 4 wt% K_2O on γ-Al_2O_3 containing 2–3% SiO_2 (*17*), "Cr20K4"). It is prepared by simultaneous impregnation of 3-mm spherical pellets with chromic anhydride and $K_2Cr_2O_7$, and was applied in its original form in the gradientless reactor, and in a fraction of 0.3–0.6 mm in the pulse reactor and in TPR. The BET surface of the catalyst was 165 m^2/g, being considerably lower than that of the support (222 m^2/g), probably due to micropore blocking by chromia (*10*). The catalyst was employed after stabilization in two reaction/regeneration cycles.

TPR experiments were also performed on catalysts containing 2.3 and 7.8 wt%, Cr_2O_3 on γ-Al_2O_3 (S_{BET} = 262 and 258 m^2/g, resp.), produced by impregnation of γ-Al_2O_3 with chromic anhydride ("Cr2.3, Cr7.8").

n-Hexane was supplied by VEB Synthesewerk Schwarzheide and contained $\approx$0.8 wt% isohexanes and $\approx$0.5 wt% methylcyclopentane, it was dried over Zeosorb 4A molecular sieve (VEB CK Bitterfeld).

2. Gradientless reactor. A gradientless reactor with internal recyclization and directed flow through the catalyst bed was employed. The reactor described in more detail in (*18*) was designed to minimize the internal free volume at the maximum recyclization ratio in view of possible blank reactions and the high reaction enthalpy of the *n*-hexane aromatization ($\Delta H_R = +267$ kJ/mole). A radial impeller with a maximum of 18,000 rpm was used as a mixing device, the internal surfaces (chromium–nickel steel) were deactivated by an aluminum treatment.

The break-in behavior was investigated at 823 K by charging the catalyst previously oxidized in air at 823 K for 2 h with 0.3–1.5 $g \cdot g^{-1} h^{-1}$ *n*-hexane. Samples of the effluent withdrawn with closable sampling columns (*19*) were injected for hydrocarbon analysis on a 9.2-m dinonylphthalate-packed column with double detector (intermediate absorption of olefines) (*20*). The H_2 content of the effluent was evaluated by balance calculations.

In reduction experiments with H_2 (50% in N_2), water was trapped with Zeosorb 4A and determined gravimetrically. Correction was made for the H_2O desorption from the carrier. A rough estimate of unreacted H_2 was given by a catharometer. CO_2, as a product of reduction by CO, was recorded by an Infralyt CO_2 analyzer (VEB Junkalor Dessau).

3. Temperature-programmed reduction (TPR). TPR was performed in a conventional flow system provided with facilities for moistening the flowing medium (5% H_2 in N_2), which established H_2O equilibrium pressure at ambient temperature, and for trapping H_2O between the reactor and the detector. The samples were heated at 30 K/min from 295 to 933 K where runs were finished with an isothermal period. H_2 consumption and evolution were measured with a catharometer.

A H_2 consumption of the empty quartz reactor was observed when the reactor had been heated in air previously. This blank effect probably due to surface silane formation (*21*) was avoided by performing oxidation of the catalysts (923 K, 2 h) outside the reactor.

H_2 and inert gases were passed over MnO/Al_2O_3 for deoxygenation and dried over $Mg(ClO_4)_2$.

4. Pulsed microreactor. The pulsed microreactor scheme employed allows alternating analyses of the hydrocarbon composition and of the C and H yield of the product pulse (Fig. 1). Product pulses may be trapped in closable sampling traps (*23*), from which they are injected on a 10-m SE-30 packed column (6 K/min, starting at 303 K) or on a 90-m UCON glass capillary column at 303 K. The H_2 evolved may be detected by the catharometer.

Alternately, product pulses are totally oxidized by CuO (973 K) and subsequently reduced by iron cuttings (873 K). In this case, the resulting mixture of CO_2 and H_2 is analyzed on the basis of nondispersive IR photometry (Infralyt CO_2 analyzer) (*22*) and, after absorption of CO_2 in natron asbestos, catharometrically. This method, which is calibrated with a nonreacted reactant pulse, supplies reliable analyses of the absolute quantities of C and H leaving the microreactor (standard deviation $\pm 3\%_{\mathrm{rel}}$ at pulse sizes of ≈ 3 μmole *n*-hexane). Analyses of free CO_2 in the product pulses (and, analogously, tests on the presence of CO) are performed with the corresponding Infralyt analyzers, bypassing the sampling trap.

Gas purification in this system (Ne, H_2) was similar to that employed in TPR. *n*-Hexane for the pulses was evaporated into flowing Ne at 285 K, the pulse quantities were corrected for slight temperature deviations by vapour pressure calculations. The results reported for each reducing agent were obtained from 1 to 3 experiments with alternating pulse analysis, parallelled by at least two experiments without the evaluation of C and H yields (0.6 g catalyst, previously oxidized in air at 823 K for 90 min, sampling loop 0.7 ml, temperature 773 K, carrier gas velocity 6 liters/h). In some cases, the temperature rise in the catalyst bed was measured with a 0.5-mm steel jacket NiCr–Ni thermocouple.

RESULTS

1. Gradientless reactor. The process observed in the gradientless reactor when the oxidized catalyst was charged with *n*-hexane resembled the phenomena reported in the literature. After an initial exothermic phase, with a temperature rise in the cata-

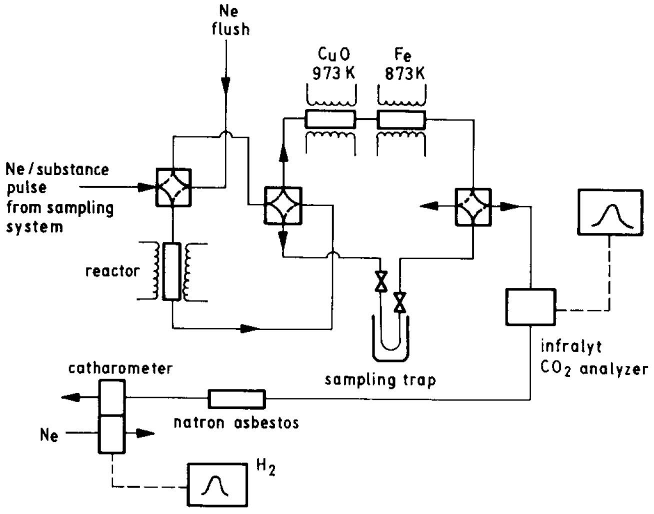

FIG. 1. Pulsed microreactor scheme.

lyst bed of 30–40 K despite recyclization ratios of 100–500, the aromatization activity was recovered slowly, starting with a low benzene content in the effluent hydrocarbon (Fig. 2). Irrespective of the feed rate, about 0.6 ml liquid *n*-hexane/g catalyst was consumed for attaining constant activity, resulting in break-in periods of 15–80 min for the applied feed rates.

As this observation seems to confirm the role of water desorption in the development of aromatization activity an interruption of the *n*-hexane feed by flushing intervals and a prereduction of the catalyst by other reducing agents (H_2, CH_4; 15 min, 823 K) would be expected to result in activity steps and a shortening of the transient period, resp. However, at variance with (*1*, *13*), none of these procedures affected the transient behavior of aromatization activity as demonstrated in Fig. 2, in which a slight deactivation between run 1 and 2 concerning overall activity should be neglected.

It was tested, therefore, if the delayed appearance of aromatization activity is due to a reduction process in which the catalytic poison H_2O is formed. Indeed, the reduction of Cr20K4 in hydrogen (Fig. 3) beginning with a violent initial phase passed over into a slow reaction at a permanently decreasing rate, the H_2O production of which could be unambiguously distinguished from water desorption from the carrier even after 5.5 h (see insert in Fig. 3). In the first phase of reduction (50 mmole H_2), the conversion of H_2 was nearly complete, while H_2O production accounted only for 40–45% of the H_2 consumed, the rest being obviously retained by the catalyst. The value of 0.34 mole H_2O/mole Cr_2O_3, roughly characterizing the water production of the rapid phase, corresponds therefore to a consumption of 1.6 g equiv. H_2/mole Cr_2O_3. Unfortunately, data about H retention are not yet available for the slow reduction step. Neglecting this retention, the overall H_2 consumption after 360 min would be estimated to be 1.90 g equiv./mole Cr_2O_3.

It should be noted that the slow reduction proceeds at a considerable H_2O partial pressure. The water content of the effluent

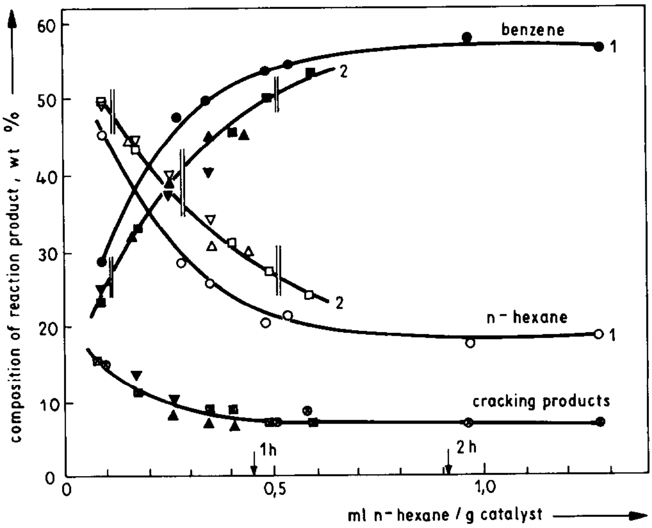

FIG. 2. Break-in behavior of aromatization activity of the Cr20K4 catalyst in a gradientless reactor. T = 823 K, m_{cat} = 56 g, b = 0.3 g · g^{-1} · h^{-1} *n*-hexane. Full symbols—benzene, open symbols—*n*-hexane, crossed symbols—cracking products; (○) undisturbed break-in process; (□) break-in process interrupted (||) by 40-min N_2 flushes (20 liters/h). (△) Prereduction with H_2, 15 min (20 liters/h) (▽) prereduction with CH_4, 15 min (20 liters/h).

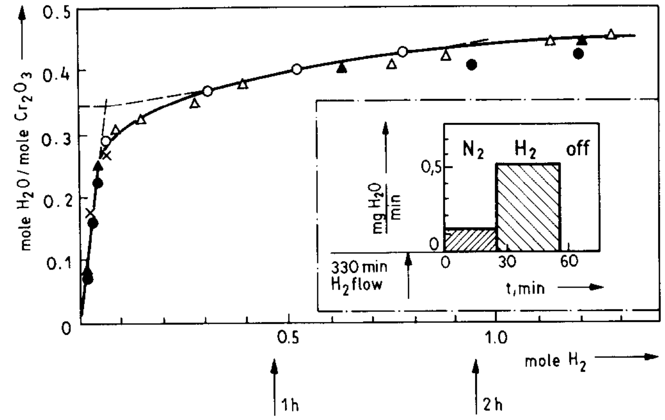

FIG. 3. Reduction of the Cr20K4 catalyst in a gradientless reactor (50% H_2 in N_2, 20 liters/h, m_{cat} = 56 g). Insert: rate of H_2O release from the catalyst after 330 min reduction in H_2/N_2. First period—H_2O desorption in carrier gas N_2, second period—reduction and desorption in the H_2/N_2 flow.

was estimated to be 0.35 vol% after 2 h reduction time.

Similar results were obtained with CO as a reducing agent, where CO_2 was still detected after 240 min. The reduction rate in the slow stage was higher under these dry conditions, which is exemplified by reduction experiments on a catalyst that had been previously charged with *n*-hexane for 50 min (823 K, $m_{cat} = 56$ g, 1.5 g · g^{-1} · h^{-1} *n*-hexane, 25 min with constant activity). After flushing the hydrocarbons from the reactor (20 liters/h N_2, 30 min) the conversion of H_2 (50% in N_2, 20 liters/h) and CO (20% in N_2, 25 liters/h) was 1.0–0.8% and 5–3%, resp., at 823 K.

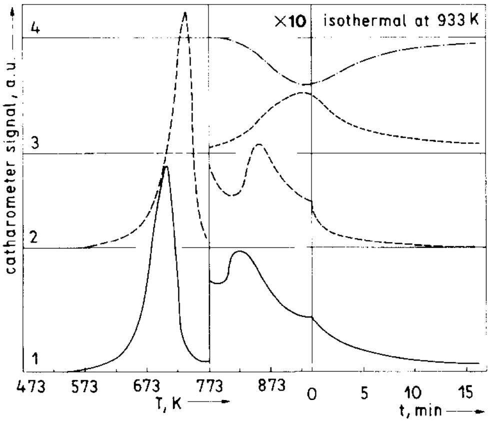

FIG. 4. Temperature-programmed reduction of Cr7.8 (stabilized). (1) TPR in dry H_2/N_2 ($x_{H_2} = 0.05$). (2) TPR in moistened H_2/N_2 ($x_{H_2O} \approx 0.02$). (3) TPR in dry H_2/N_2, subsequent to run 2 (sample cooled in moistened H_2/N_2). (4) Temperature-programmed desorption of H_2, subsequent to run 3 (sample cooled in dry H_2/N_2).

2. Temperature-programmed reduction. TPR of the Cr7.8 catalyst is reported in Fig. 4 and Table 1. Curve 1 representing reduction in dry H_2/N_2 reveals two stages of hydrogen consumption obviously corresponding to the two phases observed in the gradientless reactor. Both stages proceeded in a moist H_2/N_2 mixture, too (run 2), with the maximum of the first stage shifted by ≈35 K and a decreased rate of hydrogen consumption in the second stage, which was, however, not completely suppressed

TABLE 1

H_2 Consumption of Stabilized Cr7.8 (Fig. 4)

Run	Procedure	T_{min}[a] (K)	mole H_2/mole Cr_2O_3	
			$T \leq T_{min}$	$T > T_{min}$
1	H_2/N_2, dry	730	1.18	0.24
2	H_2/N_2, moist	808	1.23	0.11
3	Cooled in medium of run 2, heated in dry H_2/N_2	—	—	0.07
4	Cooled in dry H_2/N_2, heated in N_2	—	—	0.08

[a] Temperature of minimum between low- and high-temperature peaks (cf. Fig. 4).

by a water content of ~2 vol% in the flowing gas. When the catalyst was rapidly cooled down in this medium, no H_2 evolution was observed. A subsequent temperature sweep in dry H_2/N_2 yielded an additional H_2 consumption (run 3). The temperature-programmed desorption of chemisorbed hydrogen is presented in curve 4, which was recorded subsequent to run 3 after cooling in dry H_2/N_2.

The quantity of chemisorbed hydrogen is nearly equal to the H_2 consumption of run 3, giving rise to the suspicion that the latter might be due to an activated chemisorption suppressed in run 2 by the H_2O present, and that we are dealing with chemisorption rather than with reduction phenomena as suggested in (*24*). However, after the desorption of hydrogen (run 4) the catalyst was able to liberate H_2 from pulses of H_2O in N_2 (≈2 vol%): at a temperature of 923 K, 0.12 mole H_2/mole Cr_2O_3 was released from 12 pulses, with gradually declining H_2 yield. No H_2 was evolved when H_2O pulses were applied at 773 K after the same reduction and desorption procedure.

Conversions of dry reduction are reported in Table 2 for catalysts with different chromia contents. Though there is some uncertainty about the contribution of chemisorption and the separation between the rapid and the slow stage by the signal minimum appears to be somewhat arbitrary, general trends should not have been obscured. Slow stage conversion decreases with growing chromia content, paralleled by a decline of rapid stage conversion, which reflects the restriction of chromia oxidation to the surface of crystallites (*10*).

TABLE 2

TPR of Cr_2O_3/Al_2O_3 Catalysts (dry H_2/N_2)

Catalyst	mole H_2/mole Cr_2O_3	
	$T \leq T_{min}$[a]	$T > T_{min}$
Cr2.3	1.59	0.75
Cr2.3 unstabilized[b]	2.50	1.05
Cr7.8	1.18	0.24
Cr7.8 unstabilized[b]	2.40	0.40
Cr20K4	0.67	0.065

[a] Temperature of minimum between low- and high-temperature peaks (≈800 K).

[b] First reduction of catalyst after preparation.

Consequently, rapid stage conversion is higher in the unstabilized samples, which were used after impregnation and calcination (923 K, 2 h). It should be noted that these samples exhibit an increased slow stage conversion as well.

3. *Pulse experiments.* The pulse reduction of the oxidized Cr20K4 catalyst differs greatly from the process observed in the gradientless reactor. The results are summarized in Fig. 5, which presents yields of benzene, *n*-hexane, referred to reactant hexane, yields of H_2, CO_2, C, and H, referred to C and H in reactant hexane, and the temperature rise in the catalyst bed. Hexenes and hexadienes, which are intermediate products of the aromatization (*1*), and cracking products are omitted (maximal yields 2 and 3.5%, resp.). Peaks that could be ascribed to oxygen-containing components were not detected. The right-hand diagrams show the development of aromatization activity (measured with *n*-hexane pulses) when the catalyst was charged with a flowing *n*-hexane/Ne mixture ($x_{hexane} \approx 0.12$) at 773 K for the time shown on the abscissa subsequent to pulse reduction. The coke content after 8 min of reaction under these highly H_2 deficient conditions was ≈1 wt% of the catalyst.

The reduction of the catalyst by *n*-hexane pulses (Fig. 5a) is characterized by the fact that neither H_2O nor CO were formed and that all hydrogen and about 40% of the carbon was retained by the catalyst as long as a temperature rise could be detected. (This was similar in the reduction with CH_4 pulses not shown here, where H left the catalyst only in unreacted CH_4 and part of the C was retained, too). At the end of the reduction, the CO_2 yield declined and increasing amounts of hydrocarbons were formed, which contained a high fraction of benzene (and cracking products) initially.

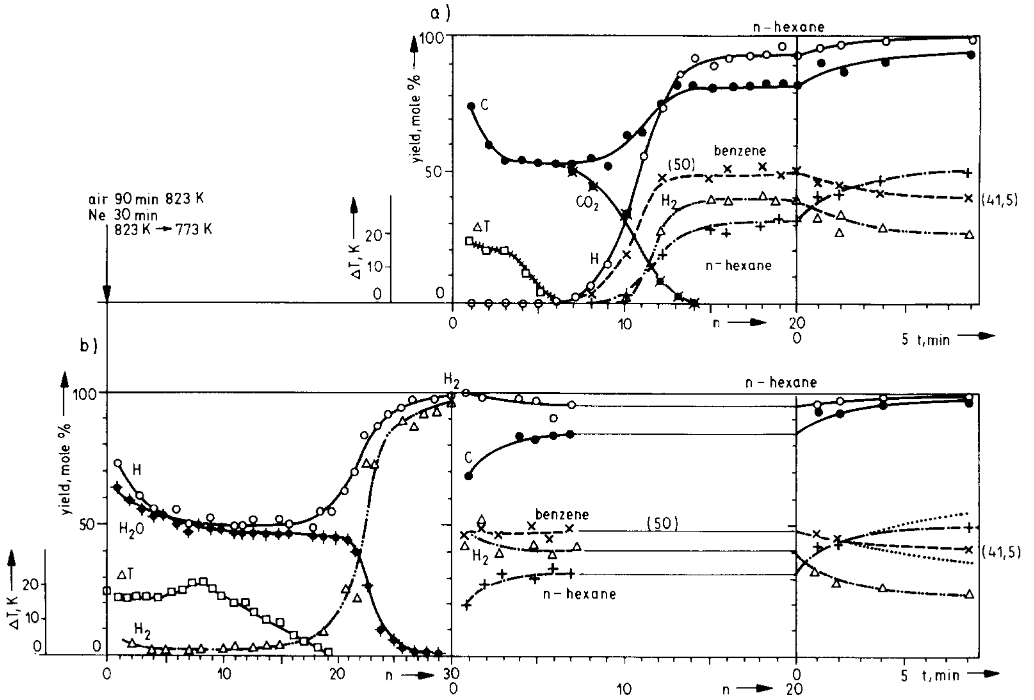

Fig. 5. Pulse reduction and aromatization activity of the Cr20K4 catalyst. T = 773 K, (×) benzene, (+) n-hexane, (△) H_2, (■) CO_2, (♦) H_2O, (●) total C yield of pulse, (○) total H yield of pulse, (□) temperature rise in the catalyst bed. (a) Reduction with n-hexane pulses (left diagram), development of activity (measured by n-hexane pulses) after operation of the catalyst in an n-hexane/Ne flow (≈12 vol% n-hexane) for t minutes (right diagram). (b) Reduction with H_2 pulses, subsequent activity test (n-hexane pulses), development of activity after operation in an n-hexane/Ne flow (diagrams from the left to the right). Dotted lines: catalyst previously reduced in H_2 at 773 K for 900 min.

Subsequently, the benzene fraction decreased due to growing hexane (and hexene) fractions, and the overall yield of benzene rose to a value stable under pulse conditions after 13–15 pulses.

The n-hexane quantity applied in these pulses corresponds to ≈0.01 ml liquid hexane/g catalyst. The consumption of redox equivalents may be evaluated assuming the hydrocarbon retained by the catalyst to be totally oxidized. The resulting 1.60 g equiv./mole Cr_2O_3 are, however, a slight overestimation as the mentioned assumption should not be valid for the last pulses. The quantities of H and C retained by the catalyst amount to 0.58 and 0.14 g atom/mole Cr_2O_3, resp. (15 pulses). This may include H and C bonded to the surface via OH—, C_xH_y—, and carbonate groups and other forms.

The activity observed after pulse reduction turned out to be a maximum. When the catalyst was subsequently charged with flowing hexane/neon the benzene yield from hexane pulses was found to decrease slightly. The pronounced simultaneous increase of unreacted n-hexane (and hexenes) reflects a decreasing coke formation rate. There is a clear parallelism with the deactivation processes observed in gradientless and flow reactors with progressing coke deposition.

When the catalyst was reduced by H_2 pulses (Fig. 5b), water was formed giving rise to a broad tailing of the catharometer signal which returned to "zero" level (determined by H_2O desorption from the Al_2O_3) after 8–10 min. Wall interactions may have contributed to this tailing though the wall temperatures were ≈420 K in the heated tubing section. The H_2 consumption in 30 pulses amounted to 1.56 g equiv./mole Cr_2O_3, with 0.77 g atom H/mole Cr_2O_3 retained.

The yields of benzene, *n*-hexane, hexenes, and cracking products from *n*-hexane pulses applied after a 10-min Ne flush or after the treatment with *n*-hexane/neon described above equaled those observed after *n*-hexane reduction. The yields of free H_2 tended to be higher at the first pulses indicating the presence of weakly chemisorbed hydrogen on the surface after reduction. Similar phenomena were observed whenever the catalyst had been charged with the *n*-hexane/neon flow: the total H yield was frequently higher than 100% at the first pulse, decreasing to the values reported in Fig. 5 with the subsequent 1–2 pulses. The effect on activity was insignificant.

Activity was not enhanced by prolonged H_2 reduction at 773 K. After 60 min reduction the initial activity and the deactivation process were identical with those shown in Fig. 5b. After 900 min reduction the initial activity was still the same, the deactivation was, however, more pronounced as indicated in the diagram (dotted lines).

The reduction of the catalyst by CH_4 pulses (not included in Fig. 5) resulted in the same initial activity and deactivation behavior as H_2 and *n*-hexane reductions. The consumption of redox equivalents (retained CH_4 assumed to be totally oxidized) was 1.62 per mole Cr_2O_3, with 0.41 g atom H and 0.08 atom C per mole Cr_2O_3 retained.

DISCUSSION

From Figs. 3 and 4 it is obvious that Cr_2O_3/Al_2O_3 catalysts are reduced in two stages.

In the rapid stage reduction of the Cr20K4 catalyst, the consumption of the reducing agent was in the range of 1.56–1.62 g equiv./mole Cr_2O_3 after oxidation at 823 K (pulse and gradientless reactors) and 1.35 g equiv./mole Cr_2O_3 after oxidation at 923 K. This is slightly more than found by the iodometrical method of Weller and Voltz (*25*): 1.32 (823 K) and 1.18 (923 K) g equiv./mole Cr_2O_3, (*25*). The difference may well cover chemisorption effects observed and the limited validity of assumptions made for calculations of redox equivalents for hexane and methane. Thus, a comparison between iodometric values and our data confirms the predominance of Cr^{3+} but does not supply unambiguous evidence for the existence of a low-valence Cr species besides Cr^{3+} already after pulse reduction. In the literature, Cr^{2+} formation is generally expected only after 20–60 min reduction in flowing H_2. A further discussion of this question will be given in Part II of this paper.

The slow reduction obviously corresponds to the process reported by Sloveckaya *et al.*, with the relations between reducibility and chromia content agreeing with (*5*). The conversions listed in Table 2 and the ability of the reduced samples (after H_2 desorption) to liberate H_2 from H_2O indicate that at least one valence state lower than Cr(III) is present after TPR, catalysts with small chromia content containing higher fractions of low-valence chromium. The incompleteness of the slow stage reduction, with significant differences between stabilized and unstabilized samples, and the nearly asymptotic behavior exhibited in the isothermal case suggest that only part of the Cr(III) is accessible to reduction. The identity of the low-valence chromium and the nature of this inhomogenity will be discussed in Part II of this paper.

In the discussion of the question if the low-valence species can be the active site for aromatization, a comparison will be made between the results from pulse and gradientless recirculation reactors. There is no doubt that the difference of reaction regimes between these reactors will affect measured activities. The rate constants for hexane dehydrogenation estimated from pulse experiments were significantly higher than those found in the gradientless reactor, reflecting inter alia hydrogen deficiency of the catalyst surface under pulse conditions. It seems, however, unlikely that the difference of reaction regimes would imply a difference in the type of reaction sites involved, the more so as hydrocarbon partial pressures in the pulses were well within the partial pressure range applied in the CSTR. Thus, the comparison of activity tendencies appears to be justified as is confirmed by the parallelism of deactivation processes observed in pulse and gradientless reactors.

Bearing this in mind we conclude from the pulse experiments that the catalyst achieves full activity after the rapid reduction stage resulting in Cr(III). As the activity is not enhanced by further reduction or treatment with flowing *n*-hexane/neon a significant activity contribution of the low-valence chromium species may be ruled out. However, detailed information on catalytic properties of this (these) species cannot be extracted from our experiments as the reduction extent was presumably low (cf. Part II). Further work on this problem is in progress.

In the gradientless recirculation reactor, the long break-in period is due to water produced in the slow stage reduction of Cr(III) by the reaction mixture blocking coordinatively unsaturated Cr^{3+} sites. Obviously, a constant activity is attained when the water content of the recirculated gas falls below a critical value (0.15–0.5% (*27*)) because of the decreasing reduction rate.

When an oxidized Cr_2O_3/Al_2O_3 catalyst is reduced with *n*-hexane in a flow reactor, several processes are superimposed that may result in break-in phenomena as reported in (*1, 13*). Slow stage reduction not relevant in the pulse system may well affect the flow reactor as the final layers of the catalyst are faced with the cumulated water production of the preceding ones. In rapid stage reduction, the absence of H_2O among the reaction products (see Fig. 5a) is typical only of the first layers of the catalyst bed. Since reduction proceeds instantaneously, giving rise to distinct reaction zones even in the catalyst bed of the recirculation reactor (which is not gradientless in respect of this reaction), the following layers are reduced by the H_2-containing aromatization product of the first ones, which results in water formation (see Fig. 5b). Moreover, there is considerable doubt concerning plug flow conditions in flow reactors used for investigations in this field (linear gas velocity estimated to be 2–6 cm/s for references in (*1*). The delayed elution of water from the rapid reduction step and a shortening of the break-in period by flushing with inert gas as reported in (*1*) is plausible on this basis.

CONCLUSIONS

Oxidized chromia/alumina catalysts are reduced in two stages. The rapid first stage supplies a surface exhibiting the aromatization activity well characterized in the literature. Most likely, this activity arises from Cr^{3+} the chromium valence predominantly if not exclusively present on this surface. In the slow second stage at least one low-valence chromium species is formed, which does not contribute significantly to aromatization activity.

Break-in periods in gradientless and flow reactors are due to water being formed in the slow reduction stage and poisoning active sites. In laboratory flow reactors far from plug flow conditions, additional retardation may arise from the delayed elution of water produced in the first stage of reduction.

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