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Activation of Phillips Cr/silica catalysts
IV. Mobility of Cr(VI)

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Abstract

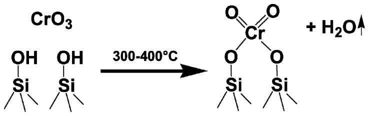
The saturation coverage behavior of Cr(VI) on silica has been used to study the mobility of hexavalent chromium during commercial activation of the Phillips catalyst in a fluidized bed. Cr(VI) was found to migrate not only within each silica particle, but even between particles. The mechanism of transfer is thought to be particle-to-particle contact during the fluid bed calcining process, and Cr migration was observed at temperatures as low as 300–400 °C in these experiments. Transfer can take place even in the absence of oxygen, which suggests that redox cycling is probably not the main method of mobility. However, once the silica is calcined at high temperatures the migration is stopped at low temperatures, indicating that the thermal history of the surface is important in the transfer process. Migration of Cr on and between alumina particles behaved in much the same way, and Cr transfer was also observed between silica and alumina in both directions. Cr(III) on deactivated commercial Cr/silica catalysts could be reclaimed to Cr(VI) surprisingly easily by co-activation with virgin support. The spreading out of Cr(VI) onto a fresh unoccupied surface probably provides a powerful force to reoxidize the otherwise seemingly inert alpha-Cr_2O_3 crystallites. The mobility has important consequences for commercial manufacture and use of the catalyst.

Keywords: Polyethylene; Ethylene polymerization; Phillips catalyst; Chromium catalyst; Polymerization catalyst; Thermal migration

1. Introduction

The Phillips Cr/silica polymerization catalyst, responsible for perhaps 40% of the world's high-density polyethylene production, is usually made by impregnation of a chromium compound, such as CrO_3, onto silica followed by calcination in dry air at high temperature. Bulk CrO_3 is unstable above about 200 °C, decomposing into oxygen and Cr_2O_3. However, on silica a small amount of hexavalent Cr is "anchored" to the surface and stabilized even up to 900 °C. This anchoring is usually thought to occur through esterification with surface silanol groups (Scheme 1). These are the species from which the active polymerization sites are later derived.

Despite being thus "anchored," even the earliest pioneers of Cr/silica research believed that this stabilized hexavalent form was in fact mobile, at least to some degree, on the silica surface during the activation step. This was inferred by J.P. Hogan, discoverer of the catalyst, and others, from the behavior of the catalyst under many different commercial treatments.[1] This was of interest because mobility of Cr has many important consequences concerning its commercial manufacture and use. During the 1960's and 1970's it was even found, in this laboratory and that of W.R. Grace,[2] that hexavalent Cr could migrate be-



Scheme 1. Anchoring of Cr(VI) to silica.

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[1] From personal communications with them.

[2] Personal communication with Dr. Rim Glemza, W.R. Grace.

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tween individual silica particles. This was established by physically mixing and co-activating sieved silica and Cr/silica particles. For example fine Cr/silica particles could be co-activated in a fluidized bed with coarse silica particles, then separated again by sieving. By this method it was found that some of the Cr had moved from one particle to another.

In more recent years these findings have been confirmed by spectroscopic methods as well. Wachs and Weckhuysen et al. [1,2] performed some studies on the differences in DRS and ESR spectra from Cr(V) and Cr(VI) when supported on titania, alumina, and silica. Cr/silica was physically mixed together in a mortar with alumina and then the mixture was co-activated at 550 °C. From DRS and ESR spectroscopy they then found that the Cr had migrated preferentially to the alumina. Cr/alumina co-activated with silica also transferred Cr, but only partially.

In another publication Cr mobility between particles was also implied by the unusual work of Jozwiak and Dalla Lana, who took a different approach [3]. They physically ground silica together with alpha-Cr_2O_3 powder. After being co-calcined, the reduction capacity of the mixture was then measured by temperature-programmed reduction with CO or with H_2. Again the transfer of Cr to silica could be detected because Cr/silica displays a significantly different TPR profile from that of unsupported alpha-Cr_2O_3. Despite the fact that alpha-Cr_2O_3 is extremely inert, they found that it transferred easily onto virgin silica during calcining. By examining the disappearance of X-ray diffraction lines they concluded that the transfer occurred around 500–700 °C. Transfer of Cr was also possible to alumina at only 360–420 °C and to magnesia at 500–700 °C.

The Dalla Lana paper seemingly contradicts some of what was thought to be known about alpha-Cr_2O_3, and it raises some important questions. Alpha-Cr_2O_3 is well known for its inert character and once deactivated by formation of alpha-Cr_2O_3, commercial catalysts are extremely difficult, if not impossible, to regenerate back to the hexavalent form. Therefore, the fact that physically mixed alpha-Cr_2O_3 could be so easily oxidized and distributed onto the silica as Cr(VI) calls for an explanation. In short, why does physically mixed alpha-Cr_2O_3 oxidize and spread whereas alpha-Cr_2O_3 formed in situ on the catalyst during deactivation does not.

Understanding the migration of hexavalent Cr during calcining has important commercial implications. It affects how catalysts are manufactured, what happens during activation, and deactivation, and how polyethylene plants should be operated for a consistent outcome. It is also important in appreciating some contamination problems during commercial production. To better understand the phenomenon, we have undertaken some further studies in an effort to better define Cr mobility in a fluidized bed under more commercial conditions, to determine what substrates are most susceptible, and why commercial deactivation seems almost irreversible.

The present study was conducted using still another, perhaps simpler, analytical technique. It relies on the previously defined tendency of supports to "saturate" with hexavalent Cr. For each substrate, and set of calcining conditions, the surface will only hold a certain maximum level of Cr(VI). If more is applied the excess simply decomposes into Cr(III) [4]. This behavior is shown in Fig. 1. Thus, a silica can be co-activated with a Cr/silica, one that contains more Cr than is allowed to be Cr(VI) by its saturation coverage. After activation the Cr(VI) content of the mixture is determined by titration. If the conversion to Cr(VI) is higher than would be possible from the Cr/silica component alone, then migration must have occurred to the pure silica in order to support the extra Cr(VI).

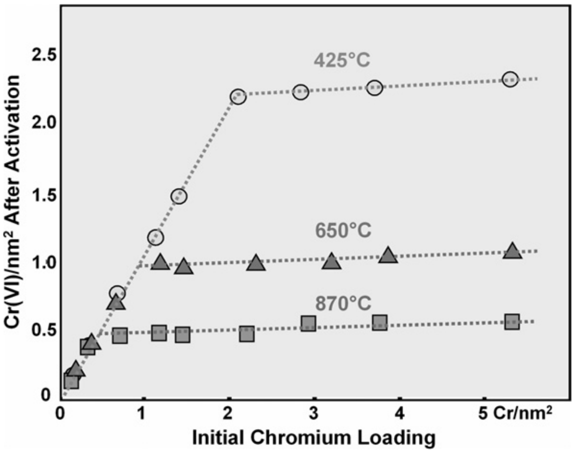


Fig. 1. Saturation coverage behavior of silica by Cr(VI).

2. Experimental

The silica base used in these studies was ES70 from Ineos Co., and used widely as a commercial, polymerization grade support. It had a 50-μm average particle size, a surface area of 300 m^2/g and a pore volume of about 1.6 cc/g. The Cr/silica component was made by impregnating the same silica to incipient wetness with 5 wt% Cr as an aqueous CrO_3 solution. It was then stir-dried by evaporation at room temperature until free flowing. The alumina base used was alumina-A from W.R. Grace, which had a 100-μm average particle size, a surface area of 300 m^2/g and a pore volume of about 1.3 cc/g. The Cr/alumina component was made by similarly impregnating the same alumina base with about 6 wt% Cr as an aqueous CrO_3 solution.

All four of these materials were then finally dried individually in a fluidized bed by raising the temperature up to 200 °C, or higher if so stated. This was done to ensure that all liquid water was removed from pores before the physical blending of these components in order to avoid chromatographic movement of pore water (and Cr) from one component to another. Unless stated otherwise the two components were then blended in an approximately 3:1 ratio in which the minor component contained the chromium. This ratio was used to obtain higher experimental precision. The two components were weighed out in the desired amount, then each added to an activator tube where they were intimately mixed by fluidization during the activation process.

Co-activation experiments were carried out by calcination in a fluidized bed. About 10 g of the mixture was placed in a 1.75-inch quartz tube fitted with a sintered quartz disk at the bottom.

While the powder was supported on the disk, pure oxygen, previously dried through 13X molecular sieve column, was blown up through the disk at the linear rate of about 1.6 to 1.8 standard cubic feet per hour to create a fluidized bed. In some cases, if so stated, dried nitrogen or air was used as the fluidizing gas in place of oxygen. An electric furnace around the quartz tube was then turned on and the temperature was raised at the rate of 400 degrees centigrade per hour to the indicated temperature, such as 600 °C. At that temperature the powder was allowed to fluidize for 24 h in the dry oxygen. Afterward the powder sample was collected and stored under dry nitrogen, where it was protected from the atmosphere until ready for testing.

The first co-activation temperature studied was usually 400 °C. After sampling, this same mixture was typically then heated to 500 °C for another 24-h period of co-activation, followed by sampling again. This process was continued up to 900 °C with a new co-activation experiment being carried out at each increment of 100 °C. In this way the last sample taken after activation at 900 °C had experienced the cumulative effect of all previous co-activations at lower temperatures. This fact sometimes becomes important in the interpretation of results later.

Hexavalent chromium content on the activated sample was then measured by titration against ferrous ammonium sulfate. About 0.5–1 g of the sample was immersed in 2 N sulfuric acid solution and stirred for 30 min prior to the titration. Two drops of phenanthroline iron (II) sulfate solution was added as the indicator. Ferrous ammonium sulfate titrant solution was calibrated against a standard solution of potassium dichromate, purchased from Aldrich Co.

3. Results and discussion

3.1. Migration in O_2 between virgin silicas

In the first experiment, one part of virgin Cr/silica was physically mixed with three parts of virgin silica and the two co-activated by fluidization at various temperatures in dry oxygen for 24 h. By “virgin” it is meant that the component had no prior heat treatment other than being dried at 200 °C to first remove any residual liquid pore water prior to mixing. Co-activation experiments were done every 100 °C between 400 and 900 °C. As a “control” for the series, similar one-component activations of Cr/silica alone were also conducted. The results of these and subsequent experiments are summarized in Table 1, which lists the retention of Cr(VI) on these samples.

All experiments in Table 1 used a mixture of approximately 3 parts support and 1 part supported Cr. Column 3 in Table 1 is the percentage of the total Cr present in the mixture that is expected as Cr(VI) if no transfer occurs at all. That is, it is the amount of Cr(VI) supportable by the donor component alone when activated alone. Column 4 in Table 1 is the percentage of Cr present that would be Cr(VI) if both the donor component and the recipient became saturated with Cr(VI) at the highest temperature to which each is exposed, either in the pretreatment or in the subsequent co-activation. Frequently this number is greater than 100% because the maximum possible loading of Cr(VI) is greater than the amount of total Cr present. In cases where the Cr donor support and the recipient are identical, including the pretreatment temperatures, then column 4 is just column 3 multiplied by the blend ratio plus one, or approximately four, because there is now about four times as much surface to hold the Cr(VI). In experiments where the two components do not use identical supports, the calculation of column 4 is a bit more complicated, because donor and recipient do not contribute equally. Column 5 in Table 1 is the percentage of Cr present that was actually measured as Cr(VI) after co-activation of the mixture. Finally column 6 shows how far the transfer has progressed relative to full equilibrium, or more precisely:

$$\text{Column 6} = [\text{Column 5} - \text{Column 3}] \\ /[\text{Column 4} - \text{Column 3}].$$

Fig. 2 shows the color of these samples in Experiment 1 through photographs taken of each after activation or co-activation. The top half of the figure shows the color from the one-component activations. The virgin Cr/silica is 100% hexavalent and therefore shows a strong orange color. As it is activated at progressively higher temperatures more of that Cr(VI) decomposes into the green Cr(III) oxide due to the saturation coverage effect (Fig. 1). Even at 400 °C there appears to be a loss of Cr(VI). However, the co-activated mixture is shown in the second line part of the figure. Here the color remains yellow even up to 900 °C, indicating little or no loss of Cr(VI). This signifies a migration of the Cr to the unpromoted silica. By spreading out the Cr on both sources of silica, the combined Cr concentration is now below or nearer to the saturation coverage, allowing much more of the Cr to remain hexavalent.

The change in Cr(VI) is quantified in Table 1 as Experiment 1, and in Fig. 3, which plots the amount of Cr(VI) retained after activation as a function of temperature. In this case the axis is not expressed as Cr(VI) atoms/nm^2, but instead as a percent of the total chromium present that is retained as Cr(VI). The lower line 3A plots the one-component activations of Cr/silica alone. This curve shows the saturation behavior in Fig. 1. The silica cannot hold more Cr(VI) than this value, so even at 400 °C there is already a loss of Cr(VI). Line 3A also represents what would be observed from the co-activated mixture of Cr/silica with silica if there were no migration of Cr between the two components. In line 3A the amount of Cr(VI) retained is limited by the amount of silica surface available only on the one component—the Cr/silica.

In contrast the upper line B in Fig. 3 represents the amount of Cr(VI) that could be expected from full equilibration of the Cr between the two silica sources. In this example where the Cr donor and recipient have the same supports, this curve is simply line A multiplied by the blend ratio plus one, usually about 4, since there is now approximately 4 times as much silica surface available (from a blend ratio of 1 part Cr/silica and approximately 3 parts silica). There is now enough surface available, if full migration and equilibration occurs, that only at 800 and 900 °C would saturation coverage be expected to result in a small loss of Cr(VI) to Cr(III). At other temperatures all of the

Table 1
Summary of co-activation experiments

Donor/acceptor	Co-activation (24 h)	Cr(VI) If no migration (%)	Cr(VI) for full equil. (%)	Cr(VI) observed (%)	% Toward equilibration (%)
Experiment 1	400 °C O_2	79.5	306.3	99.0	>9
200 °C 5% Cr/silica	500 °C O_2	50.8	195.7	98.4	>33
& 200 °C silica	600 °C O_2	39.2	151.2	97.8	>52
	700 °C O_2	29.0	111.9	97.6	>83
	800 °C O_2	22.4	86.5	77.4	86
	900 °C O_2	20.5	79.1	60.2	68
Experiment 2	300 °C N_2	89.0	343.7	100.0	>4
200 °C 5% Cr/silica	400 °C N_2	60.5	233.5	77.3	10
& 200 °C silica	500 °C N_2	21.9	84.7	38.0	26
	600 °C N_2	5.6	21.6	18.3	79
	700 °C N_2	1.9	7.1	6.3	85
	800 °C N_2	0.6	2.4	1.9	72
	900 °C N_2	0.0	0.2	0.9	
Experiment 3	400 °C O_2	19.4	77.2	22.2	5
900 °C 5% Cr/silica	600 °C O_2	19.4	77.2	23.9	8
& 900 °C silica	700 °C O_2	19.4	77.2	33.0	24
	800 °C O_2	19.4	77.2	51.4	55
	900 °C O_2	19.4	77.2	53.7	59
Experiment 4					
900 °C 5% Cr/silica	400 °C $O_2 + H_2O$	20.5	84.0	20.0	0
& 900 °C silica	600 °C $O_2 + H_2O$	20.5	84.0	24.5	6
Experiment 5	400 °C O_2	79.5	150.3	87.2	11
200 °C 5% Cr/silica	600 °C O_2	39.2	110.0	58.7	28
& 900 °C silica	900 °C O_2	20.5	91.3	61.3	58
Experiment 6	400 °C O_2	36.9	1305.8	38.5	
857 °C 1% Cr/silica	600 °C O_2	36.9	699.1	69.5	
& 200 °C silica	800 °C O_2	36.9	416.9	96.2	
Experiment 7	300 °C O_2	100.0	407.3	92.0	?
200 °C 5% Cr/alumina	400 °C O_2	96.0	391.0	89.7	?
& 200 °C alumina	500 °C O_2	85.0	346.2	92.0	3
	600 °C O_2	72.5	295.3	89.1	7
	700 °C O_2	55.3	225.1	97.8	>25
	900 °C O_2	21.0	85.5	59.4	60
Experiment 8	400 °C O_2	21.0	85.9	24.0	5
900 °C 5% Cr/alumina	600 °C O_2	21.0	85.9	26.8	9
& 900 °C alumina	900 °C O_2	21.0	85.9	61.0	62
Experiment 9	400 °C O_2	96.0	159.3	92.0	?
200 °C 5% Cr/alumina	600 °C O_2	72.5	135.8	97.8	>40
& 900 °C alumina	900 °C O_2	21.0	84.3	66.5	72
Experiment 10	400 °C O_2	21.0	319.5	27.7	2
900 °C 5% Cr/alumina	600 °C O_2	21.0	246.9	35.1	6
& 200 °C alumina	900 °C O_2	21.0	87.8	60.5	59
Experiment 11	300 °C O_2	97.5	476.2	96.2	?
200 °C 5% Cr/silica	400 °C O_2	79.5	438.4	97.0	>5
& 200 °C alumina	500 °C O_2	50.8	365.9	93.5	14
	600 °C O_2	39.2	307.4	84.5	17
	700 °C O_2	29.0	233.3	80.5	25
	800 °C O_2	22.4	166.9	75.4	37
	900 °C O_2	20.5	99.5	68.1	60
Experiment 12	400 °C O_2	20.5	96.7	28.4	10
900 °C 5% Cr/silica	600 °C O_2	20.5	96.7	36.0	20
& 900 °C alumina	900 °C O_2	20.5	96.7	54.3	44
Experiment 13	300 °C O_2	100.0	352.4	94.7	?
200 °C 5% Cr/alumina	600 °C O_2	72.5	183.8	96.0	>21
& 200 °C silica	700 °C O_2	55.3	137.5	102.3	>57
	800 °C O_2	39.0	102.7	100.0	>96
	900 °C O_2	21.0	79.8	80.3	100

Table 1 (*continued*)

Donor/acceptor	Co-activation (24 h)	Cr(VI) If no migration (%)	Cr(VI) for full equil. (%)	Cr(VI) observed (%)	% Toward equilibration (%)
Experiment 14	300 °C O_2	21.0	78.9	23.5	4
900 °C 5% Cr/alumina	400 °C O_2	21.0	78.9	33.6	22
& 900 °C silica	600 °C O_2	21.0	78.9	43.3	38
	900 °C O_2	21.0	78.9	57.6	63
Experiment 15	400 °C O_2	79.5	156.1	91.3	15
200 °C 5% Cr/silica	600 °C O_2	39.2	110.3	76.4	52
& 900 °C alumina	900 °C O_2	20.5	89.0	51.5	45
Experiment 16	400 °C O_2	20.5	352.8	32.9	4
900 °C 5% Cr/silica	600 °C O_2	20.5	272.2	44.1	9
& 200 °C alumina	900 °C O_2	20.5	95.4	51.9	42

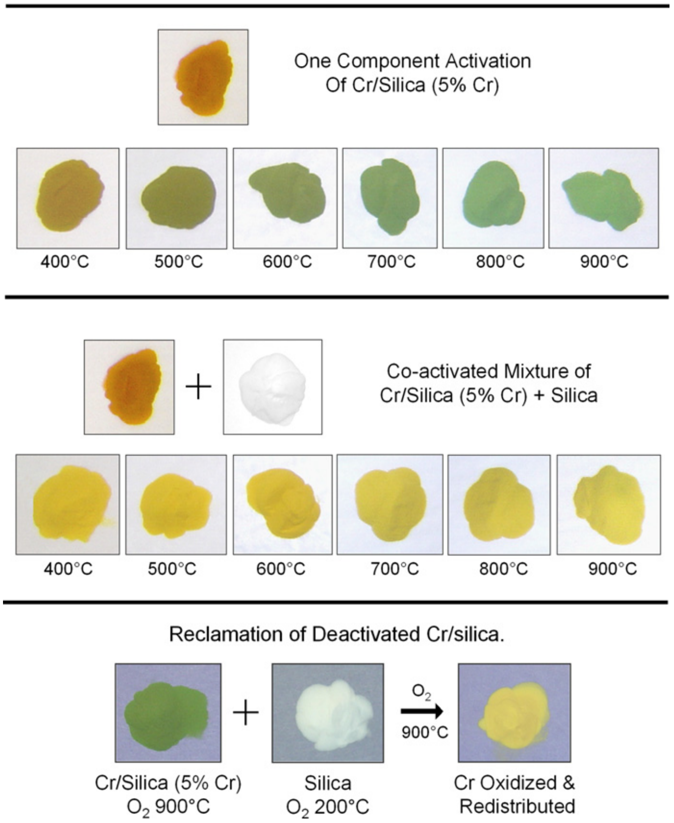


Fig. 2. Colors produced from the activation of Cr/silica.

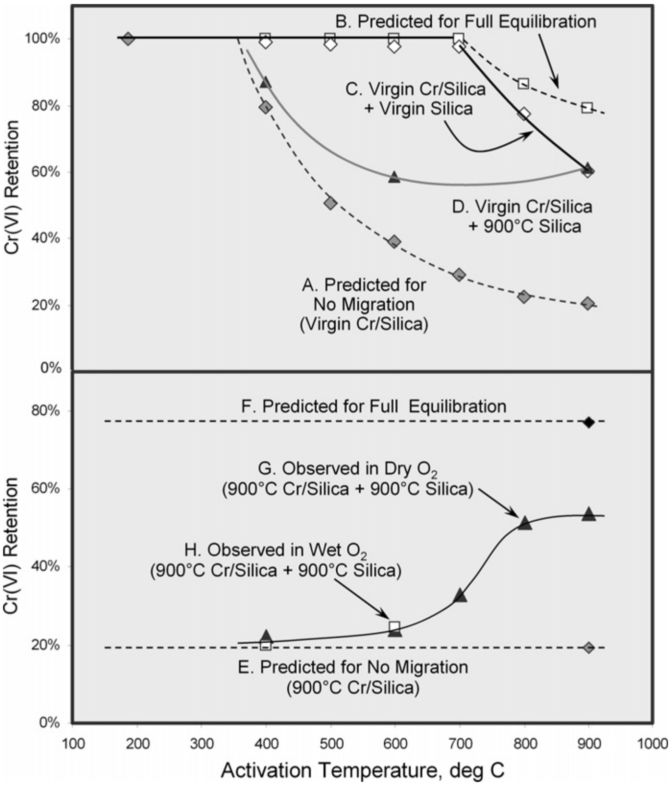


Fig. 3. Cr migration between silica particles during activation in O_2.

chromium should remain hexavalent, being not limited by the saturation coverage maximum.

Line C of Fig. 3 plots the Cr(VI) retention values actually observed from the co-activated mixtures. Since every point on line C is above that on line A, it is clear that a large migration of chromium has definitely taken place, even at 400 °C. It is possible that migration would have occurred at even lower temperatures, but this was considered beyond the reliability of the technique. Since all of the chromium is hexavalent between 400 and 700 °C, one cannot tell if full equilibration of the Cr(VI) has occurred between the two sources of silica, or something less. Table 1 lists some minimum values for the degree to which complete equilibration is reached. The points at 700–900 °C do suggest some quantification of the amount of transfer. About 85% of full equilibration has been reached under these conditions, although one cannot tell at what temperature this level of transfer occurred.

3.2. *Transfer by chromatography*

The data in Figs. 2 and 3 call for an explanation as to exactly how the transfer of chromium is accomplished from one particle to another. One possible method of Cr(VI) transfer is chromatographic movement or "wicking" during evaporation of liquid water from pores during the early stages of calcining. Commercial silicas and Cr/silica catalysts still usually contain 8–10% pore water even after drying at 100 °C. This water can be seen leaving the pores between 100 and 150 °C during TGA measurements. Depending on how the drying is accomplished, one can often visually see local gradients of Cr in the bed, carried from the interior of the bed by pore water moving to replace that lost by evaporation. Thus, Cr could transfer from one particle to another, depending on how much pore water is left behind after drying.

In some of the work by Weckhuysen et al. the particles were not mixed until after they had been calcined separately at 550 °C [2]. Thus, at least in these experiments, chromatography cannot account for the observed migration. Likewise in the Jozwiak and Dalla Lana study, Cr moved from Cr_2O_3, which is not soluble in water [3]. So again chromatography can be ruled out. In our own study, even the virgin silica and Cr/silica components were always calcined individually at 200 °C and protected from the atmosphere before use. Therefore some other mechanism must be invoked to account for the transfer.

3.3. Transfer by Cr evaporation

Another possible explanation for the movement of Cr between particles is evaporation of the chromium from one particle and re-deposition onto its neighboring particle. Although the usual oxides of Cr are not generally thought to be volatile in this temperature range, Cr volatility has nevertheless been reported in some studies [5–8], where Cr was lost from the silica. The amount of Cr lost was found to be small at the commercial loading of about 0.4 Cr/nm^2, but became more pronounced at higher loadings and at high calcining temperatures. This would be in general agreement with the fact that Cr loss has not been observed in the vast number of commercial activations carried out over half a century and using millions of pounds of catalyst.

To further probe this idea a Cr/silica catalyst containing about 2.5 Cr/nm^2 was analyzed by X-ray fluorescence before and after activation at 900 °C for 24 h in flowing oxygen. The results of this analysis indicated, within the accuracy of the technique, that no Cr was lost during activation. The experiment was then repeated but the calcining was done in nitrogen instead of oxygen. Again no loss in Cr was observed.

Still another attempt was made to detect Cr evaporation from these catalysts. A special activation vessel was constructed from quartz glass which contained a tube within a larger tube. The design is illustrated in Fig. 4. The outer tube contained Cr/silica, and the inner tube contained silica. Both materials were supported on a porous sintered quartz disk about 2 mm thick. During activation, the design forced oxygen to first move though the Cr/silica bed at high temperature, presumably carrying any volatile Cr with it, and then through the silica bed held at exactly the same temperature. Once loaded, the double-tube was surrounded by an electrical furnace and activation was carried out as described above in dry oxygen for 24 h at 900 °C. Although several tests were conducted in this way, no evidence was ever found of Cr transfer from one bed to the other. Thus Cr could not be transferred over a 2-mm distance in the gas phase at 900 °C. This agrees with a report by Dalla Lana's group that no transfer was observed at up to 900 °C between alpha-chromia particles and silica particles separated by a 3-mm distance [3].

These results would seem to argue against Cr evaporation, but perhaps they do not totally rule it out. One could still speculate that, once vaporized, the Cr is highly prone to re-adsorption upon contact with another surface, keeping the Cr overall vapor pressure extremely low, even if it is higher locally in and around particles. Perhaps this could restrict Cr transfer to nearest neighbor particles, a behavior very difficult to distinguish from physical particle-to-particle contact (see below).

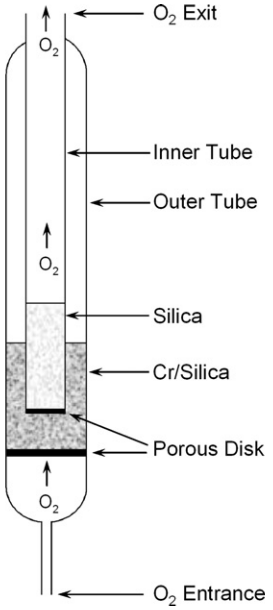


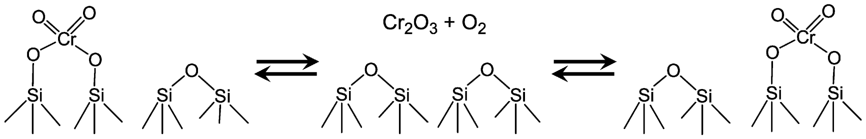
Fig. 4. Double-tube activator.

3.4. Transfer by redox cycling (migration in N_2)

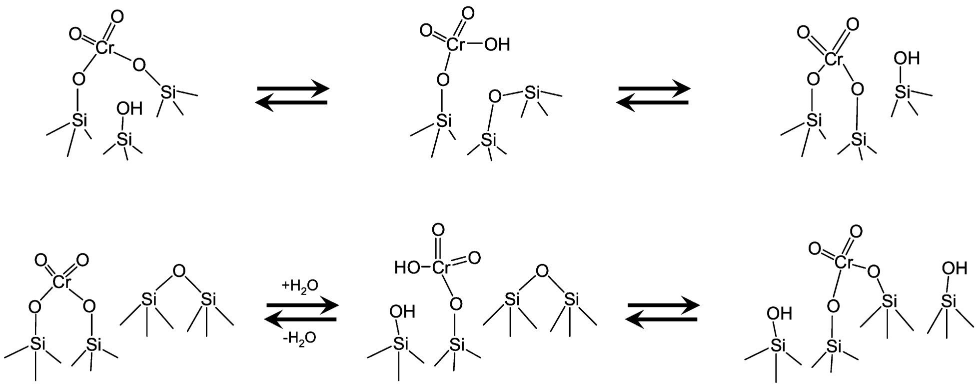
Transfer of Cr through physical contact between particles was also considered [9]. This requires a mechanism by which Cr can move across a silica surface, both within and (upon contact) between particles. One possibility that might account for this movement is that Cr migrates through a cycling between Cr(III) and Cr(VI) on the surface, such as in Scheme 2.

Such cycling requires oxidation of Cr(III) by oxygen gas. In the absence of oxygen transfer should not be possible. Therefore the above experiment was repeated, except that the calcining was done in flowing dry nitrogen instead of oxygen. Cr(VI)/silica, containing about 5% Cr and dried at 200 °C, was mixed in an approximately 1:3 ratio with unpromoted silica, also previously dried at 200 °C. The mixture was then heated to various temperatures, ranging from 300 to 900 °C, and held there for 24 h fluidized under flowing nitrogen. After each heating step, a sample was taken for analysis, and then the remaining mixture was heated up to the next progressively higher temperature. For comparison a control series was also made using only the Cr(VI)/silica alone, exposed to the same heating procedure. The results of these experiments are listed in Table 1 under Experiment 2, and this data can also be plotted to produce a graph like that in Fig. 3 A, B, and C.

As expected there is a major loss in Cr(VI) when the calcining is done in nitrogen. Cr(VI) decomposes into Cr(III) and oxygen at an early temperature, and the oxygen by-product is swept away by the nitrogen, making reoxidation impossible. Despite the severe and early loss of Cr(VI) however, it is clear



Scheme 2. Cr mobility by redox cycling.



Scheme 3. Cr mobility by hydrolysis.

that the some transfer did occur. The "no migration" column in Table 1 shows the control runs again, Cr/silica heated alone. As above, this is the result to be expected if no transfer occurs. These values represent the maximum amount of Cr(VI) that can be supported by original Cr/silica component under nitrogen. The next column labeled "full equilibration," or Fig. 3B, is just the previous column multiplied by the blend ratio plus one, or approximately four. It represents the results expected in the event that there is complete equilibration between the two silica sources. The column labeled "observed," or Fig. 3C, lists the actual results obtained from the co-activation of the mixture. These values lie intermediate between "no migration" and "full equilibration," indicating that some transfer occurred, even at 300 °C, despite rapid decomposition of Cr(VI). At 600 °C the migration became so strong that it almost reached full equilibrium. This suggests that redox cycling, although it almost certainly occurs, is not the only or even the primary means of Cr movement.

3.5. Transfer by hydrolysis (migration between 900 °C silicas)

An alternate mechanism of Cr migration considered was the hydrolysis and reformation of Cr–O–Si bonds, either by neighboring surface silanols or by traces of moisture in the fluidization gas, such as in Scheme 3. Cr transfer between particles by this mechanism will also require particle-to-particle contact. To test this possibility Experiment 3 was conducted, in which Cr/silica and silica were again co-activated, except that each component had first been activated alone in oxygen for 24 h at 900 °C before mixing. Cr/silica containing 5% Cr was activated alone at 900 °C and silica was also calcined alone at 900 °C. Then they were mixed together in a ratio of approximately 1:3 (Cr/silica to silica) and co-activated at various temperatures from 400 to 900 °C in dry oxygen for 24 h. If moisture is required for Cr migration, then transfer of Cr should be severely inhibited under these conditions. The results of these experiments are also plotted in Fig. 3, and listed in Table 1 as Experiment 3.

Again three lines are shown. Line 3E shows the control run—the 900 °C Cr/silica. Having been already calcined at 900 °C, re-activation at lower temperatures changes nothing. The Cr(VI) amount is irreversibly set by the 900 °C treatment, and therefore a horizontal straight line is obtained. This line also represents the results expected from the mixture if no migration occurs. Line 3F is line 3E multiplied by approximately four, from the blend ratio, representing the Cr(VI) values expected if there is full equilibration of the Cr between the two components. Then line 3G plots the results actually obtained from the mixture.

In this example there is almost no migration of Cr at 400 °C and even up to 700 °C the migration is rather minor. Only at the highest temperatures, 800–900 °C does the transfer become more significant, reaching about 60% of full equilibration (see Table 1). This result is a strong indication that the extent of surface annealing or dehydration governs the transfer of Cr(VI). Whether this indicates the direct participation of surface silanols or not is uncertain. It could also reflect the general annealing and reorganization of the surface that accompanies high temperatures. It is possible that for the Cr to be mobile, the silica surface itself must also be somewhat mobile. Once annealed at 900 °C, it may require similar temperatures to obtain significant mobility again. Alternatively one might speculate that traces of moisture in the gas stream are needed for migration, and that once calcined at 900 °C, the supports do not release moisture until that temperature is again approached.

To distinguish between these two possibilities, the experiment was repeated, except that the co-activation was performed in oxygen that was first sparged through distilled water, to reach 100% humidity at 25 °C (Table 1, Experiment 4). That is, Cr/silica, calcined at 900 °C in dry oxygen, was mixed with silica, also calcined at 900 °C in dry oxygen, and the two were co-activated in wet oxygen at 400 and 600 °C. If moisture in the gas stream is primarily responsible for transfer, one might expect to see more migration than was seen in line 3G. The results are shown in line 3H. There is no change in migration compared to 3G. This suggests that moisture in the gas stream is not the primary driver of Cr transfer, or that 900 °C silica is not easily rehydrated under these conditions.

3.6. Only one silica component calcined

Little migration occurred at low temperatures when the individual components had first been dehydrated at 900 °C. Therefore it was of interest to see if migration would be improved if only one of the components had been dehydrated before mixing. Virgin Cr/silica (dried at 200 °C) was mixed with three parts silica that had already been calcined at 900 °C (Experiment 5). This mixture was then co-activated at 400–900 °C in oxygen for 24 h. The results of this experiment are shown in Fig. 3, line D.

Comparing the experimental line 3D with control lines 3A and 3B, one can see that little migration occurred at 400 °C. This is in agreement with Fig. 3G, and suggests that both surfaces need to be hydrated for effective transfer at low temperatures. More migration occurred at 600 °C, but still not as much as in line 3C between virgin components. By 900 °C, however, significant migration has occurred, representing about 58% of the equilibrium value. Also shown in Fig. 3 for comparison, is line 3C derived from co-activation of virgin Cr/silica with virgin silica. There is a major difference between lines 3C and 3D, strongly indicating that Cr moves more easily on the hydrated materials at low temperature. At 900 °C, however, both curves merge as might be expected.

The reverse experiment was also carried out, in which 900 °C Cr/silica was co-activated with 200 °C silica. In this case the Cr/silica was a commercial grade sold by Ineos as EP30X containing 1% Cr and having an average particle size of about 100 μm. It was commercially activated in dry air, then co-activated with three parts of virgin silica in dry oxygen for 5 h. The results are listed in Table 1, Experiment 6. Again no migration was observed at 400 °C. By 600 °C the transfer of Cr became more significant, and by 800 °C all of the Cr was converted into Cr(VI). Thus if either the donor or the recipient surface has been pre-annealed at high temperature, the transfer is greatly inhibited at low and intermediate temperatures. However, the transfer at high temperature becomes respectable. Fig. 2 shows photographs of the two components before and after co-activation at 900 °C. The dramatic color change indicates that Cr_2O_3 on the “deactivated” catalyst is re-dispersed as Cr(VI).

3.7. Rate of Cr transfer

In an effort to understand how quickly the transfer of Cr occurs between silicas under these conditions, two experiments were done using intermediate temperatures. Cr/silica and silica, both individually calcined at 600 °C, were physically mixed in approximately a 1:3 ratio, then co-activated in oxygen for various times ranging from 1 to 24 h. One series of samples was co-activated at 400 °C and another at 600 °C. The results of these experiments are plotted in Fig. 5. It is clear from the graph that equilibration is not immediate, but takes prolonged contact under these conditions. Equilibrium has not been reached even after 24 h. Predictably, migration was somewhat faster at 600 °C than at 400 °C.

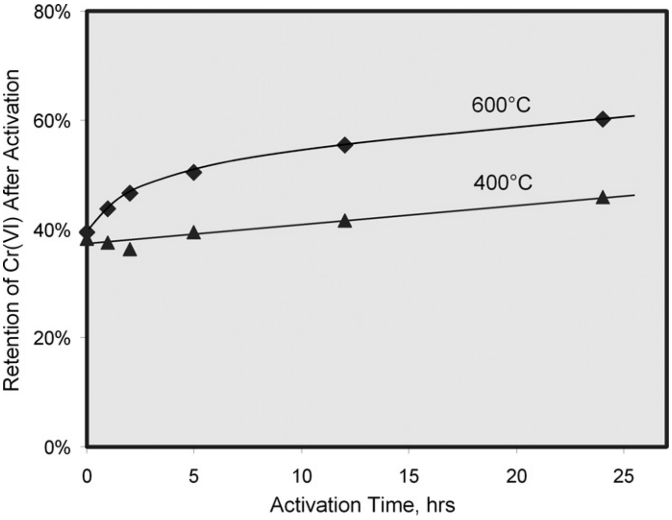


Fig. 5. Co-activation of 600 °C Cr/silica and 600 °C silica in O_2.

3.8. Difficulty of reoxidizing Cr_2O_3

Alpha-chromia has a reputation for being almost inert. It is insoluble, even in aqua regia, and those who work with commercial Cr/silica catalysts at high temperatures often observe this lack of reactivity. The loss of Cr(VI) into Cr(III) during activation seems almost irreversible. The saturation behavior in Fig. 1 raises the issue. The Cr(VI) saturation level depends on temperature as shown. Saturation at 650 °C was around 1.0 $Cr(VI)/nm^2$, but raising the temperature up to 870 °C produced alpha-Cr_2O_3 and cut the Cr(VI) in half to $0.5/nm^2$. The process is not reversible. Once the alpha-Cr_2O_3 has formed at 870 °C, one cannot reoxidize it at 650 °C to restore the original 1.0 $Cr(VI)/nm^2$. This might be attributed to the difficulty of reoxidizing alpha-Cr_2O_3, but another interpretation is that the ability of the silica surface to stabilize Cr(VI) depends on its level of dehydroxylation or thermal annealing, which is not reversed by simply lowering the temperature again.

Other evidence, from two-step activation procedures, suggests that both explanations are correct and can contribute to the final Cr(VI) level [10]. These procedures were developed to enhance the melt index potential of the catalyst. They consist of two steps: (1) the support is calcined at maximum temperature in the absence of Cr(VI), then (2) Cr(VI) is added or created at a lower temperature. In this way the support experiences the high temperature, but not the Cr(VI). In such cases the maximum Cr(VI) level is determined by the thermal history of the support, and not by the final, and lower, oxidation temperature of the Cr. However, within this maximum allowed Cr(VI) limit, some procedures that yield large crystallites of alpha-Cr_2O_3

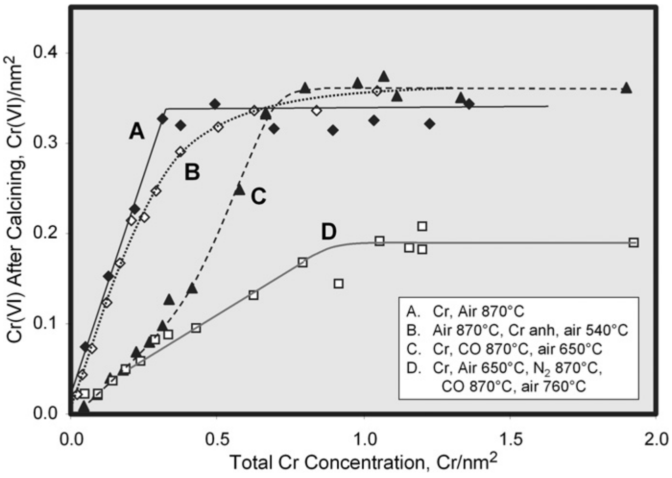


Fig. 6. Cr(VI) coverage after various calcining treatments.

also produce a lower Cr(VI) level, indicating the difficulty of reoxidizing alpha-Cr_2O_3.

An example is shown in Fig. 6. In each of the four cases the silica–titania support was calcined at 870 °C for 3–5 h, contained various levels of Cr added in different ways. Fig. 6 plots the Cr(VI) content found on the catalyst after the activation treatment as a function of the total Cr loading. Line 6A is the normal one-step activation. The catalyst was impregnated with Cr, then calcined in dry air at 870 °C. It produces the usual saturation behavior that was also shown in Fig. 1. The initial slope of the line is 1, indicating that at first all of the Cr is converted into Cr(VI), until the maximum level is reached, then the excess is converted to Cr_2O_3. In line 6B the support alone was first calcined at 870 °C, then it was impregnated with a pentane solution of dicumene Cr(0) to prevent rehydrating the support. Cr(VI) was generated by a final oxidation in dry air at 540 °C (which produces maximum melt index). This two-step procedure generated the same maximum level of Cr(VI) as the one-step activation in line A. Therefore the saturation Cr(VI) concentration is determined by the thermal history of the support, and not that of the Cr.

However, line 6C represents another case. The support was impregnated with Cr(III) acetate then calcined in carbon monoxide at 870 °C. This treatment produces some Cr(II) and Cr(III) oxides. Oxidation to Cr(VI) was then accomplished by calcining in dry air at 650 °C (which produces maximum melt index). Notice that again the same maximum level Cr(VI) resulted, however, it now requires a higher loading to achieve that level. The initial slope is no longer unity, indicating that right from the beginning some of the Cr is never oxidized at this temperature.

Line 6D represents a more extreme case of this same phenomenon. Sometimes called the "fluxing" treatment [11,12], the support was first impregnated with Cr, then calcined in dry air at 650 °C to fully oxidize the Cr into the hexavalent form. Then it was calcined for 3 h in nitrogen up to 870 °C. This causes the Cr(VI) to largely decompose into alpha-Cr_2O_3 and when conducted at high temperature in the presence of some Cr(VI) to act as a "flux," large crystallites are formed. The catalyst was then also treated with CO at 870 °C followed by reoxidation at 760 °C (which produces maximum melt index). In this case both the initial slope and the final Cr(VI) level reached are still lower than previous experiments.

In each of the four experiments in Fig. 6 the support was calcined at 870 °C, but a progressively higher secondary temperature was needed to oxidize the Cr to a reasonable value, and to achieve the maximum melt index. This indicates increasing difficulty in re-dispersing the Cr. Thus both the state of the Cr, and also the thermal history of the support, contribute to the maximum Cr(VI) level obtained.

Commercial activation often provides further evidence that alpha-Cr_2O_3 can be difficult to reoxidize. The typical 1% Cr catalysts can be easily activated in the laboratory at 800–900 °C, achieving full conversion to Cr(VI). However, when activated in the commercial process at perhaps 20 times the bed depth and a corresponding increase in moisture level, much, or even most, of the chromium remains in the trivalent state as alpha-chromia. An example is shown in Table 2, comparing a laboratory activation of EP30X from Ineos Co. to a commercial activation of the same catalyst. Thus although the silica surface is capable of holding more Cr(VI), coverage remains low in the commercial activation.

This has usually been attributed to the difficulty of reoxidizing the large, relatively inert, crystallites of alpha-chromia [4,10]. Commercial activations produce less Cr(VI) because of the higher levels of moisture released into the deeper bed, which destabilize Cr(VI). However, near the end of these 12–15-h hold periods at maximum temperature, moisture levels decrease significantly, without restoring the Cr(VI) back to lab-generated values. Similarly, one can see in Table 2 the results obtained from a low-Cr(VI) catalyst, formed by commercial activation, by reactivating it in the usual laboratory procedure. Only about 11% of the lost Cr(VI) was restored. Longer times in the laboratory restored more of the lost Cr(VI) but even a 72-h hold recovered only about a third of the lost Cr(VI). This suggests that the alpha-chromia formed from commercial activation is indeed very difficult to reoxidize within the usual industrial time frames.

We wondered if the degree of hydration of the silica surface might contribute to the ease of reoxidizing alpha-chromia. In one experiment in Table 2 the same commercially activated catalyst was soaked in liquid water for 24 h in order to rehydroxylate the surface. Then it was dried to retain all forms of Cr, and finally reactivated in the laboratory. The Cr(VI) was no different from the same catalyst after a similar lab activation without the water treatment.

In still another experiment listed in Table 2, Cr(VI) was removed from the commercially activated catalyst by leaching with water. Only the Cr(III) remained. Then the catalyst was dried and reactivated in the laboratory, yielding 0.103% Cr(VI). Again no major recovery of the lost Cr(VI) was observed.

Finally, in the last experiment in Table 2, the commercial catalyst was impregnated with an aqueous solution of an additional 1% Cr as chromium(III) acetate. When this catalyst was dried and reactivated, it did result in a major improvement of Cr(VI), generating almost the expected full saturation level. In

Table 2
Difficulty of oxidizing Cr_2O_3

Treatment of 1% Cr/silica catalyst	Calcined	% Cr(VI)
Lab activation	5 h, 857 °C	0.957
Commercial activation	12 h, 857 °C	0.363
Further treatment of commercially activated catalyst		
Lab reactivation	5 h, 857 °C	0.427
Lab reactivation	12 h, 857 °C	0.445
Lab reactivation	72 h, 857 °C	0.576
Soak 24 h in water, dry, then lab reactivation	5 h, 800 °C	0.427
Remove Cr(VI) by water leaching, then lab reactivation	5 h, 800 °C	0.103
Impregnate 1% Cr(III) as acetate, then lab reactivation	5 h, 800 °C	0.866

Note. EP30X (1% Cr/silica) calcined in dry air in all; lab = 4 in bed, commercial = 7. 7 ft bed.

this case the new source of Cr was fully capable of oxidation to Cr(VI) and dispersion throughout the silica surface.

All of these results suggest that the alpha-chromia formed from commercial activation is indeed difficult to reoxidize within the usual industrial time frames. This conclusion might seem to contradict some of the migration results reported above, where significant reoxidation of alpha-chromia did occur, followed by redistribution onto a fresh silica surface. This is especially true in Experiments 3, 4, and 6 (Table 1). Clearly the reoxidation was more vigorous when the Cr was allowed to spread out onto a virgin, as opposed to a calcined, surface. In fact, Experiment 6 used the same commercially activated EP30X described in Table 2. These seemingly opposing results require some attempt at explanation.

During activation, the alpha-chromia is probably in equilibrium with surrounding Cr(VI), which exists both on the surface of the alpha-Cr_2O_3 crystallites [11,12], and also on the neighboring silica surface. Thus it is conceivable that the ease of oxidation of alpha-chromia depends on the size of the crystallites and also on the concentration of Cr(VI) on the silica surface surrounding the crystallites. A surrounding surface relatively low in Cr(VI) may provide the strongest driving force for redistribution of Cr from the crystallites. Thus a large crystallite of alpha-chromia may redistribute more easily onto a virgin silica containing no Cr(VI), when available, than onto its own silica support already containing a medium level of Cr(VI). In essence, the alpha-chromia expands onto the empty surface to fill a Cr vacuum. No doubt the large ratio of catalyst to silica used in these experiments helped this process.

The following experiment demonstrates that principle. The commercially activated catalyst in Table 2 was diluted with various amounts of virgin silica, from 0 to 3 parts of silica per part of Cr/silica. Then each mixture was co-activated at 800 °C in dry air for 5 h. Fig. 7 plots the conversion of Cr to Cr(VI) after co-activation. The amount of alpha-chromia reoxidized to Cr(VI) was not constant, but instead it depended on the amount of silica added to the mixture. Fig. 7 also shows that although the overall conversion of Cr into Cr(VI) increases with the amount of silica, the final Cr(VI) level, now distributed over both silica sources, actually decreases. This is probably the driving force for the migration, and it also explains why alpha-chromia cannot so easily be reoxidized on the original catalyst surface.

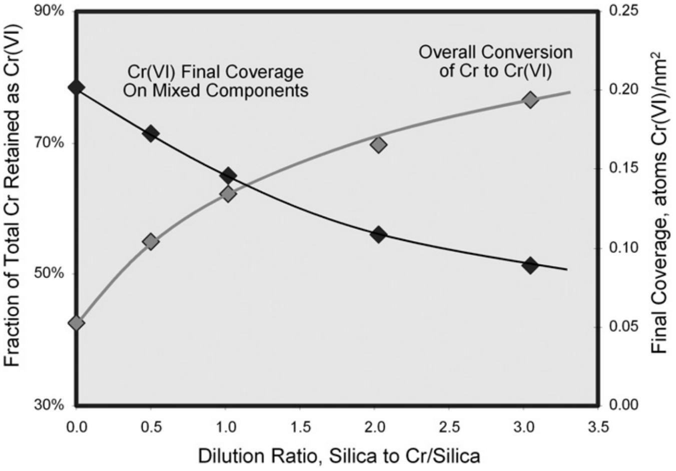


Fig. 7. Co-activation of 857 °C Cr/silica and virgin silica in dry air.

3.9. Migration between aluminas

Similar tests were also made to determine whether Cr(VI) could transfer between alumina bases. Fig. 8 plots the result of co-activating 1 part virgin Cr/alumina with approximately 3 parts virgin alumina at various temperatures (Experiment 7). Line 8A shows the saturation behavior of Cr/alumina, and also represents the level of Cr(VI) expected if no Cr migration occurs. Line 8B shows line 8A multiplied by approximately four, representing the maximum level of Cr(VI) that can be stabilized by both supports if full migration occurs. Line 8C shows the actual observed results. Although the test becomes more uncertain for alumina, it is still obvious from these three lines that the same pattern of Cr migration seen between silicas also applies to aluminas. At 400 °C the results are inconclusive, but migration can be clearly seen at temperatures as low 500–600 °C. At 900 °C the transfer reached about 60% of the value expected from full equilibration. This behavior is similar to what was observed between virgin silicas in Fig. 3 under the same conditions.

The two alumina components were also calcined before mixing and co-activation to determine what effect this had on the Cr migration. Cr/alumina, previously calcined at 900 °C, was mixed with three parts alumina, which had also been calcined at 900 °C (Experiment 8). These two components were mixed

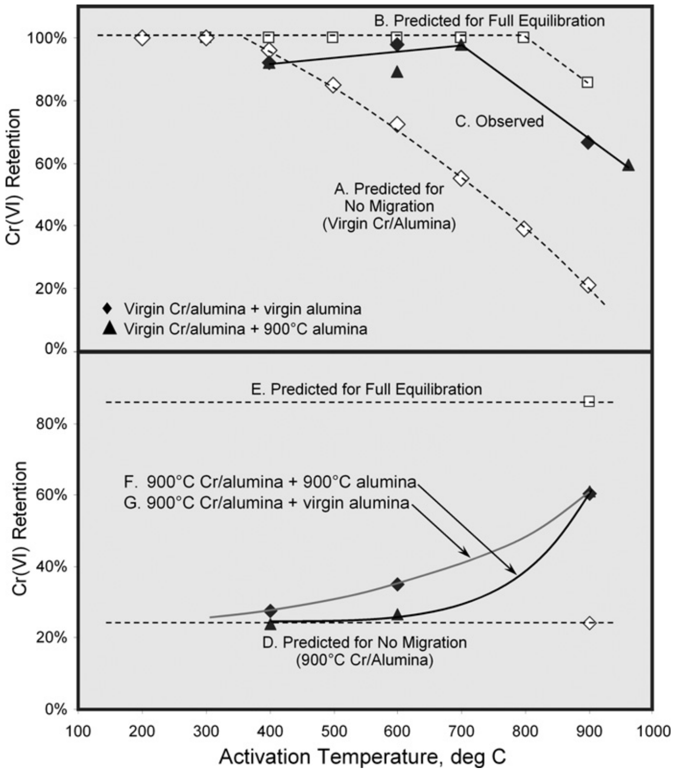


Fig. 8. Cr migration between alumina particles during activation in O_2.

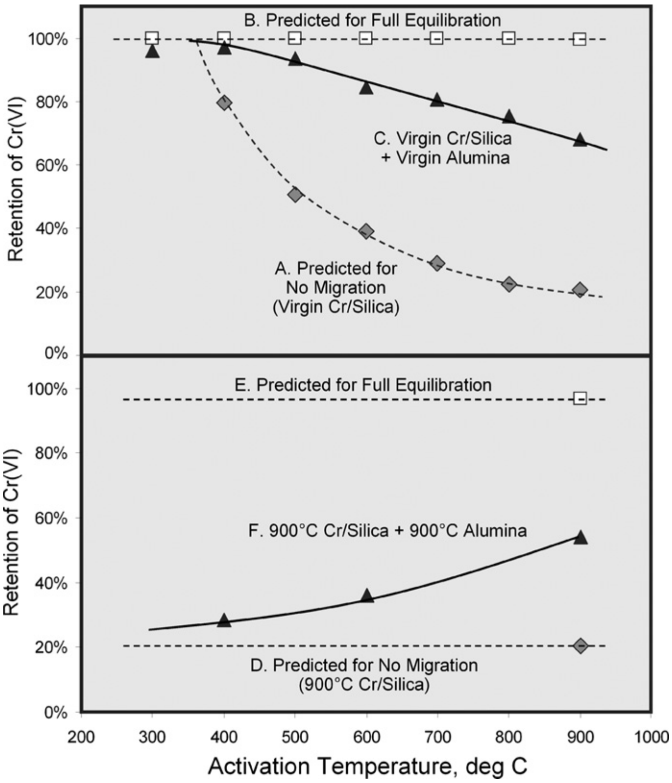


Fig. 9. Cr migration from silica to alumina during activation in O_2.

and then co-activated in oxygen at various temperatures as described above. The results of these experiments are also shown in Fig. 8. Line 8D shows the values expected from no Cr transfer, and line 8E shows the maximum amount of Cr(VI) that can be stabilized by both supports, representing full transfer. Line 8F shows the actual experimental results obtained. No migration at all was observed at 400 °C, and barely a trace at 600 °C. By 900 °C, however, Cr transfer did occur, achieving about 60–65% of the value expected from full equilibration. Again this behavior is very similar to that observed between calcined silicas in Fig. 3. It is another indication that the extent of surface annealing or dehydration strongly influences the transfer of Cr(VI).

Fig. 8 also plots the degree of Cr migration when only one of the two alumina components was pre-calcined. Another set of points in Fig. 8 (near line 8C) shows the results of mixing virgin Cr/alumina with alumina that had already been calcined at 900 °C, followed by co-activation at various temperatures (Experiment 9). At 400 °C it is not clear whether migration occurred, but given the result in Fig. 8F, it seems likely that little transfer may have occurred. Some migration can be seen at 600 °C and at 900 °C about 70% of full equilibration was reached. Thus the transfer behavior between aluminas was similar to that observed between silicas, in Fig. 3.

Fig. 8 also shows the opposite combination. Calcined Cr/alumina was co-activated with virgin alumina (Experiment 10). Line 8D shows the expected behavior from no transfer, line 8E from full transfer, and the experimental results are shown in line 8G. At 400 °C little or no migration occurred. Even at 600 °C only about 6% of full equilibration was reached. At 900 °C, however, migration became more significant occurred, reaching about 59% of full equilibration. Thus once again the transfer behavior between aluminas seems very similar to that between silicas, as shown in Fig. 3 for comparison.

3.10. Migration between silica and alumina

Chromium could also be transferred during co-activation from silica to alumina and vice versa. Fig. 9 shows the results of an experiment in which virgin Cr/silica was mixed with virgin alumina in approximately a 1:3 ratio, then co-activated in oxygen at various temperatures for 24 h as described above (Experiment 11). Line 9A represents saturation from Cr/silica alone, indicating no migration. Line 9B represents the combination of full saturation by both the silica and alumina components at each temperature. The actual results are plotted in line 9C. Transfer from silica to alumina seemed to be very similar to that from silica to silica in Fig. 3. Mobility was observed at the lowest temperature tested, 400 °C. By 900 °C transfer had reached about 60% of full equilibration.

Transfer was also possible from calcined silica to calcined alumina (Experiment 12). Fig. 9 plots the results obtained when Cr/silica, previously calcined at 900 °C, was co-activated with three parts of alumina, also previously and individually calcined at 900 °C. Again the experimental results are plotted in line 9F, to be compared to lines 9D and 9E. The transfer behavior was once more very similar to that between two calcined silicas, shown above in Fig. 3. Little or no migration was observed after co-activation at 400 °C. Slightly more was observed at 600 °C,

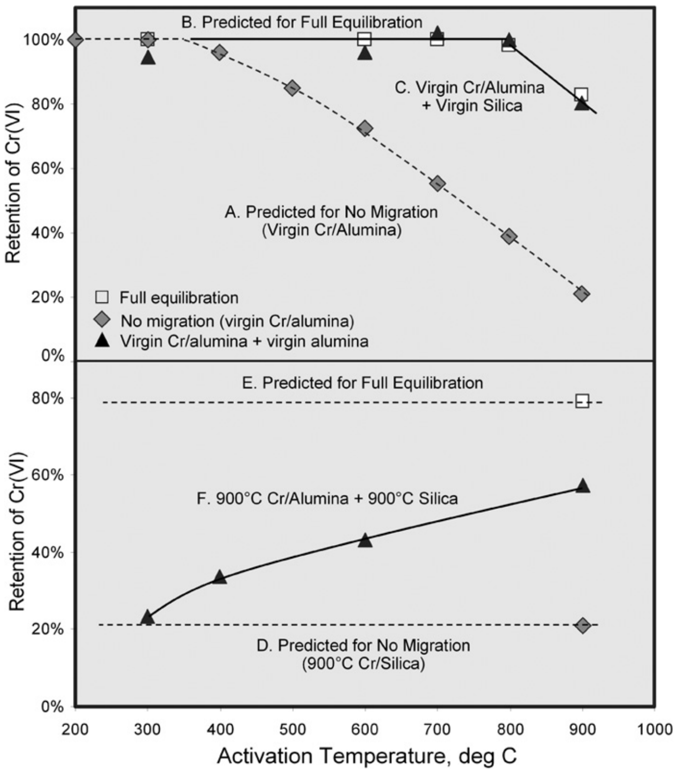


Fig. 10. Cr migration from alumina to silica during activation in O_2.

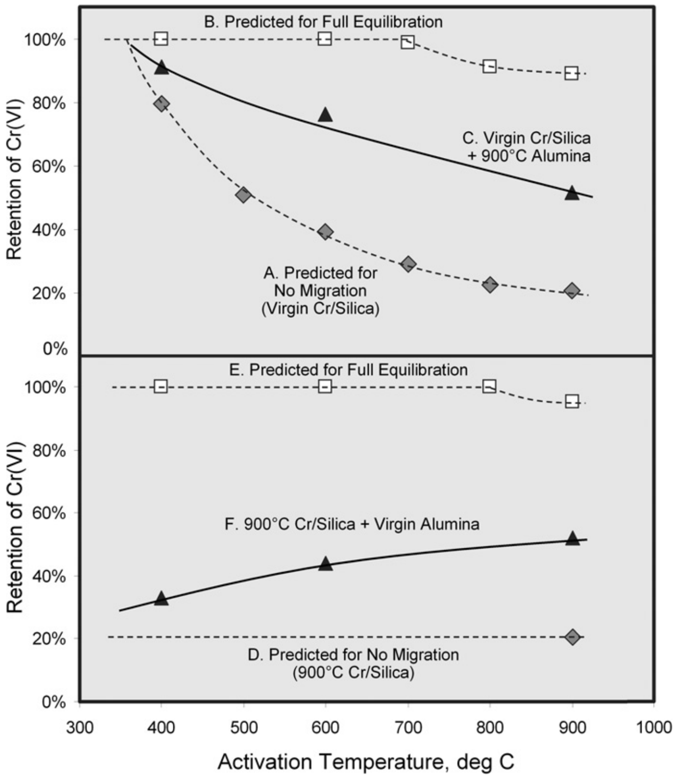


Fig. 11. Cr migration from silica to alumina, one component calcined.

and significantly more at 900 °C, where 44% of full equilibration was reached.

Transfer in the opposite direction, from alumina to silica, seemed to occur a little more willingly as shown in Fig. 10. Line 10C plots the results of an experiment in which virgin Cr/alumina was mixed with virgin silica in a 1:3 ratio, then co-activated as before (Experiment 13). Line 10C is to be compared to line 10A (no transfer) and line 10B (full transfer). At all temperatures 100% of the Cr was stabilized in the hexavalent form. Table 1 shows that how this translates into a fraction of the full transfer value. All numbers above 700 °C are quite high. At 900 °C the transfer was 100% of equilibrium, the only such case where this value was reached.

Migration from calcined alumina to calcined silica (Experiment 14) is also shown in Fig. 10. Line 9F plots the results obtained from co-activation of 900 °C Cr/alumina with three parts of 900 °C silica. Again it is to be compared to lines 10D (no transfer) and line 10E (full transfer). The pattern of migration is familiar in that little transfer occurred at low temperatures, but transfer became more significant at higher temperatures, reaching 63% of equilibration was at 900 °C. In both cases, calcined and uncalcined, more transfer seemed to occur from alumina to silica than from silica to alumina.

Finally two other experiments were also performed in which Cr was transferred from silica to alumina, shown in Fig. 11. In Experiment 15 virgin Cr/silica was co-activated with alumina that had already been calcined at 900 °C. This is plotted in line 11C, to be compared with 11A and 11B. Migration was low at 400 °C, and by 900 °C it had reached about half the equilibrium value. Also in Fig. 11 the opposite combination was used. Cr/silica, previously calcined at 900 °C, was co-activated with virgin alumina (Experiment 16). These results are shown in line 11F, to be compared to lines 11D and 11E. Little transfer occurred at 400 and 600 °C, but by 900 °C about 46% of the equilibrium value was reached.

3.11. Particle-to-particle contact

If the mechanism of Cr migration is dependent on particle-to-particle contact, then it seems likely that the type of contact (fixed or fluidized bed) should be important, as well as the particle size of the components. Early published work used a fixed bed type of contact in which, before co-activation, the two components were ground together in a mortar [2,3] followed in one case by granulation. While not actually stated, this may have resulted in some very intimate contact between the two components. Two of these studies even used pyrogenic silica, where the effective particle size may be sub-micron [1,3]. In contrast, the present study has investigated the use of a fluidized bed, using 50–100 µm average particles, in order to faithfully represent commercial activation conditions. Assuming that the components are fully mixed, one might expect inter-particle contact to be more intense in a packed fixed bed. In contrast, the fluidized bed takes up more volume because the particles are floating in the air, providing less time in contact with other particles. However, this presumed disadvantage may be offset by the constantly changing network of contacts in a fluidized bed, which might discourage local gradients from forming around particles.

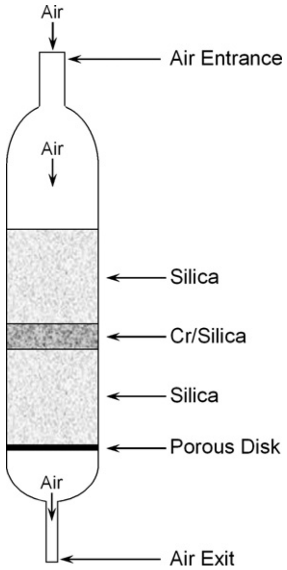


Fig. 12. Fixed bed with layered components.

For comparison between a fixed and fluidized bed, several experiments were done with these same silica and Cr/silica components. In one experiment the same activator tube used for fluidization was first filled with 10 cm of white virgin silica in a static bed. Then a layer of about 1 cm of green Cr/silica, activated commercially at 900 °C, was added on top of the silica bed. Finally another 10 cm layer of silica was added on top, so that the Cr/silica was sandwiched between two silica layers. Then a reversed gas flow was turned on. That is, dry air was introduced from the top of the tube, instead of the bottom. Air was forced to flow down through the bed instead of up, so that the bed remained fixed. Otherwise all conditions were unchanged, including the amount of air flow. This arrangement is shown in Fig. 12. The temperature was raised at 150 °C/h to 900 °C where it was held for 24 h.

When the experiment started there was a sharp demarcation between the layers. Since the Cr/silica had a dark green color, the boundary was easy to see visually. From particle-to-particle contact, it was expected that migration would cause a blurring of the layer boundaries, upper and lower, as Cr gradients formed due to macroscopic movement of Cr into the silica layers. In contrast, any movement through Cr evaporation would be expected to occur only in a downward direction. However, after the experiment was concluded the boundary demarcations were still found to be very sharp. A yellow transition band of only about 0.5 to 1 mm was seen at the upper and lower interface of the two layers. The experiment was then repeated with virgin 5% Cr(VI)/silica sandwiched between virgin silica, and the fixed bed was calcined 24 h at 400 °C. The same sharp demarcation of both boundaries was maintained during the experiment.

This result suggests that there is considerable resistance to Cr flow. Probably a particle of Cr/silica at the boundary does lose some fraction of its Cr into its immediate contact sphere of silica particles. Those recipient particles in turn then pass on an even smaller fraction of their Cr to their sphere of contacted particles. Thus a sharp gradient develops in a short distance and the drive for bulk flow is lost. In contrast, a fluidized bed continually exposes each Cr/silica particle to a well-mixed representative sample of the un-promoted silica particle population.

Another type of fixed bed experiment was also carried out. Into the same type of activator tube was added a 50/50 mixture of the same virgin silica and green 900 °C commercial Cr/silica sample described in the above experiment. In this case, however, the two components were allowed to fluidize for an hour at room temperature to ensure homogeneous mixing. Then the air flow was reversed to create a fixed bed of already mixed components. Activation was carried out again at 900 °C with air flow from the top to prevent particle movement. Reoxidation of the Cr(III) occurred very quickly in this environment, indicating movement of the Cr. When the tube had been at 900 °C for only 1 h, it was cooled and examined. The bed had already changed from green to orange-beige, indicating a very fast migration in the fixed bed. After 5 h at 900 °C the sample had turned completely orange. The Cr(VI) values obtained are listed in Table 3, where it can be seen that after 5 h about 95% of the Cr had become hexavalent. The success of Cr transfer in this fixed bed experiment, compared to the failure of Cr transfer in the above fixed bed, again suggests a very limited transfer distance. That is, Cr probably transfers (in this time frame) from a Cr/silica particle to a shell of surrounding particles that are only few particles deep. When the bed is already well mixed, this is not a handicap.

Finally one additional experiment was also carried out. For comparison, the same activation described above using a 50/50 mixture activated using a fixed bed, was identically repeated but with the air flow reversed to create a fluidized bed. Air flow and temperatures used were unchanged. After 1 h at 900 °C the fluidized bed had also taken on an orange-beige color, and was almost indistinguishable from the fixed bed catalyst. After 5 h it had also turned orange. The Cr(VI) values are listed in Table 3, and are almost indistinguishable between the two bed types. Thus, at least in this experiment, the two modes of activation, fixed and fluidized bed, seemed to be similarly effective provided the fixed bed is pre-mixed. Thus even if the inter-particle contact is more intense and prolonged in a well-mixed packed bed, the fluidized bed completely compensates by providing a constantly changing network of contacts, which probably helps to discourage local gradients.

4. Conclusions

The saturation coverage behavior of Cr(VI) has been used to show that hexavalent chromium is mobile during activation, migrating within each silica particle, and even from one particle to another. Migration of Cr was observed at temperatures as low as 300–400 °C in these experiments, and may occur at even lower temperatures, although this could not be established by the present technique. Transfer can take place even in the absence of oxygen, which suggests that redox cycling is probably not the main method of mobility. However, the migration is nearly stopped at 400 °C if the components, or even one of them, has first been dehydrated at 900 °C. The migration then resumes at 900 °C. This could be interpreted to mean that water, or perhaps surface silanol groups, are involved in the migration.

Table 3
Comparison of Cr transfer in fixed versus fluid bed

First component	Second component	Co-activation[a] at 900 °C	Fixed bed results		Fluid bed results	
			% Cr(VI)	Conversion to Cr(VI)	% Cr(VI)	Conversion to Cr(VI)
850 °C Cr/silica	None	None	0.525	58%	0.525	58%
850 °C Cr/silica	Virgin silica[a]	1 h	0.341	81%	0.352	80%
850 °C Cr/silica	Virgin silica[a]	5 h	0.401	95%	0.417	94%

[a] Co-activation in same dry air flow. Cr/silica to silica blend ratios, fixed bed: 1.14 to 1, fluid bed: 1.03 to 1.

However, adding water to the gas stream to create 100% humidity did not restart the migration at 400 °C between the calcined components. An alternate interpretation of these facts is that Cr mobility depends on surface mobility, and that high temperature annealing modifies the surface to reduce its mobility at lower temperatures.

In agreement with some earlier reports, all of this behavior suggests that the mechanism of transfer is likely to be particle-to-particle contact during the fluid bed calcining process. One might still argue that the actual transfer is due to localized Cr evaporation and re-adsorption, but it is unclear why vaporization would depend on prior annealing history as observed above. We were unable to find evidence of Cr loss during calcining under these commercial conditions.

Alpha-chromia, a by-product of commercial activation, is indeed very difficult to reoxidize and redistribute onto the original catalyst surface. In this sense these crystallites deserve their reputation for being almost inert. The degree of inertness probably depends on the size of the Cr_2O_3 crystallites, which in turn may be influenced by their thermal history. In contrast, these same deactivated alpha-chromia/silica catalysts readily reoxidize and redistribute the Cr when co-activated with an excess of virgin silica. A possible explanation for these seemingly contradictory facts may be that the alpha-chromia crystallites are in equilibrium with Cr(VI) on the surrounding surface. Adding a large excess of virgin silica draws away the surrounding Cr(VI), lowering its concentration around the crystallites, thus driving a larger overall conversion of alpha-chromia to Cr(VI). In agreement with this idea, the amount of reoxidation was found to be a function of the amount of extra support added, as if the Cr expands to fill the available "space" up to a certain concentration.

The fixed-bed experiments also seemed to suggest that the available "space" offered by the silica is limited to a very short distance. Cr was only capable of moving from a Cr/silica particle through a shell of silica neighbors about 1 mm thick. Otherwise the resistance to flow became overwhelming, and the driving force for Cr movement was not transmitted over much of a distance. Prior mixing, or a continually fluidized bed, avoids this limitation.

The "space" offered by a silica surface must also depend on its thermal history. Catalysts activated at 400 °C can hold more Cr(VI) than those activated at 900 °C. Once annealed at 900 °C, however, the coverage cannot be reversed by a second activation at 400 °C. This seems to be a function of the surface condition itself, and not of the chromium. For example, silica alone can be calcined at 900 °C and then impregnated anhydrously with Cr. When finally activated at 540 °C, it takes on the Cr(VI) coverage of a catalyst activated at 900 °C [10].

Alumina behaved much like silica in these same respects. Transfer of Cr between alumina particles readily occurred, although again migration was inhibited at 400 °C when the alumina components had first been calcined at 900 °C. Cr also transferred between silica and alumina particles in both directions. Although counter-intuitive, migration seemed to be more complete when the Cr moved from alumina to silica, rather than the reverse. It is unclear whether this behavior is universal or just a result of the experimental conditions chosen.

Migration at low temperature was severely inhibited when one of the components had been pre-calcined at 900 °C. However, given that all of these experiments ended with a 900 °C exchange, one might expect a similar final result from all. Indeed, in most experiments the extent of transfer at 900 °C was similar, reaching about 60–70% of full equilibrium (Table 1). Of all the possible combinations tested, the most migration seemed to occur when the donor was virgin alumina and the recipient was virgin silica, where full equilibration was reached at 800 °C if not lower. Transfer between virgin silicas was also quite high. It is conceivable that in some cases, significant Cr movement occurs between the virgin materials before reaching 900 °C, that is not necessarily duplicated at 900 °C.

Finally, Cr mobility has some important implications for commercial usage. For example one need not worry about inhomogeneous impregnation of Cr, as happens during some spray drying operations. Redistribution of Cr is expected during activation. On the other hand, cross-contamination of un-promoted supports by Cr can be seen as likely if care is not taken during activator clean-out. This in turn can result in imperfections in film grade polymers.

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