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The Effect of Alkali Metal Doping on the Performance of Cr/Silica Catalysts in Ethylene Polymerization

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Sodium contaminants are known to promote sintering of silicas during calcination at high temperatures such as 900°C. This study examines the effect of doping the Phillips Cr/silica polymerization catalyst with larger amounts of various alkali metals followed by calcination at milder temperatures, like 500–700°C. The presence of 0.8 mmol of extra alkali metal per gram of catalyst shifts the sintering process about 300–400°C lower in temperature. Both Cr/silica and Cr/silica-titania catalysts were similarly affected. The effect on the physical properties of the catalyst and on catalyst performance during the polymerization of ethylene have been investigated. Activity, melt index potential, and polymer molecular weight distribution were all influenced to varying degrees, depending on the amount of alkali metal added. These responses were then compared to that of sintering the undoped catalyst at higher temperatures. © 1998 Academic Press

INTRODUCTION

The Phillips Cr/silica ethylene polymerization catalyst is used in the manufacture of a major portion of the world's 40 billion pound high density polyethylene supply. During this production the type of silica used and its calcination history are of great importance in determining, not only the activity of the catalyst, but also the type of polymer it yields (1, 2). For example, the melt index potential of the catalyst, which is related to the molecular weight of the polymer produced, is no less important to plastics producers than the activity (3). The catalyst must be calcined to develop activity and in general the higher the calcination temperature, the better (higher) the melt index potential and the activity of that catalyst will be. Changes in the active site bonding and coordination with the surface are thought to cause this behavior (2).

At some temperature, however, usually around 900°C, commercial silicas begin to sinter, which causes a loss of surface area and porosity (3). The polymerization behavior of the catalyst is highly influenced by its porosity (2). Thus calcination above the sintering temperature results in a decrease in both the activity of the catalyst and its melt index potential.

That alkali metals can promote sintering of silica by acting as a flux at high temperatures like 900°C has long been appreciated (4, 5). Commercial silica manufacturers, who typically use sodium silicate as a feedstock, take great care to wash, or ion exchange, out the last traces of residual sodium ions from their polymerization grade silicas. To fail to do so would enhance sintering at the highest calcination temperatures. The effect of sodium ion is to promote the making and breaking of Si–O–Si bonds, which increases the mobility of the structural elements.

Despite general acceptance of this phenomenon and its importance, we are aware of no published studies which have deliberately examined the effect of alkali metal doping on the Cr/silica catalyst and its performance in ethylene polymerization. In fact, at lower calcination temperatures the effect of small amounts of alkali metal, if any, has not been reported to our knowledge. Therefore in this paper we have examined the behavior of some typical commercial catalysts before and after doping with alkali metal in an effort to better characterize the process.

EXPERIMENTAL

Aluminophosphate catalysts were made for this study by quickly neutralizing with ammonium hydroxide a concentrated solution of aluminum nitrate and ammonium phosphate. The gel was washed, dried, and then impregnated with a solution chromium nitrate to equal 1 wt% Cr (10). Silica-titania catalysts were made by adding sodium silicate solution to a concentrated aqueous solution of titanyl sulfate and sulfuric acid. Gellation occurred at pH of 5 to 6, and afterward the gel was "set" at a pH of 7 to 8 at 80°C for 5 h. After thorough washing to remove sodium down to less than 0.05% soda, the gel was azeotropically dried by refluxing in ethyl acetate to remove water. During this step, aqueous chromic acetate solution was added to make the finished catalyst 1.0% Cr. The gel was then calcined at 425°C (6).

Catalysts were doped with alkali metal as follows; The dry catalyst was usually impregnated with a 0.1 *M* solution

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of the formate salt dissolved in methanol. For lower loadings, a lower concentration of the alkali metal formate in methanol was used so that the catalyst would at least be impregnated to incipient wetness. Afterward, the methanol was evaporated on a hot plate, followed by vacuum drying overnight at 100°C.

Catalysts were calcined as follows: About 10 g was fluidized in a dry air stream for 3 h at 350–850°C, as specified in each experiment. A quartz tube was used with sintered glass disk to support the sample, which was heated to temperature at 400°C/h with a 1-cm/s flow rate through the bed. Before use, gasses were dried through activated alumina, or where possible through CO-reduced Cr/SiO_2 pellets to remove the oxygen as well.

Activity tests were conducted under slurry conditions at temperatures between 105 and 109°C, as indicated in each experiment. The reactor consisted of a stainless steel 2-liter stirred autoclave. A pressurized jacket filled with boiling alcohol held the internal temperature of the reactor constant to within 0.5°C. About 0.05 g of the catalyst was charged under dry nitrogen, then one liter of liquid isobutane diluent, and finally ethylene was supplied on demand at 550 psig unless otherwise stated until about 200–250 g of solid polyethylene had been made. Under these conditions the polymer does not go into solution but remains as a slurry. The rate of polymerization was followed by monitoring the flow of ethylene into the reactor through a calibrated differential pressure cell. Isobutane and ethylene stock were Phillips polymerization grade, further purified through activated alumina and, in the case of isobutane, through a CO-reduced Cr/SiO_2 column. When an aluminophosphate catalyst was tested, it is common and preferable to use triethylboron (TEB) cocatalyst as an activity enhancer (15, 16). Such co-catalysts act by accelerating the reduction of initial hexavalent chromium to the lower valent active state. They may also assist with the initial alkylation of the site. Thus, in aluminaphosphate runs, TEB was added to the isobutane as a cocatalyst in the concentration of 5×10^{-5} moles/liter of the reaction diluent, or generally about 5 B/Cr. In the study using chromium on Davison Grade 952 silica, triethylaluminum was used a cocatalyst at 8 ppm of the isobutane to improve activity. Thus the effect of alkali metal doping was seen under three different, but common, commercial modes of operation.

Melt index (MI) and high load melt index (HLMI) values were obtained from the resultant polymer at 190°C according to ASTM procedures (8). Inherent viscosity measurements were taken on a Schott Automated Viscometer, with Ubbelohde type Oc orifice using solutions of polymer in 1,2,4 trichlorobenzene at 130°C (9). Size exclusion chromatography was done at 140°C on a Waters model 150 GPC equipped with infrared detector. The solution concentration, 0.25% polymer in 1,2,4 trichlorobenzene, was chosen to give reasonable elution times.

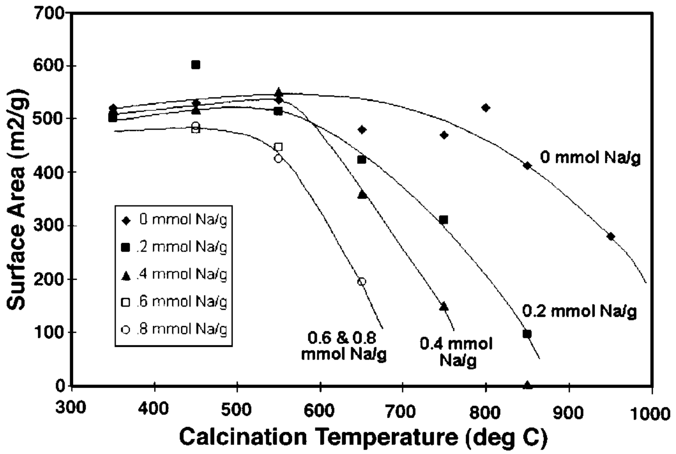

FIG. 1. Surface area of Cr/silica-titania catalysts doped with various levels of sodium formate and calcined at the temperature indicated.

RESULTS

Figures 1 and 2 show the effect of sodium on the physical properties of a commercial catalyst as measured by nitrogen sorption. In this case the starting material was a Cr/silica-titania containing 8.3 wt% titania. Titania is added as an activity promoter, and it also tends to broaden the molecular weight distribution on the low MW side (6). This catalyst was chosen for the experiment because the initial surface area and pore volume were both rather high, at 500–550 m^2/g and 2.1 cc/g, and the initial sodium content was low, at 0.01 mmoles Na per gram of catalyst. Samples of this catalyst were impregnated with a methanol solution of sodium formate to yield various levels of sodium on the surface. After evaporation of the methanol solvent each sample was calcined at various temperatures by fluidization in dry air for three hours.

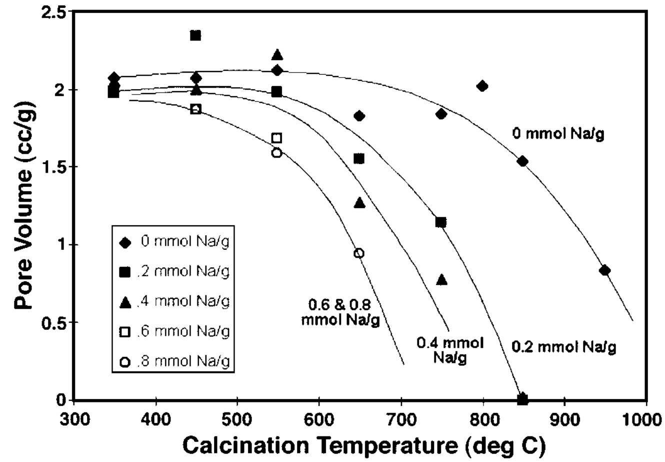

FIG. 2. Pore volume of Cr/silica-titania catalysts doped with various levels of sodium formate and calcined at the temperature indicated.

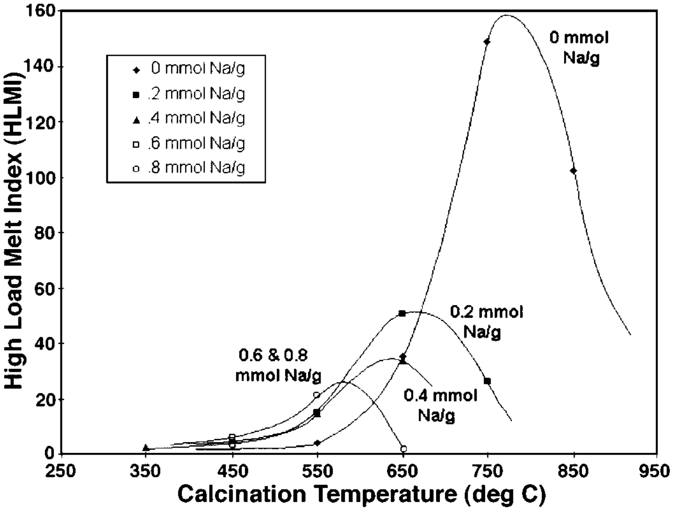

FIG. 3. Cr/silica-titania catalysts were doped with various levels of sodium formate, calcined at the indicated temperature, then tested for ethylene polymerization at 105°C. Plotted is the high load melt index (21.6 kg) of the polymers obtained.

Notice in Fig. 1 that in the absence of extra sodium there is no great loss of surface area until after 900°C. As the sodium level was raised, however, not only did the loss at 900°C become more pronounced, but the sintering process itself commenced at lower temperatures. When the catalyst contained 0.8 mmol Na/g serious sintering began at as low as 550°C. Notice also that in terms of sintering, calcining the untreated catalyst at 850°C, the point of optimal performance, is equivalent to calcining the 0.2 mmol Na/g catalyst at 650°C, or the 0.8 mmol Na/g catalyst at 550°C, etc.

Figure 2 shows the pore volume of these samples, which can also serve as a gauge of sintering. Notice that the pattern is very similar to that in Fig. 1, and thus the remarks above also apply. It has long been observed that frequently during sintering the pore volume decreases roughly in proportion to the loss in surface area, leaving pores of similar size, although fewer in number (4, 7). Notice that this also seems to apply in Figs. 1 and 2, approximately, whether the sintering is caused by sodium or not.

Figure 3 shows the melt index potential of these catalyst samples. Melt index is a measure of how much of the molten polymer can flow through a standard orifice under a set pressure in 10 min, and it is very important to resin producers and users (8). In general a high melt index, indicating a less viscous polymer and thus normally a lower molecular weight, is considered desirable for production. Figure 3 plots the high load melt index, or HLMI, which refers to a specific test condition (21.6 kg). The regular melt index, or MI (2.16 kg), was also obtained but is not shown because it yielded essentially the same pattern.

Notice in Fig. 3 that the melt index potential rises with the calcination temperature up to a maximum of near 750–850°C for samples containing no added sodium. This behavior has been reported previously (3). Dehydroxylation of the silica surface results in an increase in chain transfer up to the point where sintering begins. The presence of sodium, however, shifts this curve to lower temperatures, which parallels the shift due to the sintering described in Figs. 1 and 2. The more sodium that is added, the greater the shift. In similar tests with the Group II metals calcium, magnesium, and strontium, this effect was not observed.

However, it would be a mistake to conclude that the presence of sodium merely shifts the normal chemistry to lower temperatures, because the maximum melt index values achievable without sodium were not possible at lower temperatures with sodium. Maximum melt index values obtained with 0.2 mmoles Na/g added were less than half that obtained from the untreated catalyst. Thus the situation is a bit more complicated than a simple shift of events to lower temperatures.

Despite the lower melt index maxima, however, the effect of sodium could be viewed as positive in one sense. Notice that at the lower calcining temperatures like 650°C, which is commonly used in commercial operations, the sodium-treated catalysts often exhibit more melt index potential than those not treated. This effect will be shown in more detail below.

Figure 4 shows another measure of viscosity, the inherent viscosity (IV) of the polymer in solution (9). Although inversely related to melt index, it reveals a similar trend. IV decreases with calcination temperature for undoped catalysts, going through a minimum near 750–850°C. Catalysts doped with sodium exhibited the same pattern but shifted to lower temperatures and higher minima.

Of course the pattern of melt index and inherent viscosity curves are due to the changing molecular weight of the polymer. Usually molecular weight is more difficult to measure than IV or MI, and the results are not as

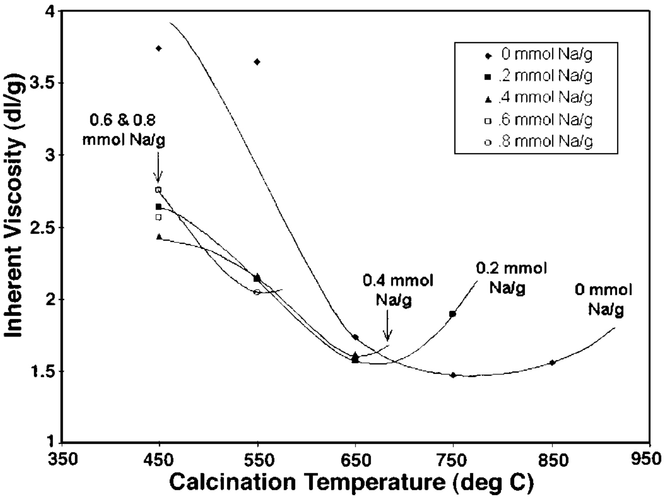

FIG. 4. Inherent viscosity of polymers obtained from sodium doped Cr/silica-titania catalysts calcined at the indicated temperature.

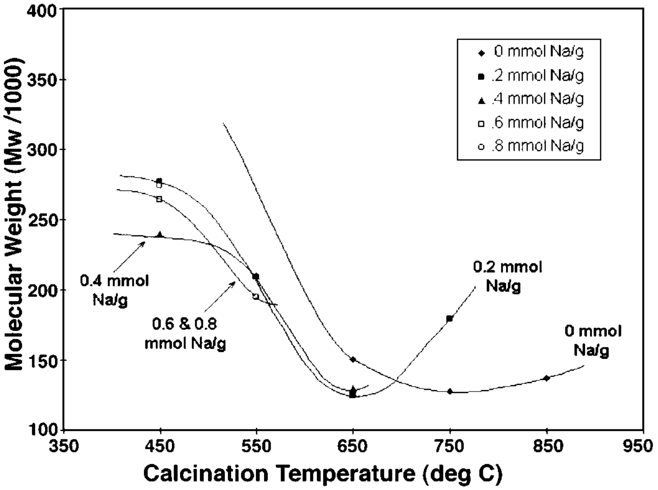

FIG. 5. Weight average molecular weight of polymers obtained from Cr/silica-titania catalysts doped with sodium formate and calcined at the indicated temperature. Polymerization at 105°C and 550 psig.

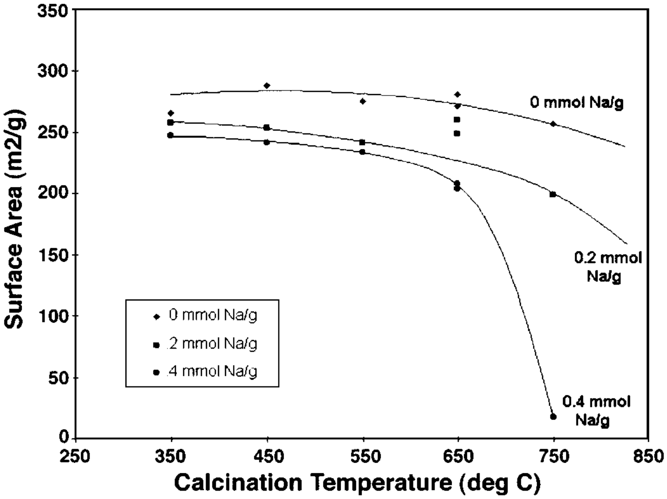

FIG. 7. Surface area of sodium doped Cr/silica catalysts made from Davison Grade 952 silica and calcined at the temperature indicated.

accurate. Nevertheless some measurements of weight average molecular weight were made by gel permeation chromatography on these samples and the results are plotted in Fig. 5. The pattern resembles the inherent viscosity plot in Fig. 4, as expected. Mw decreases with calcination temperature down to a minimum near the sintering temperature. Adding sodium causes a downward shift in that transition temperature.

Figure 6 plots the activity of these catalyst samples. Here the pattern seems to be different. Activity rises with the calcination temperature for untreated samples, reaching a broad peak at 750–850°C. The sodium-doped samples display comparable activity to the undoped samples until the sintering temperature is reached, which comes at lower temperatures and is related to the amount of sodium present. Thus in terms of activity, unlike molecular weight, there seems to be little benefit from doping with sodium. Higher activity is not obtained from sodium addition, except perhaps at the lowest temperatures. Thus again the sodium seems to bring some of the characteristics of high temperature calcination to lower temperatures, but not all of them.

The preceding data was obtained on a high porosity silica-titania. In order to see if this response was typical of other Cr/silica catalyst types, the above experiments were repeated with a standard silica from W.R. Grace, grade 952, which had no titania and a lower porosity (SA = 280 m^2/g, PV = 1.6 cc/g). The results are shown below in Figs. 7, 8,

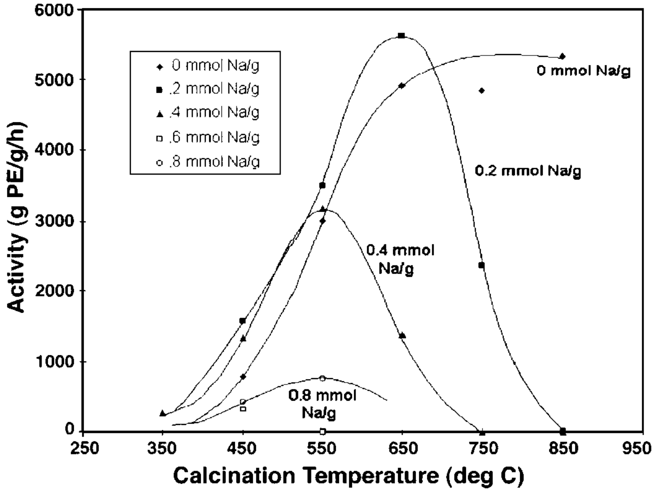

FIG. 6. Ethylene polymerization activity of sodium doped Cr/silica-titania catalysts calcined at the temperature indicated. Polymerization at 105°C and 550 psig.

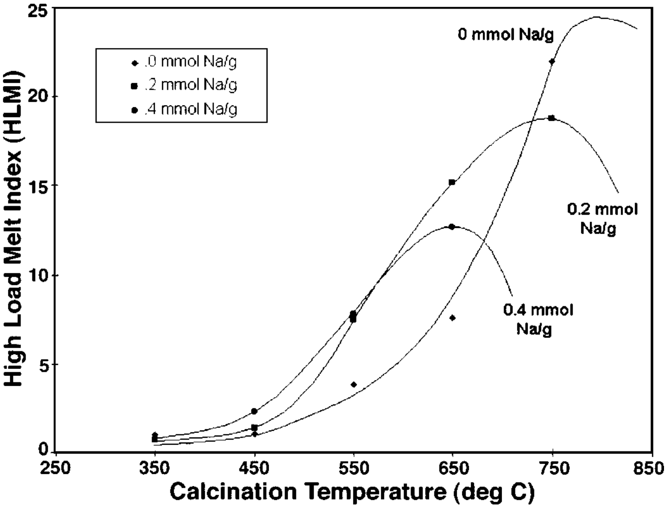

FIG. 8. High load melt index (21.6 kg) of polymers obtained from sodium doped Cr/silica catalysts made from Davison Grade 952 silica and calcined at the temperature indicated. Polymerization at 105°C, 550 psig, 8 ppm triethylaluminum.

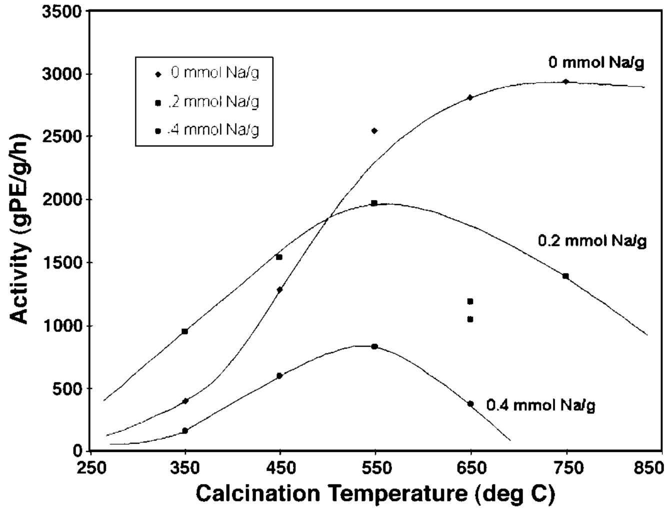

FIG. 9. Ethylene polymerization activity of sodium doped Cr/silica catalysts made from Davison Grade 952 silica and calcined at the indicated temperature. Polymerization at 105°C and 550 psig with 8 ppm triethylaluminum.

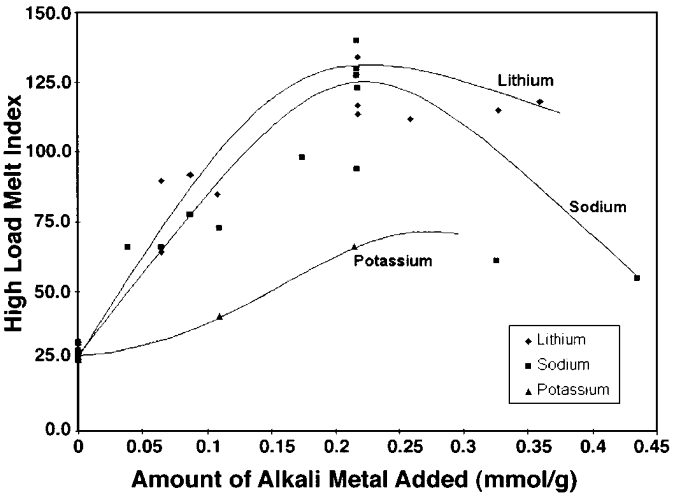

FIG. 10. High load melt index (21.6 kg) of polymers obtained from Cr/silica-titania catalysts doped with the indicated amount of alkali metal and calcined at 650°C.

and 9. These curves are very similar to those obtained earlier. Although these silica samples were doped with a similar level of sodium per gram of catalyst, they actually contained more sodium per square nanometer of surface because of the lower surface area. Nevertheless, it is hard to see that the doping effect was any more pronounced. The lower surface area catalyst responded in about the same way, and perhaps to a slightly lesser degree.

Since 650°C is a commonly used lower calcination temperature, an attempt was made to maximize the melt index enhancement at this temperature by varying the level of alkali metal present. In another series of experiments high porosity silica-titania (this time the titania level was 4.2%, PV = 2.5 cc/g, and SA = 550 m^2/g) were again doped with various levels of alkali metal formate from methanol solution. In addition to sodium formate, lithium formate, and potassium formate were also tested. All samples were then calcined at 650°C in dry air for 5 h.

Figure 10 plots the high load melt index obtained from these experiments against the amount of alkali metal added. From sodium the maximum boost in melt index seems to occur around 0.2 mmol/g, and as expected, adding more can be detrimental. Lithium produced an effect similar to that from sodium, although going beyond 0.2 mmol Li/g did not seem to be as harmful. Potassium yielded a smaller melt index enhancement than sodium or lithium.

Figure 11 plots the activity of these samples against the amount of alkali metal added. Again the activity boost from alkali metal is not great in comparison to the melt index response. Nevertheless, some enhancement was noticed for sodium and lithium and the effect seemed to be maximized somewhere around 0.2 mmol/g. Beyond 0.2 mmol/g, activity dropped off rather quickly for the sodium-doped samples, but less so for those treated with lithium. Potassium decreased the activity of these samples, even at the lowest level tested.

In addition to the formate, other salts of alkali metals were also impregnated from methanol, including hydroxide, chlorate, acetate, ethoxide, and nitrate. However, no great difference between anions could be detected within the error limits of these experiments. Since the anion is burned off during calcination this was expected.

In another experiment a silica-titania hydrogel was made from sodium silicate and washed to remove the sodium. Samples were taken from the gel at varying stages during the wash procedure and then finished into catalysts and tested for polymerization. Although we were unable to determine the optimum level of residual sodium for a 650°C

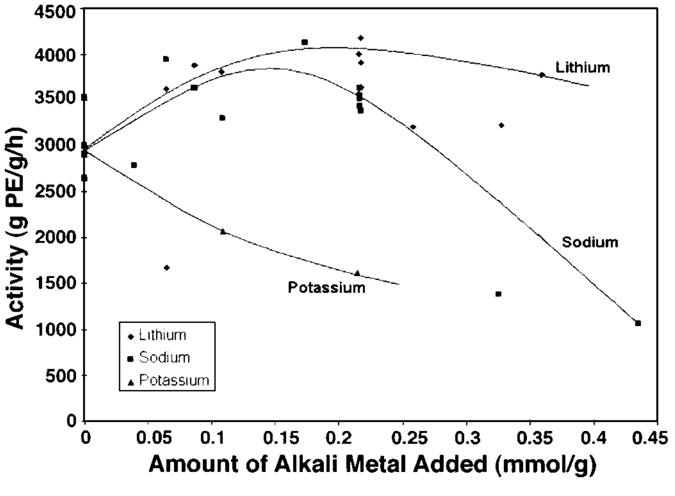

FIG. 11. Ethylene polymerization activity of Cr/silica-titania catalysts doped with alkali metal and calcined at 650°C. Polymerization at 109°C and 550 psig.

calcination, it was clear that residual sodium left in the gel this way has an influence similar to sodium impregnated from methanol onto the dry finished catalyst.

Another question considered was whether calcining the catalyst before introduction of the sodium might make a difference. Therefore several identical sample pairs were made in which one sample was calcined at 450–550°C before doping with alkali metal formate from methanol solution. The other sample from each pair was doped identically but without the extra calcination step. Afterwards both samples were then calcined at 650°C in the normal way. In subsequent polymerization tests we were unable to establish that this extra calcining step made any difference to the performance of the catalyst.

The effect of alkali metal doping on the molecular weight distribution was also examined. Polymers prepared in the first series described above from Cr/silica-titania (8.3 wt% titania) were analyzed by gel permeation chromatography (GPC). An example of GPC results is shown in Fig. 12, where two polymers from this series are compared. It is known that increasing the calcination temperature of the catalyst tends to cause a narrowing the MW distribution and a shift to lower MW. This can be seen clearly in Fig. 12, which compares polymers from catalyst calcined at 850 and 450°C.

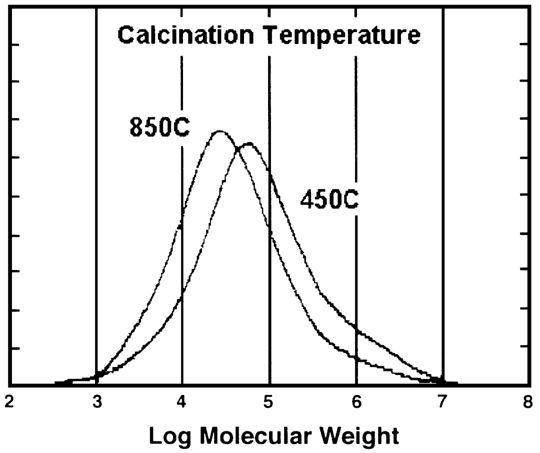

FIG. 12. Gel permeation chromatography (GPC) showing difference in molecular weight distribution between polymers from two Cr/silica-titania catalysts, one activated at 850°C (Mw/Mn = 11.6) and the other at 450°C (Mw/Mn = 16.9).

GPC data is compiled by decade analysis in Table 1 for the Cr/silica-titania catalyst. This data indicates, as shown in Fig. 5, that doping the catalyst with sodium usually also shifts the entire curve to slightly lower MW values. However, the effect of sodium is not exactly equivalent to the effect of temperature, because sodium seemed to narrow the MW distribution slightly more than temperature alone. Notice in Table 1 that at each temperature the amount of low MW polymer, that in decades 10^2–10^4, decreases as sodium is added. Likewise the high MW decades 10^6–10^8 also usually decreases somewhat, indicating a narrowing.

An attempt was made to compare the pore size distribution of an undoped catalyst sintered by high temperature to one sintered by alkali metal at a milder temperature. The Cr/silica-titania catalyst used in Figs. 1–6 was calcined at 800°C to represent the optimum activation temperature in Fig. 3 (top of the curve for the undoped catalyst). Another sample of this catalyst was severely sintered by calcining at 950°C. Then for comparison a sample containing 0.8 mmol Na/g was also calcined but at 650°C, which was chosen from Fig. 3 to represent a similar degree of sintering. The physical properties are shown in Table 2. Normal sintering at 950°C

TABLE 1

Decade Analysis of Polymer MW Distribution

Calcination temp. (deg C)	Sodium added (mmol/g)	10^2 to 10^3 (percent)	10^3 to 10^4 (percent)	10^4 to 10^5 (percent)	10^5 to 10^6 (percent)	10^6 to 10^7 (percent)	10^7 to 10^8 (percent)	Mw/Mn
450	0.2	0.89	10.97	50.84	31.15	6.11	0.04	16.9
450	0.4	0.47	10.51	52.71	30.92	5.38	0	12.9
450	0.6	0.95	11.62	50.51	30.96	5.92	0.03	17.0
450	0.8	0.83	8.82	47.52	36.36	6.46	0	15.6
550	0.2	0.62	13.6	54.67	26.82	4.24	0.05	13.8
550	0.4	0.1	12.62	56.19	26.82	4.23	0.04	11.0
550	0.8	0.02	12.03	57.88	26.13	3.91	0.03	9.4
650	0	0.44	17.21	56.2	23.05	3.1	0	10.9
650	0.2	0.23	16.4	57.57	23.67	2.14	0	8.2
650	0.4	0.47	15.46	58.14	23.59	2.33	0	8.9
750	0	0.92	20.56	58	18.24	2.27	0.01	12.0
750	0.2	0.62	15.55	56.76	23.55	3.48	0.04	12.9
850	0	0.69	19.59	58.15	19.05	2.48	0.03	11.6

TABLE 2

Physical Properties of Sintered Catalysts

Cr/silica-titania catalyst	Surface area (m^2/g)	Pore volume (cc/g)	Pore radius (ang)
Unsintered (0 mmol Na/g; 800°C)	522	2.02	77
Normal sintering (0 mmol Na/g; 950°C)	282	0.84	60
Sodium induced sintering (0.8 mmol Na/g; 650°C)	195	0.94	97

severely decreased the surface area and the pore volume. Sodium-induced sintering decreased the surface area even more drastically, but had slightly less effect on the pore volume. Thus the average pore radius was decreased slightly by normal sintering but increased by sodium induced sintering.

The pore size distributions from nitrogen adsorption for these three samples are shown in Fig. 13. It is clear that the sodium treatment was more effective at collapsing the smallest pores, with the result that the remaining pore size distribution is narrower and larger. Since the polymer MW is related to pore radius (2), it is conceivable that the narrower MW distribution from sodium sintered catalysts reflects the narrower pore size distribution.

Finally aluminophosphate catalysts also were tested. Stoichiometric $AlPO_4$ is isoelectronic and isostructural with silica and, therefore, aluminophosphates are sometimes used as a support for chromium-based polymerization catalysts (2, 10). In one experiment, a nonstoichiometric Cr/aluminophosphate catalyst having a molar P/Al ratio of 0.4 was doped with lithium formate up to a loading of 0.22 mmol/g and then calcined at 600°C. Results of polymerization tests on these samples were much like that of Cr/silica samples. Melt index potential increased steadily with added lithium, while activity was little affected.

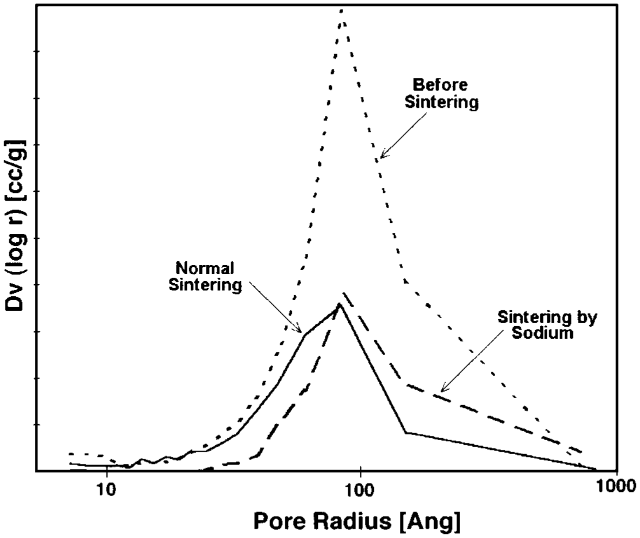

FIG. 13. Pore size distribution of Cr/silica-titania catalysts: (a) undoped and calcined at 800°C (before sintering); (b) undoped and calcined at 950°C (normal sintering); and (c) doped with 0.83 mmol Na/g and calcined at 650°C (sodium sintering).

DISCUSSION

The polymerization behavior of Cr/silica catalysts is strongly influenced by the porosity of the silica carrier in ways that are not completely understood (2). The chromium always remains on the silica surface, which can only stabilize a limited amount as Cr(VI) from which the active sites evolve. The remainder decomposes to inactive alpha Cr(III) oxide crystallites. Thus, higher surface area might be expected to yield higher activity, which is often observed. However, the picture is more complicated because the polymer immediately fills up the pores. If the catalyst structure is fragile enough it fragments into billions of smaller pieces which continue to produce polymer. If the structure is too rigid, fragmentation does not occur, the pores remain blocked by polymer, and no subsequent activity is observed. Fragility is often correlated with pore volume. Cr/silica catalysts containing much less than 1.0 cc/g pore volume usually do not exhibit polymerization activity.

Mysteriously, the molecular weight of the polymer produced also depends on the catalyst porosity (2). Larger pore diameter seems to yield lower MW. Long chain branch reincorporation has been suggested as a possible explanation, albeit not a very satisfying one. Sintering changes the porosity of silica by fusing particles together. Other changes include an increase in shear response despite a sometimes narrower MW distribution, which indicates an increased degree of long chain branching. It is possible that fragmentation patterns are changed substantially by sintering, which in turn affect diffusion of the monomer in some unknown way.

Alkali metals have long been known to enhance the formation and breakage of Si–O–Si bonds (4). Thus, doping a Cr/silica catalyst with alkali metal, followed by calcination at low temperatures has been found to yield many of the same effects on porosity and polymerization performance as calcining the undoped catalyst at higher temperatures. The shift in the MW distribution and the melt index response to temperature are observed in both cases.

However, there are differences too. The maximum melt index response to alkali metal at 650°C does not come close to matching that of the undoped catalyst calcined at 850°C. Neither is there much benefit to the activity of the catalyst from alkali metal doping, even though the temperature itself yields a strong activity boost. A close look at the MW distribution indicates that sodium narrows the distribution more on the low MW side.

Some writers have postulated that the effect of sodium is to cause localized sintering, where primary particles of silica in contact with sodium can coalesce, but other nearby particles cannot (4, 11). Whether the sintering is localized or not, it seems likely that the surface environment would not be exactly identical between a 850°C undoped catalyst and a 650°C catalyst containing sodium. The hydroxyl population is probably different, and the sodium itself may exert an electronic influence of its own on chromium neighbors. A connection between the activity and surface hydroxyl population has long been noted (3). However, it is unknown whether OH groups participate directly, as by coordination with active centers, or indirectly, by merely reflecting the surface rearrangement that occurs with dehydroxylation. Either way, it seems likely that alkali metal could introduce some unique effects.

It is also possible that the various alkali metals may yield slightly different results in terms of catalyst performance. Lithium may be slightly preferred over sodium as a melt index promoter, and both may be preferred over potassium. Previous workers have also reported such differences in studies on silica doped with 5 mol% of alkali metal and calcined at 700°C. Lithium caused crystallization to quartz while sodium and potassium caused conversion to cristobalite (4, 11–14).

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