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The Role of Sulfur in Deactivation of Pt/MgAl$_2$O$_4$ for Propane Dehydrogenation

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Platinum supported on magnesium aluminate spinel is shown to be an efficient catalyst for high-temperature, long-cycle dehydrogenation of lower paraffins. Trace amounts of sulfur in the feed (25–500 ppm) suppress both hydrogenolysis and coke formation. Propane conversion in excess of 28 mol% with a propylene selectivity of 92–94% was maintained over six 24-h reaction/regeneration cycles at 600°C. Catalyst activity fell off sharply after six cycles. This was due to a gradual decrease in platinum dispersion, observed after each catalyst regeneration. The deactivation occurred only in catalysts exposed to sulfur since coke burn-off did not cause platinum sintering in catalysts run without hydrogen sulfide addition to the feed. Platinum on alumina was much more prone to metal sintering in oxidizing environments. The results are discussed in terms of metal–support interactions and their perturbation by sulfur compounds.

INTRODUCTION

Platinum supported on magnesium aluminate (MgAl$_2$O$_4$) is remarkably stable (*1, 2*) in environments which lead to platinum sintering when silica (*3*), alumina (*4*), or silica–alumina (*5*) are used as supports. The spinel is therefore an attractive support for platinum-catalyzed reactions at high severity.

We have studied the dehydrogenation of propane, isobutane, and isopentane over platinum supported on magnesium aluminate, in the presence of excess hydrogen and at temperatures of 500–600°C. Under these conditions, dehydrogenation could be carried out for extended periods at these temperatures and the catalyst oxidatively regenerated, without loss of catalytic activity and with no significant change in platinum dispersion. Platinum supported on silica, γ-alumina and η-alumina lost catalytic activity and showed pronounced growth in platinum crystallite size when used in comparable cycles.

Trace amounts of sulfur (25–500 ppm) when added as H$_2$S or thiophene increased selectivity to olefin and suppressed both hydrogenolysis and coke formation over platinum on magnesium aluminate. With addition of 200 ppm sulfur as H$_2$S, for example, propane conversion in excess of 28 mol% with 92—94% selectivity to propylene was maintained over six 24-h reaction cycles at 600°C. Sulfur addition eventually led to loss of catalyst activity, however, which was not observed in dehydrogenation/regeneration cycles in its absence. We show that the activity loss resulted from increases in platinum particle size which occurred during coke burn-off but only in catalysts exposed to sulfur during the dehydrogenation cycle. Exposure to sulfur had this effect despite reduction in pure hydrogen at 600°C prior to oxidative regeneration.

METHODS

The magnesium aluminate spinels used in this study were prepared by coprecipitation from aqueous solutions of Al(NO$_3$)$_3$ · 9H$_2$O and Mg(NO$_3$)$_2$ · 6H$_2$O by addition to a solution of NH$_4$OH at a pH of 10. The precipitate was dried at 120°C for 16 h then calcined in two stages, first at 400°C for 16 h, then at 600°C for 16 h. X-Ray diffraction analysis showed the material to be MgAl$_2$O$_4$, having the spinel structure. The

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$MgAl_2O_4$ composition was confirmed by neutron activation analysis. The supported catalysts were prepared by impregnating the calcined $MgAl_2O_4$ with an aqueous solution of chloroplatinic acid by the technique of minimum excess solution (incipient wetness). After impregnation, the catalysts were dried overnight at 120°C, then calcined for 16 h at 500°C. Platinum was supported on silica, η-alumina, and γ-alumina following the same procedure.

All dehydrogenation experiments were carried out in a $\frac{3}{8}$-in. i.d. tubular quartz reactor surrounded by a 13-in. tube furnace. Furnace temperatures were controlled by a thermoelectronic regulator. Temperatures within the catalyst bed were determined by a movable thermocouple mounted in a concentric thermocouple well running the length of the reactor.

All experiments were carried out at a 2-to-1 or 3-to-1 molar ratio of hydrogen to paraffin. Gas feeds were controlled by calibrated gas flow regulators; liquid was supplied through either liquid flow regulators or mechanical pumps. The top section of the reactor was packed with corundum pellets and used to preheat and mix the feeds. Sulfur was added to the feed either as H_2S or thiophene. Catalyst charges of 10 cm^3 of 10- to 20-mesh catalysts were used without dilution.

Before the reactions were carried out, the catalysts were prereduced in flowing hydrogen for at least 30 min at 500°C. Again, prior to regeneration, the catalysts were reduced in flowing hydrogen from 30 min to 2 h at reaction temperatures. Regenerations were carried out at 450–500°C in either flowing air or an air–helium mixture. These were monitored by GLC and were considered complete when the production of CO_2 had ceased.

Platinum metal surface areas were determined by hydrogen adsorption (*6*) or were calculated from platinum size distributions obtained from electron micrographs (*6*).

Hydrocarbon conversions and selectivities were calculated from gas chromatograms obtained with an 18-ft. by $\frac{1}{8}$-in. column of bisethoxy-2-ethyl sebacate at 25 or 50°C using a thermoconductivity detector. Unless otherwise stated, conversions and selectivities were determined over a standard 5-h reaction period. Values reported here are for the lined out catalyst and were taken at the end of the 5-h reaction period.

RESULTS

Paraffin Dehydrogenation

Initial studies were carried out on the dehydrogenation of isopentane to isoamylenes over platinum on various supports. Table 1 lists results obtained for the dehydrogenation of isopentane over 0.5% Pt supported on SiO_2, γ-Al_2O_3, η-Al_2O_3 and $MgAl_2O_4$. After each 5-h reaction period, the catalysts were reduced and oxidatively regenerated. The most selective catalysts for this reaction were Pt/SiO_2 and $Pt/MgAl_2O_4$. The Pt/SiO_2 gave low isopentane conversion, however, and lost most of its activity upon regeneration. $Pt/MgAl_2O_4$ gave higher conversion, initially, and could be regenerated repeatedly with no change in activity or selectivity. Neither Pt/γ-Al_2O_3 nor Pt/η-Al_2O_3 was selective for dehydrogenation, and each tended to lose activity upon regeneration, although not to the same catastrophic extent as Pt/SiO_2. Transmission electron microscopy showed that

TABLE 1

Dehydrogenation of Isopentane over Platinum Catalysts

Catalyst	*T* (°C)	Time (h)	Conversion (mol%)	Selectivity (mol%)
0.5% $Pt/MgAl_2O_3$	530	1	47	70
		4	42	80
0.5% $Pt/MgAl_2O_3$	530	1	32	82
		4	29	86
0.5% Pt/γ-Al_2O_3	550	1	17	40
		4	17	41
0.5% Pt/η-Al_2O_4	550	1	33	36
		4	26	40
0.5% Pt/SiO_2	575	1	16	91
		4	15	91

$H_2/C_5 = 2$ LHSV = 3.4

activity loss correlated with growth in platinum crystallite size. Platinum crystallites on $MgAl_2O_4$ were essentially unchanged after regeneration. Gross sintering, to create crystallites as large as 120 Å, was observed with platinum–silica. The platinum–aluminas were intermediate in behavior.

A series of experiments was then carried out over $Pt/MgAl_2O_4$ wih trace quantities of sulfur (80–625 ppm) added to the feed as thiophene. Sulfur increased both isopentane conversion and selectivity to isoamylenes. Results of these experiments are shown in Table 2. The addition of 80 ppm sulfur increased selectivity to isoamylenes from 76 to 86 mol%. Further increases in sulfur concentration from 80 to 625 ppm had only a small effect on selectivity but did cause a significant increase in conversion due to decreased coke formation. As a result, conversion was maintained at a high level over the entire reaction period. In subsequent experiments carried out at 525°C with 200 ppm sulfur added as H_2S, an average isopentane conversion of 30 mol% was obtained over a 48-h reaction period with a selectivity to isoamylenes of 96%. Similar results were obtained for the dehydrogenation of isobutane at 560°C with 200 ppm sulfur added as H_2S.

In propane dehydrogenation, temperatures of 600°C or higher must be employed in order to obtain reasonable yields of propylene. This reaction was not selective over $Pt/MgAl_2O_4$ in the absence of sulfur. The principal reaction was hydrogenolysis, with methane and coke the main products. The addition of sulfur in concentrations as low as 25 ppm changed the nature of the reaction. The exothermic hydrogenolysis reaction was suppressed and the overall reaction became endothermic. Yields of propylene increased dramatically and olefin selectivities of 90 mol% were obtained. Sulfur also decreased coke formation, as before, and reaction could be carried out for up to 10 days before regeneration became necessary. Table 3 shows the effect of sulfur addition on the dehydrogenation of propane over $Pt/MgAl_2O_4$, $Pt/\eta\text{-}Al_2O_3$, and $Pt/\gamma\text{-}Al_2O_3$. In the case of $Pt/MgAl_2O_4$, as little as 25 ppm sulfur increased propylene selectivity from 47 to 84%. Ninety-five percent selectivity was obtained at 425 ppm sulfur. The addition of 425 ppm sulfur had little or no effect with $Pt/\eta\text{-}Al_2O_3$, and 850 ppm sulfur decreased both conversion and selectivity with $Pt/\gamma\text{-}Al_2O_3$.

TABLE 2

Dehydrogenation of Isopentane over 0.5% $Pt/MgAl_2O_4$ at 550°C in the Presence of Thiophene

Sulfur (ppm)	Reaction time (h)	Conversion (mol%)	Selectivity (mol%)
0	1	48	70
	6	37	82
80	1.5	48	82
	6	41	91
160	1.5	48	81
	6	43	88
310	1	55	78
	6	44	86
625	1	55	88
	5.5	51	89

$H_2/C_5 = 3$ LHSV = 3.4

TABLE 3

Effect of Sulfur on the Dehydrogenation of Propane over Supported Platinum Catalysts

Catalyst	S[a] (ppm)	Conversion (mol%)	Selectivity (mol%)
0.5% $Pt/MgAl_2O_4$	0	31	47
	25	32	84
	425	29	95
0.5% $Pt/\eta\text{-}Al_2O_3$	0	22	51
	425	23	57
0.5% $Pt/\gamma\text{-}Al_2O_3$	0	28	63
	850	16	38

$T = 600°C$ $H_2/C_3 = 3$ GHSV = 4800 h^{-1}

[a] Added as H_2S.

Effect of Regeneration

During the dehydrogenation of isopentane in the absence of sulfur, the $Pt/MgAl_2O_4$ was regenerated repeatedly with no observable loss in catalyst activity.

TABLE 4

Effect of Regeneration on the Dehydrogenation of Propane over a 0.5% $Pt/MgAl_2O_4$ Catalyst at 200 ppm S

Days on-stream	Number of regenerations	Conversion (mol%)	Selectivity (mol%)
4	3	29	92
6	5	28	94
8	7	21	98
8.2	8	19	98

$T = 600°C$ $H_2/C_3 = 3$ GHSV = 4800

Even in the presence of sulfur, no change in activity was observed after the catalyst had been subjected to five regenerations at 500°C in flowing air. In dehydrogenating propane in the presence of sulfur, however, catalyst activity decreased after repeated regenerations. This loss of activity was normally observed between the sixth and eighth regeneration. Table 4 shows the effect of air regeneration on conversion and selectivity for the dehydrogenation of propane with 200 ppm sulfur added as H_2S. The conversions and selectivities shown in Table 4 were determined at the end of 24-h reaction periods after which the catalyst was oxidatively regenerated. Catalyst activity decreased after the seventh regeneration and continued to decline after each subsequent regeneration.

Transmission electron micrographs were obtained for the fresh catalyst and for the catalyst after eight regenerations. They showed that platinum particles in the fresh catalyst were between 10 and 20 Å in diameter, while those in the spent catalyst had grown to between 25 and 80 Å in diameter.

The same experiment was repeated with another sample of $Pt/MgAl_2O_4$, but in this case the catalyst was sampled after each regeneration and transmission electron micrographs obtained for each sample. Platinum crystallite size distributions were generated from a large number of micrographs, sizing some 300–400 crystallites for each sample. It was found that platinum crystallite size increased continuously with each dehydrogenation–regeneration cycle. Figure 1 (A–C) shows the platinum size distributions obtained for fresh catalyst, and the same catalyst after three and after eight regenerations. The progressive growth of platinum crystallite size is apparent.

These results were checked by hydrogen chemisorption measurements in a flow system. Good agreement was obtained with the fresh catalyst which had an H/Pt ratio of 0.71. None of the regenerated samples would adsorb hydrogen. It was later determined that this was only true for regenerated catalysts which had been used in the presence of sulfur. Reasonable agreement was obtained between hydrogen adsorption and the electron microscope in the case of regenerated catalysts which had been run in the absence of sulfur.

In order to determine which part of the

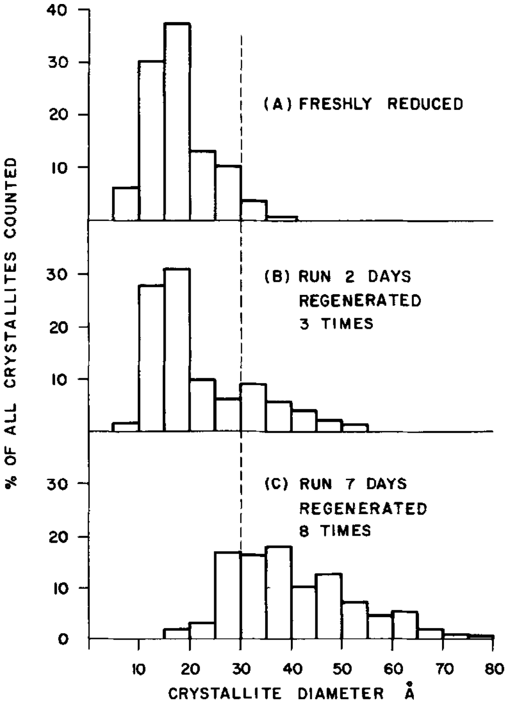

FIG. 1. Platinum crystallite size distributions for 0.5 wt% $Pt/MgAl_2O_4$ reduced 1 h in H_2 at 500°C and after use in propane dehydrogenation/air regeneration cycles. Sulfur (200 ppm) was added as H_2S during propane dehydrogenation.

overall reaction–regeneration sequence was responsible for platinum sintering, a series of Pt/MgAl$_2$O$_4$ catalysts was run in a variety of environments and examined by electron microscopy. First, two samples of Pt/MgAl$_2$O$_4$ were run for 6 days at 600°C, one in flowing hydrogen and one in hydrogen with 200 ppm H_2S. Hydrogen flow in each case was equivalent to that employed in the dehydrogenation experiments. Platinum size distributions, determined after 6 days for each sample, are shown in Fig. 2. Neither sample showed any significant increase in crystallite size. Hydrogen chemisorption on the sample run in hydrogen alone gave an H/Pt ratio of 0.69, identical to the value obtained with fresh catalyst. The sample run with sulfur adsorbed very little hydrogen.

Experiments were next carried out to differentiate between the effects of the dehydrogenation reaction itself and the regeneration in air. Two samples of 0.5% Pt/MgAl$_2$O$_4$ were used for propane dehydrogenation at 600°C with 200 ppm sulfur added as H_2S. Reaction was continued for 7 days. At the end of this time, one sample was removed from the reactor without regeneration; the other was regenerated at the end of the reaction period. As shown in Fig. 3, platinum crystallite size in the catalyst run 7 days without regeneration was unchanged from that of fresh catalyst. Catalyst run 7 days with one regeneration was equivalent to samples run 1 day and regenerated once. These results suggest that platinum crystallite size was unaffected by the dehydrogenation reaction but was a function of the number of regenerations carried out.

To be completely sure, a large sample of 0.5% Pt/MgAl$_2$O$_4$ was charged to the reactor and run for 24 h at 600°C. As before, the feed comprised propane, hydrogen and hydrogen sulfide. After 24 h, the catalyst was

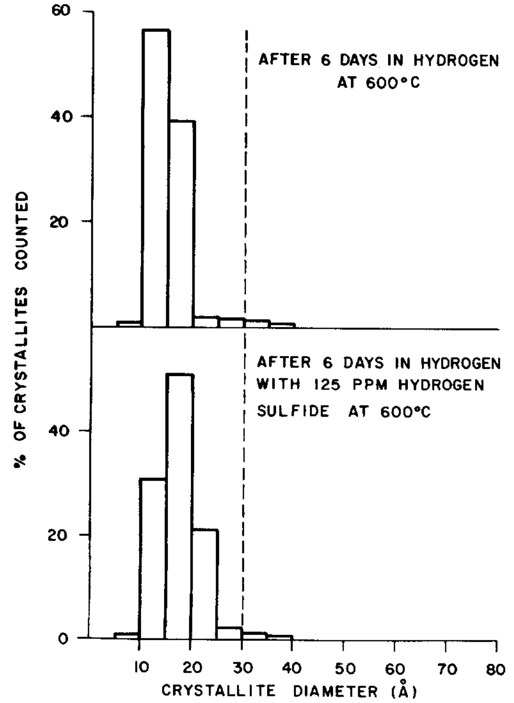

FIG. 2. Platinum crystallite size distributions for 0.5 wt% Pt/MgAl$_2$O$_4$ after 6 days at 600°C in hydrogen and in hydrogen with 125 ppm hydrogen sulfide added.

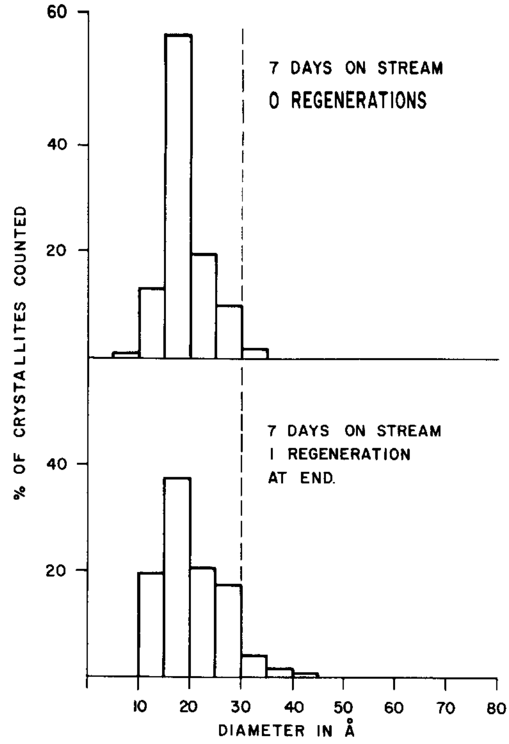

FIG. 3. Platinum crystallite size distributions for 0.5 wt% Pt/MgAl$_2$O$_4$ after 7 days propane dehydrogenation (200 ppm H_2S added), before and after regeneration.

reduced in hydrogen for 2 h at 600°C and cooled to room temperature in helium. One-half of the catalyst was then removed from the reactor. The other half was given a standard regeneration, as described previously, and cooled in helium. A small sample of each half of the catalyst was removed for electron microscopy, the unregenerated half recharged, the entire charge given a standard pretreatment, and a second 24-h reaction period begun. This procedure was repeated six times. Examination of the samples generated in this experiment confirmed that platinum sintering became progressively worse with each regeneration and showed that all seven samples which had not been regenerated had good platinum dispersion. The platinum crystallite size distribution obtained for catalyst run 7 days with no regeneration again was essentially the same as that of the fresh catalyst.

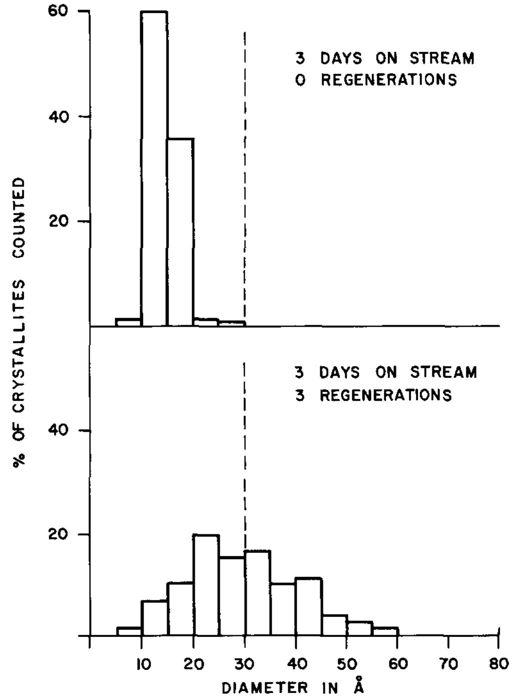

FIG. 4. Platinum crystallite size distributions for 0.5 wt% Pt/$MgAl_2O_4$ used 3 days for propane dehydrogenation at 600°C (125 ppm H_2S added) and used 3 days with three regenerations in air.

The sample run for 7 days with seven regenerations showed extensive growth in platinum crystallite size. Figure 4 compares platinum distributions for samples run for 3 days with no regeneration and 3 days with three regenerations. The change in platinum size distribution is apparent in the sample regenerated three times.

Two further experiments of this type were carried out. In one case hydrogen sulfide was withheld from the feed, while in the other, only hydrogen and hydrogen sulfide were passed over the catalyst. (Obviously no coke was formed in the latter experiment, but a series of pseudoregenerations was carried out under standard conditions.) It was hoped that these experiments would determine whether coke burn-off alone caused platinum sintering, or if the presence of sulfur in the feed was involved. The study showed that sulfur is indeed an integral part of the sintering mechanism. All 14 samples generated in the sulfur-free program had good platinum dispersions. Large platinum crystals were not observed in any sample. Quantitative data were obtained for the final sample, regenerated seven times. The Pt size distribution obtained was very similar to that of fresh catalyst (Fig. 5). The sample run without propane did not show the extensive platinum sintering observed previously. Qualitative examination of these 14 samples showed no substantial growth in platinum particle size. Quantitative data for the sample given seven simulated regenerations showed a small increase in Pt crystallite size compared to fresh catalyst (Fig. 5), but this was small relative to the changes which occurred during the course of a normal run. Thus, gross platinum sintering occurred only during carbon burn-off and then only when the catalyst had been run with sulfur present in the feed.

Platinum surface areas for some representative samples are given in Table 5. These were calculated from the surface mean diameters of platinum crystallites in each sample, as determined by electron mi-

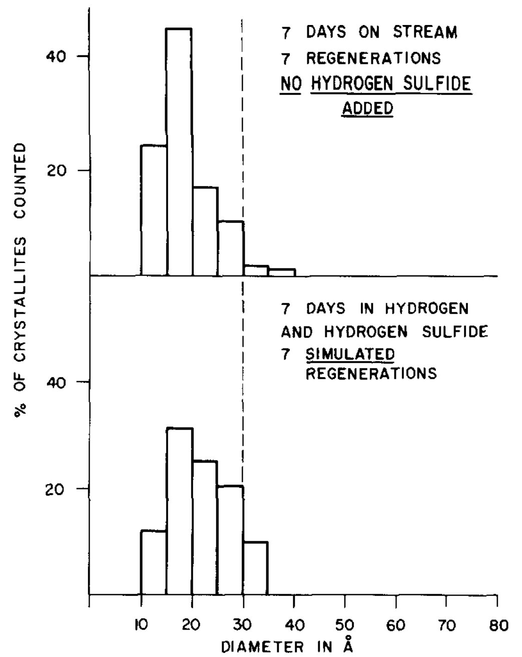

FIG. 5. Platinum crystallite size distributions for 0.5 wt% $Pt/MgAl_2O_4$ after runs in which H_2S or propane were withheld from the feed.

croscopy (*6*). They show about a threefold loss of platinum surface area in a sample exposed to sulfur and regenerated nine times.

An 0.5% $Pt/\eta\text{-}Al_2O_3$ catalyst was tested in the same way. Qualitatively, the electron microscope showed that platinum crystallite size was little affected by reduction in hydrogen for 4 days at 600°C, and no significant sintering occurred after 4 days of propane dehydrogenation at 600°C. Thus the platinum in Pt/Al_2O_3 behaved in much the same way as platinum in $Pt/MgAl_2O_4$ in reducing environments. Platinum in Pt/Al_2O_3 was less stable in oxidizing environments. Significant platinum sintering was observed in a sample run 4 days in hydrogen and given a simulated regeneration every 24 h. A single regeneration after 24 h of propane dehydrogenation gave extensive sintering, and four such regenerations at 24-h intervals resulted in extremely large platinum crystals. Significantly, Pt/Al_2O_3 run in hydrogen at 600°C with 125 ppm sulfur as H_2S and given three to four simulated regenerations was also highly sintered.

DISCUSSION

Isopentane dehydrogenation at 550°C over platinum on the various supports gave results consistent with known differences in the properties of the catalysts. The η- and γ-alumina supports have high surface acidity compared to silica or magnesium aluminate, and this is known to catalyze coke formation. Conversion was high over platinum on these alumina supports, but selectivity was low. Pt/SiO_2 and $Pt/MgAl_2O_4$ were comparable in selectivity, but conversion was much lower on Pt/SiO_2 than on any other catalyst. This we attribute to the calcination of Pt/SiO_2 in air at 500°C prior to use. Such calcination causes extensive platinum sintering in Pt/SiO_2 catalysts (*3*, *6*) but has little effect on platinum on the other supports.

For propane dehydrogenation, thermodynamics show that acceptable yields of propylene can be expected only at 600°C and above in the presence of excess hydrogen. At this temperature, hydrogenolysis and coke formation were substantial over all catalysts. Any influence of the support was overwhelmed by the hydrogenolysis activity of platinum itself at 600°C, and acceptable selectivity required suppression of this hydrogenolysis activity. The use of sul-

TABLE 5

Platinum Surface Areas of $Pt/MgAl_2O_4$ Catalysts[a]

Sulfur (ppm)	Days on-stream	Regenerations	Platinum areas (m^2/g Pt)
0	0	0	139
150	2	3	112
150	3	4	108
150	8	9	57
0	Hydrogen only, 600°C, 6 days		163
125	Hydrogen–H_2S only, 600°C, 6 days		144

[a] Calculated from particle size distributions obtained by transmission electron microscopy (*6*).

fur compounds to suppress hydrogenolysis and coke formation over platinum is well known, and hydrogen sulfide addition gave the needed change in selectivity (*1*). It also led to eventual platinum sintering and activity loss in $Pt/MgAl_2O_4$, which was a remarkably stable catalyst in the absence of sulfur. The remainder of this discussion will be concerned with this effect of hydrogen sulfide on the $Pt/MgAl_2O_4$ catalyst.

The present results show that platinum dispersion was relatively stable on all supports in reducing environments at 600°C. This was true in hydrogen, in hydrogen with added hydrogen sulfide, and also during propane dehydrogenation. Large differences in the behavior of platinum on the various supports were observed only in the presence of oxygen at high temperatures. As discussed previously, for example, calcination of Pt/SiO_2 catalysts in air at 500°C leads to extensive platinum sintering (*3*, *6*), yet this procedure is used routinely to calcine Pt/Al_2O_3 catalysts without ill effect. This suggests that there must be a mechanism for pinning or stabilizing oxidized platinum species in Pt/Al_2O_3 which is inoperative in Pt/SiO_2, an interaction which has been the subject of numerous studies (*7–15*).

Platinum dispersion was even more stable on magnesium aluminate than on alumina in the presence of oxygen at high temperatures. With Pt/Al_2O_3 significant growth in platinum crystallite size was observed after cycles of reduction in hydrogen (600°C) followed by oxidation in air (500°C). More extensive platinum sintering occurred during regeneration of Pt/Al_2O_3 in air after use as a propane dehydrogenation catalyst. This sintering grew progressively worse after each coke burn-off, and it occurred whether hydrogen sulfide was present in the propane feed or not. $Pt/MgAl_2O_4$, on the other hand, was stable in all experiments except those where coke was burned off a catalyst which had been exposed to hydrogen sulfide during propane dehydrogenation.

Adamiec *et al.* (*16*) studied the stability of platinum dispersion on magnesium oxide. Using hydrogen chemisorption and transmission electron microscopy, they showed that platinum sintering did not occur in oxygen at 550–650°C conditions which caused extensive platinum sintering in Pt/Al_2O_3 (16). The authors postulate that platinum forms PtO_x–MgO complexes in the presence of oxygen at these temperatures, which stabilizes platinum to a greater extent than occurs in Pt/Al_2O_3.

The stability of $Pt/MgAl_2O_4$ in oxygen at high temperatures is more like that of Pt/MgO than Pt/Al_2O_3. (Temperatures during coke burn-off must have exceeded the nominal 500°C reactor temperature considerably, since undiluted air was used as oxidant.) Possibly surface oxide ions which have magnesium cations as neighbors pin PtO_x species in much the same way as with magnesia itself, i.e., more strongly than in the case of alumina.

This still leaves the question of why the stability of $Pt/MgAl_2O_4$ during coke burn-off was reduced if the catalyst was exposed to hydrogen sulfide during propane dehydrogenation. We suggest a reaction sequence of the following type

$$Pt_s + H_2S = Pt_s(S)_a + H_2$$

$$Pt_s(S)_a + O_2 = Pt_s + SO_2$$

$$SO_2 + \tfrac{1}{2}O_2 = SO_3$$

$$4SO_3 + MgAl_2O_4 = MgSO_{4(s)} + Al_2(SO_4)_{3(s)}$$

where (a) denotes an adsorbed species and (s) a surface species, may lead to reconstruction of the support surface through sulfate formation and weaken the bonding between PtO_x species and the spinel surface during oxidative regeneration. Each of the reactions is thermodynamically favored at the conditions used in the present experiments, and flow microbalance studies carried out by Massoth (*17*) show that the reactions do occur over $Pt/MgAl_2O_4$. Figure 6 shows Massoth's microbalance results for 0.5% $Pt/MgAl_2O_4$ in various gaseous atmo-

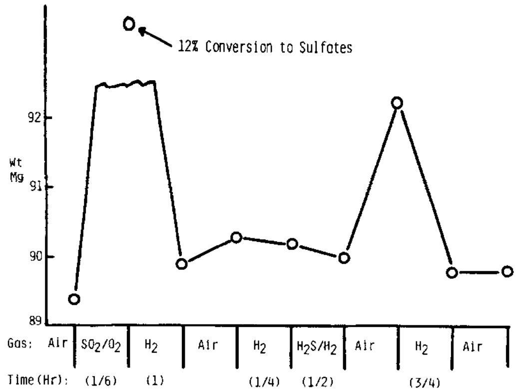

FIG. 6. Flow microbalance results (*17*) for 0.5 wt% $Pt/MgAl_2O_4$ exposed to the gas environments shown at 600°C.

spheres. Treating $Pt/MgAl_2O_4$ with SO_2 and air gave a significant weight gain, i.e., sulfate formation on the support. Subsequent hydrogen treatment gave a corresponding weight loss (sulfate reduction). When the same catalyst was treated with a H_2S/H_2 mixture followed by air, a similar weight gain was observed, showing that oxidation of adsorbed H_2S will lead to sulfate formation on the spinel support. Again, the sulfate could be reduced with hydrogen. X-Ray diffraction analysis of the reduced catalyst after this experiment showed a good spinel pattern with no evidence of either MgO or Al_2O_3. Significantly, however, the catalyst did show a strong pattern for platinum metal, indicating extensive platinum sintering.

We have no direct evidence for sulfur retention in reduced $PtMgAl_2O_4$ prior to coke burnoff. The sulfur content of samples reduced at 600°C before coke oxidation was below the detection limit of combustion methods. A recent study by Mathieu and Primet (*18*), however, provides direct evidence for a similar cycle on Pt/Al_2O_3. They found that H_2S adsorbed dissociatively on Pt above 100°C with release of hydrogen and full coverage of surface platinum atoms by sulfur. Oxygen treatments removed sulfur from the platinum and led to formation of sulfate groups on the support which were detected by infrared spectroscopy. High-temperature treatment in hydrogen reduced these sulfate groups but led to renewed poisoning of the platinum surface, as evidenced by catalyst selectivity in several test reactions; a conclusion also reached in the work of Apesteguia *et al.* (*19*) on sulfurized Pt/Al_2O_3.

This result demonstrates the formation and reduction of surface sulfate species in Pt/Al_2O_3 exposed to hydrogen sulfide, and the retention of sulfur by platinum, when the catalyst is reduced. The amount of sulfur which could be retained in this way by 0.5% $Pt/MgAl_2O_3$ is sufficiently small to be below the detection limit of the combustion method. We theorize that it could nevertheless be sufficient to disrupt the bonding between platinum and spinel by the proposed mechanism if surface sulfate is formed in close proximity to the platinum crystallites.

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