

Sulfur Poisoning of Bi- and Trimetallic γ -Al₂O₃-Supported Pt, Re, and Sn Catalysts

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Bifunctional metal/acid catalysts with Pt, Pt–Re, Pt–Sn, and Pt–Re–Sn as metallic functions supported on chlorided γ -alumina were prepared by successive impregnation or by coimpregnation of aqueous solutions of the metal precursors. They were tested in cyclohexane dehydrogenation (400 °C, 1 atm, weight hourly space velocity = 10, and H₂/CH = 30) with an intermediate step of sulfur poisoning (1, 3, 5, or 7 ppm S). The addition of Sn and/or Re produces a decrease in the catalytic activity of Pt. Both this activity decrease and the increase in sulfur poisoning follow the order trimetallic > bimetallic > monometallic catalysts. The catalysts prepared by coimpregnation are more affected than those prepared by successive impregnations. In the last case, the activity and poisoning depend on the order of addition of the metal precursors during preparation.

Introduction

Commercial naphtha-reforming catalysts are bifunctional. A group VIII noble metal provides metallic function properties (dehydrogenation), while the support, usually chlorided alumina, provides the required acid function properties (skeletal rearrangement). The ratio of the catalytic activities of both functions is optimized for the best performance of the catalyst. The naphtha-reforming catalyst is a very sensitive material, and it can be deactivated by many causes. One or both functions can be deactivated, producing an unfavorable imbalance of the metal/acid ratio. Coking deactivates both functions but mainly the acid one. It is one of the fastest deactivation agents and determines the cycle length between regenerations. Sintering also affects both functions but mainly the metal one. The dispersion of the metal can be recovered in the regeneration step, while the sintering of the support is irreversible. There are poisons that can be present in the feed and can deactivate the metal (sulfur and metals) or the acid function (nitrogen compounds). The elimination of chlorine from the alumina support *also* deactivates the acid function. The most important poison of the metal function is sulfur, and its compounds are always present in the naphtha cuts to be reformed. For this reason, a hydrodesulfurization unit is always located upstream of the reforming reactor. The allowed sulfur concentration depends on the catalyst sensitivity. There are several reviews on sulfur poisoning. Barbier et al.¹ studied the poisoning of metal catalysts in hydrogenation reactions, while Beltramini² studied the poisoning of mono- and bimetallic catalysts in naphtha-reforming reactions.

Feed sulfur compounds are hydrogenolyzed over the reforming catalyst, producing H₂S, the true poison of the metal function:



Many studies on sulfur adsorption on Pt have been published.^{2,3} When Pt is covered by a very small amount of S (about one S atom per four Pt atoms), some reactions that require a particular structure (electronic or geometric) are impeded. The hydrogenolysis reaction is practically stopped, while reactions such as hydrogenation–dehydrogenation are slightly inhibited. Pt–Re catalysts have a great hydrogenolytic activity that is passivated in common industrial practice by adsorption of very small amounts of S on the metal. This S is beneficial for the selectivity of the reforming reactions and is the reason Pt–Re catalysts are provided pre-sulfided or are sulfided in the reactor to prevent “hydrocracking runaway”. This is a great temperature increase due to the occurrence of exothermic hydrocracking of the feed during the startup of the reactor. Pt–Sn poses no danger of initial hydrocracking runaway. Similarly to Pt–Re–S, its activity is also poisoned by S in the feed. A very small amount of S remains on the metallic function during the process, which is usually referred as irreversible sulfur^{4,5} (S_i). If sulfur compounds are also present in the feed, they produce S_r, which is adsorbed reversibly depending on its partial pressure and temperature. This reversible sulfur (S_r) adds to S_i and inhibits completely the catalytic activity of the metal function when the total S is about 1 S atom per 2 Pt surface atoms.



For this reason, S in the feed must be limited to stop the increase of S_r and the deactivation of the metal. In summary, S_i is beneficial, but S_r is harmful. Sulfur not only poisons the metal but also produces an imbalance

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in the metal/acid functions. A poisoned metal cannot dissociate H_2 and spill it over the support. Then coke precursors cannot be hydrogenated, and more deactivating coke is produced on the acid support.

The objective of this work is to compare the poisoning effect of sulfur on the metallic activity of naphtha-reforming catalysts prepared by coimpregnation of the metal precursors or by the method of successive impregnations: monometallic Pt/ Al_2O_3 , bimetallic Pt-Re/ Al_2O_3 and Pt-Sn/ Al_2O_3 , and trimetallic Pt-Re-Sn/ Al_2O_3 .

Experimental Section

Preparation of Catalysts. The support was commercial γ -alumina (Cyanamid Ketjen CK 300) with Na (5 ppm), Fe (150 ppm), and S (50 ppm) as the main impurities. The extruded material was ground and sieved. The 35–80 mesh fraction was separated and calcined in air at 650 °C for 3 h. Its specific surface area was 180 m² g⁻¹, and its pore volume was 0.49 cm³ g⁻¹.

The catalysts were prepared by impregnating the support in one step with a solution of the three metals (coimpregnation) or by successively impregnating it with aqueous solutions of Pt, Re, and Sn. Concentrations were regulated in order to have 0.3% of each metal on the final catalyst. The salt solutions used were $H_2PtCl_6 \cdot 6H_2O$ (3.345 mg of Pt mL⁻¹), NH_4ReO_4 (20.18 mg of Re mL⁻¹), and $SnCl_2 \cdot 2H_2O$ (25 mg of Sn mL⁻¹).

In the successive impregnation method, a 0.2 M HCl solution (1.5 mL g⁻¹) and a solution of the first metal to be impregnated (Pt, Re, or Sn) were added to 5 g of the alumina support. The slurry was slowly stirred at 70 °C until the solvent was eliminated. Then the sample was dried at 120 °C overnight, calcined in air (60 mL min⁻¹) at 500 °C for 4 h, and reduced in hydrogen (60 mL min⁻¹) at 500 °C for 4 h. A monometallic catalyst was thus obtained. Bimetallic catalysts were prepared by repeating the previous steps while taking the monometallic catalyst as the starting material. Trimetallic catalysts are prepared in the same way with the bimetallic catalyst as the starting material. The catalyst's name indicates the order of addition of the metal precursors. For example, in the case of Sn-Pt-Re, Sn was the first promoter impregnated, Pt was the second, and Re was the last.

In the coimpregnation method, the alumina support was first dipped in a 0.2 N HCl solution and then a solution of the two or three metal precursors was added. Heat treatments were the same as those described in the last paragraph.

A catalyst was also prepared by coimpregnating two metals over a monometallic catalyst. In this case, the names of the elements that were coimpregnated appear within parentheses: Re-(Pt + Sn).

The final chlorine content after calcination was about 0.9–1.0% for all samples.

Catalytic Test, Poisoning by Sulfur. The dehydrogenation of cyclohexane (CH) to benzene at 400 °C and 1 atm was used as a test reaction of the metal function and of its poisoning by sulfur. Catalyst samples of 50 mg were charged to the reactor and reduced in H_2 at 500 °C for 2 h. The reaction test had four steps. In step I, CH dehydrogenation was carried out at weight hourly space velocity = 10 and a molar ratio $H_2/CH = 30$ for 1 h. The same reaction conditions were used in step II, but the CH feed was doped with CS_2 in order to have sulfur concentrations of 1, 3, 5, or 7 ppm S. In step

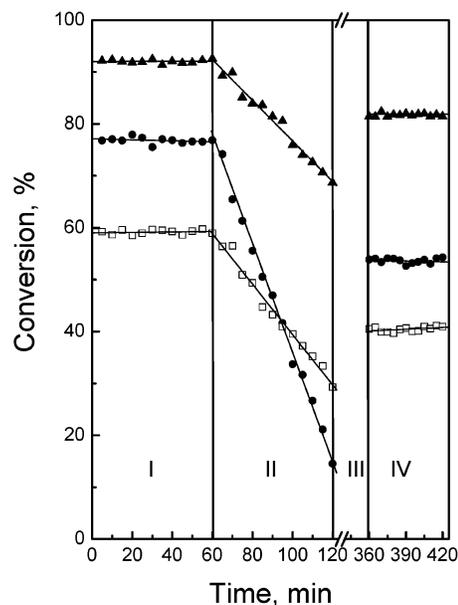


Figure 1. Conversion during dehydrogenation of CH and its poisoning with 1 ppm S. Catalysts prepared by coimpregnation: (I) sulfur-free feed; (II) feed poisoned with 1 ppm S; (III) hydrogen passage; (IV) recovery of conversion, sulfur-free, CH feed. (▲) (Pt + Re)/ Al_2O_3 . (●) (Pt + Sn)/ Al_2O_3 . (□) (Pt + Re + Sn)/ Al_2O_3 .

III, the CH feed was stopped and pure H_2 was allowed to flow over the sample for 4 h at 400 °C in order to eliminate reversible adsorbed sulfur. Finally, in step IV, the CH feed was again injected and the reaction was carried out under the same conditions of step I in order to test the recovery of the catalytic activity. Step I of the reaction test assesses the catalytic activity, step II the rate of sulfur poisoning, and step IV the recovery of the catalytic activity after hydrogen treatment. The reaction products were analyzed in a Varian 3400CX gas chromatograph equipped with a flame ionization detector and a column of FFAP on Chromosorb P.

Results and Discussion

Thirteen catalysts, one monometallic Pt, four bimetallic Pt-Re and Pt-Sn (two by coimpregnation and two by successive impregnation), and eight trimetallics Pt-Re-Sn (one by coimpregnation, the six possible by successive impregnations, and one by successive coimpregnation of a monometallic) were tested with the CH dehydrogenation reaction. Plots showing the CH conversion levels of the coimpregnated catalysts in each step of the test as a function of time on stream are shown in Figure 1 in the case of sulfur poisoning with 1 ppm S. It can be seen that (Pt-Re)/ Al_2O_3 has the lowest deactivation rate (lowest slope in step II), (Pt-Sn)/ Al_2O_3 has the highest, and the trimetallic catalyst has an intermediate value. The conversion on (Pt + Re + Sn)/ Al_2O_3 and its recovery in step IV are lower than those of the bimetallic catalysts. These results are also included in Table 1, where they can be compared with those of monometallic Pt/ Al_2O_3 and the bimetallic catalysts prepared by successive impregnation. In the case of Pt-Re/ Al_2O_3 and (Pt + Re)/ Al_2O_3 , the addition of Re to Pt produces a decrease in the catalytic activity and an increase in the sulfur susceptibility (greater deactivation rate in step II and lower percentage of activity recovery in step IV). In the case of Pt-Sn/ Al_2O_3 and (Pt + Sn)/ Al_2O_3 and in comparison with the previ-

Table 1. Values of CH Conversion in Step I, Deactivation Rate in Step II (CH Doped with 1 ppm S), and Conversion in Step IV^a

catalyst	step I	step II	step IV	
	X_I (%)	deactivation rate (% h ⁻¹)	X_{IV} (%)	X_r (% recovery)
Pt/Al ₂ O ₃	79 ^b	11 ^c	75 ^b	95
(Pt + Re)/Al ₂ O ₃	92	23	81	88
(Pt + Sn)/Al ₂ O ₃	77	62	54	70
Pt-Re/Al ₂ O ₃	97	12	91	94
Pt-Sn/Al ₂ O ₃	77	42	61	79
(Pt + Re + Sn)/Al ₂ O ₃	59	29	40	68
Re-(Pt + Sn)/Al ₂ O ₃	59	36	29	49

^a X_I = conversion during step I; X_{IV} = conversion during step IV; X_r = percentage of step I conversion recovered in step IV. Metal names within parentheses indicate that metal precursors were coimpregnated. Metal names separated by hyphens indicate the order of addition during impregnation. ^b Conversion with 0.025 g of Pt/Al₂O₃, 0.05 g for the other catalysts, and 0.05 g of Pt/Al₂O₃ produce 100% conversion. ^c Calculated extrapolation for 0.05 g of mass.

ous case, the addition of Sn to Pt produces a greater decrease in activity and a greater increase in sulfur susceptibility. The results of the CH test for the six catalysts prepared by successive impregnations show that they have, in comparison to the corresponding bimetallics, the same behavior as those prepared by coimpregnation.

All trimetallic catalysts have a smaller activity than Pt-Re/Al₂O₃, and most of them also have a lower activity than Pt-Sn/Al₂O₃. Then, the deactivation of the catalytic activity of Pt by Re and Sn in trimetallics is additive; i.e., the metallic activity order is Pt > bimetallic > trimetallic. In contrast, the poisoning rate of the trimetallic catalysts by S has an intermediate value between those of the bimetallics, and the activity recovery is intermediate or lower. The intermediate rate of deactivation could indicate that the metal sites are independent, with Pt-Re, Pt-Sn, and Pt sites being simultaneously poisoned by sulfur. Another conclusion is that the active metal sites are not only free Pt sites unaffected by Re or Sn because in the trimetallic catalysts and because of the additive action of Re and Sn the number of free Pt sites is the smallest. Then, if only unaffected Pt were the active site, the slope of deactivation should be the greatest, but this is not the case. Also, if only free Pt sites are the active sites, the recovery of activity in step IV as a percentage of step I must be equal for all of the catalysts, and this is not the case. These results indicate that Pt sites affected by Re and/or Sn are indeed catalytically active, with a smaller activity than free Pt and with a higher sensitivity to sulfur.

The different S poisoning of Pt when alloyed or interacted with Re and Sn shows that the geometrical effect alone (Pt blocking or dilution by Sn or Re) is insufficient to explain the results. A rationalization based on the classical concept of electronegativity is also possible and coincides with other reported experimental results.

In the CH reaction, the active site is always Pt, interacting or not with the promoters, but never the promoters themselves. The Pauling electronegativity values of the interacting elements are Pt = 2.28, S = 2.58, Re = 1.9, and Sn = 1.96. Because of the difference in electronegativity of Pt and S, in the Pt-S bond there is a transfer of electronic charge from Pt to S, which was shown experimentally by Gallezot et al.⁶ When Pt

interacts with Re or Sn, it draws electrons from them because of their lower electronegativity. This was shown experimentally for Pt-Re⁷ and Pt-Sn.⁸ These elements increase the electronic density of Pt, and then its bond with S is stronger, explaining the greater S susceptibility of bi- and trimetallic catalysts.

The donation of electrons to Pt by adsorbed hydrocarbons is the reason for the statement of Boudart and Ptak⁹ that a high electronegativity of the metal is necessary for hydrocarbon reactions. Dalla Betta and Boudart¹⁰ have indeed found that electron-deficient, small Pt clusters supported on acid zeolites are very active in ethylene hydrogenation. In our case, when Re and Sn interact with Pt, they transfer charge to Pt and produce a decrease in its electronegativity. The active sites of Pt-Re, Pt-Sn, or Pt-Re-Sn would then be less active than Pt. The higher the charge transfer, the higher the activity decrease.

The CH dehydrogenation is also decreased because of the smaller capacity for hydrogen chemisorption of the interacted Pt sites.¹¹ This produces a decrease in the capacity of Pt to subtract hydrogen from CH.

Re-Pt-Sn/Al₂O₃, among the trimetallic catalysts prepared by successive impregnation, had the lowest activity and the highest S susceptibility. Its behavior is similar to that of Pt-Sn/Al₂O₃ and less similar to that of Pt-Re/Al₂O₃. When Re is added first, it likely interacts in a strong way with the bare support, and when Pt and Sn are added next, they have fewer available sites for strong chemisorption because these have already been partly blocked by Re. Then, Pt and Sn mainly interact between themselves, and the resulting catalytic surface is similar to the surface of Pt-Sn/Al₂O₃. The opposite occurs when Sn is added first in Sn-Pt-Re/Al₂O₃. Sn interacts more with the support, while Re and Pt interact more between themselves. The resulting trimetallic catalyst has active sites similar to those of Pt-Re/Al₂O₃.

When the catalysts prepared by coimpregnation are compared with those prepared by successive impregnation, it can be seen that coimpregnated bi- and trimetallic catalysts have a smaller catalytic activity and a higher sulfur susceptibility; i.e., the contact or effect of Re and Sn on Pt is higher. In the case of Pt-Sn/Al₂O₃, it was shown^{12,13} that coimpregnation produces a greater Pt-Sn interaction than successive impregnation. When both promoters are in solution, they form a Pt-Sn complex that upon reduction leaves Pt and Sn in good interaction. To verify this, we prepared the catalyst Re-(Pt + Sn)/Al₂O₃ by coimpregnating Re/Al₂O₃ with the solution of Pt and Sn precursors. The last line of Table 1 shows the results of the reaction test, which verify that the better Pt-Sn contact and the additive action of Re in Re-(Pt + Sn)/Al₂O₃ produce a catalyst less active and with less recovery to S poisoning than the bimetallic catalysts and the successively impregnated trimetallic catalysts (Re-Pt-Sn/Al₂O₃ and Re-Sn-Pt/Al₂O₃).

When the concentration of CS₂ in step II is increased, the deactivation rate is also increased, as shown in Figure 2 for the 5 ppm concentration. As was the case with the poisoning with 1 ppm S, Pt-Re/Al₂O₃ has the lowest deactivation rate and Pt-Sn/Al₂O₃ the highest. Once the equilibrium between gas-phase H₂S and adsorbed S is achieved (eq 2), the catalysts still display some residual catalytic activity, which is called thiotolerance. The length of step II and the S concentration in

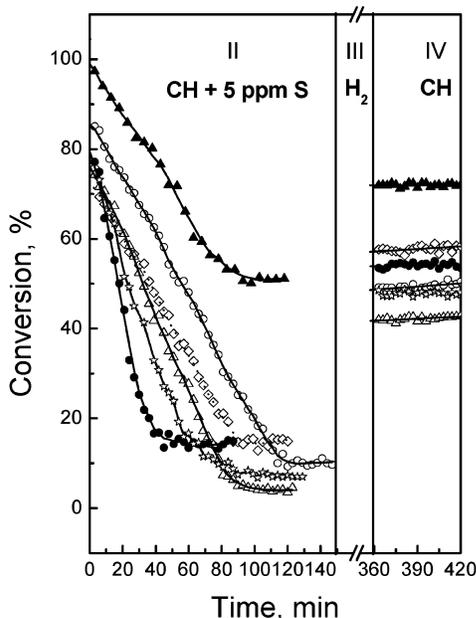


Figure 2. Poisoning of CH dehydrogenation with 5 ppm S. Catalysts prepared by successive impregnation: (II) dehydrogenation of a feed of CH with 5 ppm S; (III) sulfur removal with hydrogen; (IV) conversion recovery, sulfur-free, CH feed. (\blacktriangle) Pt-Re/Al₂O₃. (\bullet) Pt-Sn/Al₂O₃. (\circ) Sn-Pt-Re/Al₂O₃. (\diamond) Pt-Sn-Re/Al₂O₃. (\triangle) Re-Pt-Sn/Al₂O₃. (\star) Re-Sn-Pt/Al₂O₃.

Figure 1 were not enough to reach the S adsorption equilibrium, which was attained in Figure 2. Pt-Sn/Al₂O₃ is very sensitive to S and not only has a curve with a greater slope in step II but also reaches the S adsorption equilibrium much faster than Pt-Re/Al₂O₃. The trimetallic catalysts have an intermediate value of the deactivation rate and a lower value of thiotolerance and activity recovery than the bimetallic catalysts. The magnitude of the poisoning by sulfur of the trimetallic catalysts depends, as was the case with the catalytic activity, on the order of addition of the elements during the preparation of the catalysts. The Re-Pt-Sn/Al₂O₃ catalyst is again the worst trimetallic catalyst, with a high deactivation rate and the lowest thiotolerance and activity recovery. Conversely, Sn-Pt-Re/Al₂O₃ is the best, with the lowest deactivation rate and a good thiotolerance and activity recovery.

Thiotolerance depends on the S concentration in the gas phase, as is shown for Pt-Re/Al₂O₃ in Figure 3, where step I is not included. The time to reach the thiotolerance value is smaller at higher S concentrations. After the hydrogen treatment (step III), only the irreversible adsorbed sulfur remains, with its amount depending on the temperature and the catalyst, which in this case are the same. Therefore, the catalytic activity recovery should be independent of the S concentration in the feed. However, the level of activity recovery decreased when the S concentration was increased. This might indicate that the time span of step III was too short for the desorption of all of the reversible S in the case of the high sulfur treatments (5 and 7 ppm). Figure 4 is a summary of the results of the poisoning experiments performed on Pt-Re/Al₂O₃. The thiotolerance is important because it is the steady-state activity during the passage of a feed with S. When the sulfur concentration in the feed is increased, the thiotolerance is decreased because new metal sites are

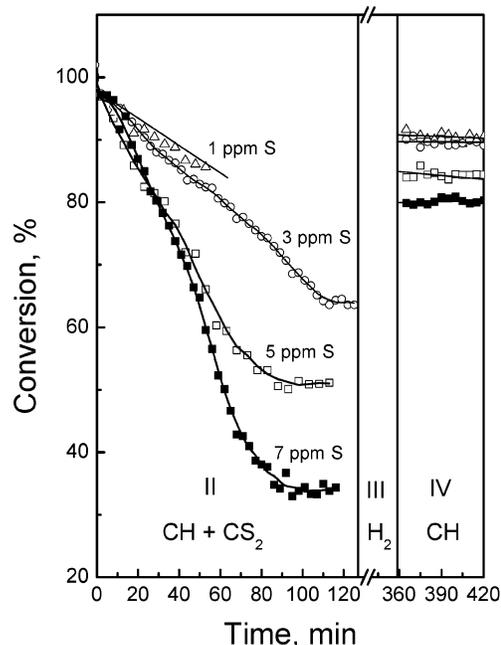


Figure 3. Poisoning, thiotolerance, and activity recovery of a Pt-Re/Al₂O₃ catalyst. Poison: 1, 3, 5, and 7 ppm S (CS₂) in CH.

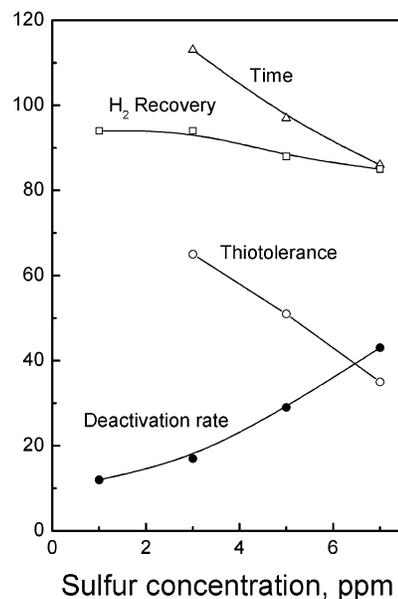


Figure 4. Influence of the sulfur concentration on the poisoning of Pt-Re/Al₂O₃. Initial conversion of CH: 97%. (Δ) Time to reach equilibrium, min. (\square) Recovery of conversion after passage of hydrogen, % of initial conversion. (\circ) Thiotolerance, % of initial conversion. (\bullet) Deactivation rate, % h⁻¹.

covered by S. For every S concentration, the greatest value of thiotolerance corresponds to Pt and the lowest to the trimetallic catalysts.

Conclusions

Sulfur poisoning of the metal function of bimetallic Pt-Re/Al₂O₃ and Pt-Sn/Al₂O₃ catalysts is greater than the poisoning of monometallic Pt/Al₂O₃ and lower than the poisoning of the trimetallic catalysts, which is the most severe.

When trimetallic catalysts are prepared by successive impregnation, both the metallic catalytic activity and the magnitude of its poisoning by sulfur depend on the

order of the addition of the metals. The non noble metal added first interacts more with the support, and the one added last interacts more with Pt. A trimetallic catalyst is produced that has a behavior similar to that of a bimetallic catalyst composed of Pt and the metal added last.

The decrease in the metal activity produced by Re and Sn addition and the S susceptibility are greater for the coimpregnated catalysts than for the catalysts prepared by successive impregnation. The reason is the better interaction between Pt, Re, and Sn in the coimpregnated catalysts.

Sn addition decreases the Pt catalytic activity to a greater extent than Re does. Sn also increases the strength of the Pt–S bond more than Re, therefore producing a greater deactivation rate and a lower thiotolerance and activity recovery.

Trimetallic catalysts have the lowest metal activity, with some variation between them, which depends on the order of addition of the metals. They also have the lowest thiotolerance and capacity for activity recovery. These results justify the extreme conditions currently employed to eliminate sulfur from the feed. In the operation of reforming units, a S concentration in the feed of lower than 20 ppm is suggested for monometallic Pt/Al₂O₃. This limit is lowered to 1 ppm for bimetallic Pt–Re/Al₂O₃ catalysts.² Because trimetallic catalysts are even more sulfur sensitive, the S concentration should be as low as possible. Ultralow sulfur levels cannot be attained by normal hydrodesulfurization units, and a sulfur guard unit must be incorporated before the reforming reactor.

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Received for review July 10, 2003

Revised manuscript received December 30, 2003

Accepted December 30, 2003

IE030579K