

EFFECT OF SOME PLATINUM METALS ON THE REGENERATION BEHAVIOUR OF ZEOLITIC CRACKING CATALYSTS

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ABSTRACT

A simple method is described by which a clear distinction can be made between fluid cracking catalysts, whether they contain oxidation promoters or not. It was shown that by incorporating 1 part per million of platinum into an unpromoted catalysts, its CO-oxidation activity could be improved drastically. Palladium proved about ten times less effective. The regenerability of the catalyst, characterized by the temperature belonging to the CO-conversion of 0.5 changes linearly with the one third power of the platinum concentration. High temperature steam treatment of the platinum metal impregnated catalysts levelled activity differences by decreasing the activity of platinum containing catalysts and increasing that of palladium containing ones.

INTRODUCTION

Synthetic zeolite containing catalysts are used practically exclusively in catalytic cracking units all over the world because of the higher gasoline yield, lower coke make etc. In order to make full use of these advantages a coke level far less than 0.1 % by weight on the recycled catalyst is imperative, since already small amounts of coke left on the catalyst would block the zeolite pores, preventing the molecules to be cracked to enter. The effect of the coke content on cracking yield was shown by Wachtel and coworkers (1).

Highly efficient coke removal can be attained by high temperature regeneration (2), by two-step regeneration (3) and/or by the use of coke oxidation improving agents incorporated into the fluid cracking catalyst (4), or used along with the catalyst in liquid or solid form (5). Using these means, a practically complete oxidation

of the coke to carbon dioxide (and water) with a near-stoichiometric amount of air is possible, that, by decreasing the catalyst-to-oil ratio, brings about higher gasoline yields, more efficient use of the thermal and kinetic energy of the regenerator flue gases in expander turbines, lower carbon monoxide emissions, etc.

Oxidation improvers belong to the class of platinum metals. In spite of the wide-spread use of these so called promoters, no literature is known presenting data on the specific effects of different platinum group metals, how their concentration influences the burning of the coke, how their catalytic effect is influenced by conditions occurring during the cracking/regeneration cycle, etc.

The effectiveness of oxidation improvers is tested either by determining the carbon monoxide/carbon dioxide ratio in the flue gas of a batch regeneration experiment of coked catalysts (2), or by measuring the carbon monoxide conversion of a carbon monoxide containing gas led over the catalyst under specified conditions (6, 7).

The aim of the present work was to investigate how platinum and palladium impregnated zeolitic cracking catalysts behave in carbon monoxide oxidation, what are the metal concentration effects, and how hydrothermal treatment affects their oxidation activity.

EXPERIMENTAL

The apparatus used consisted of an electrically heated upflow isothermal quartz reactor of 20 mm i.d. and 400 mm height with a sintered porous plate in the middle and two thermowells extending from both ends, pressure bottles for compressed air and carbon monoxide, and flow control valve and rotameters for controlling and measuring the flow of gaseous reactants. The temperature inside the reactor was controlled to ± 1 deg. C by means of temperature controllers.

The carbon monoxide content of the feed gas as well as that of the effluent from the reactor was measured by means of calibrated infrared gas analyzers, type Elkon S-205, operating at a wave-length of 4660 nm.

Measurements were carried out with air containing 2 % by volume of carbon monoxide, at a flow rate of 30 liters/hour, measured at room temperature and atmospheric pressure, using 6.2 ml catalyst samples placed on the porous plate.

Measurements with the same batch of catalyst were carried out at different temperatures. The carbon monoxide content of the effluent was corrected by subtracting the carbon monoxide converted in

the empty (i.e. catalyst not containing) reactor at the same temperature. The correction was negligible at temperatures below 400 deg. C.

Catalyst samples have been stabilized by pretreating the catalyst for 2 hours at 500 deg. C with the same 2 % (volume) CO-containing air used for the activity determination. Industrial fresh and equilibrium fluid cracking catalysts from two different manufacturers have been used, some of them containing promoters of unspecified nature and concentration. Data of the catalysts are summarized in Table 1.

Table 1
Data of the catalysts used

Catalysts	Unpromoted			Promoted		
	Al _F	Al _E	B _F	A2 _{FP}	A2 _{EP}	B _{EP}
<u>Chemical composition</u>						
Al ₂ O ₃ %	23,2	21,5	46,8	28,0	26,5	-
Na ₂ O %	0.24	0.19	0.25	0.20	0.28	-
Fe %	0.01	0.12	0.76	0.08	0.25	-
Coke %	0	0.13	0	0	0.09	0.01
<u>Physical properties</u>						
Apparent Bulk Density (g/ml)	0.46	0.75	0.84	0.53	0.85	0.96
Pore Volume (ml/g)	0.68	0.41	0.27	0.50	0.25	0.23
Surface Area (m ² /g)	565	172	122	390	97	81

-: no data available

Early measurements with these catalysts presented problems as fines leaving the reactor plugged outlet lines. This difficulty was overcome by a previous air elutriation of the catalyst samples, by which about 21-23 % of the original batches have been removed as fines.

In order to test the promoting effect of platinum group metals fresh Al_F catalyst samples were impregnated with aqueous platinum or palladium salt solutions (H₂(PtCl₆) and PdCl₂), dried at 120 deg. C for 3 hours and calcined at 600 and 750 deg. C for 3 and 6 hours in air, respectively.

To simulate hydrothermal effects occurring during fluid catalytic cracking, catalyst samples were treated in the laboratory at 750. deg. C for 6 hours with steam.

RESULTS AND DISCUSSION

Figure 1. shows the carbon monoxide conversion vs. temperature curves for commercial fluid cracking catalysts made by manufacturers A and B. The samples tested were the following:

- unpromoted fresh $A1_F$ and B_F ,
- unpromoted equilibrium $A1_E$,
- promoted fresh $A2_{FP}$ and B_{FP} , further
- promoted equilibrium $A2_{EP}$ and B_{EP} ,

where subscripts F, E and P refer to fresh, equilibrium and promoted catalysts, respectively.

Figure 1. clearly shows that the oxidation of carbon monoxide starts and is completed at much lower temperatures with promoted catalysts as in the presence of unpromoted ones. Promoted fresh catalyst $A2_{FP}$ was of lower oxidation activity than its equilibrium counterpart $A2_{EP}$, indicating that one or more of the conditions prevailing during the cracking-regeneration cycle improves carbon monoxide conversion behaviour of certain fluid catalytic cracking catalysts.

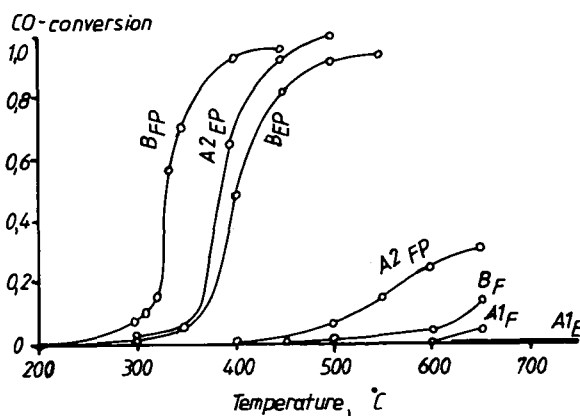


Fig. 1. Carbon monoxide conversion vs. temperature with different commercial cracking catalysts

The carbon monoxide conversion vs. temperature curves for most promoted cracking catalysts were steep, probably because the temperature within catalyst particles was much higher than the

measured bulk gas temperature, due to the heat of combustion of carbon monoxide and the low heat conductivity of the catalyst particles.

Fresh catalyst Al_F was impregnated to different platinum contents of 1 to 200 ppm, with solutions of hexachloroplatinic acid. Data of carbon monoxide conversion vs. temperature for these catalysts, along with those of unpromoted Al_F catalyst are plotted in Figure 2. This figure shows that already the extremely low concentration of 1 part per million of platinum drastically reduces the temperature needed for a given carbon monoxide conversion. Increasing the platinum concentration to 200 ppm further enhances the activity of the catalyst. Reaction temperatures measured at a CO-conversion of 0.5 plotted in function of the one third power of platinum concentration show a linear correlation.

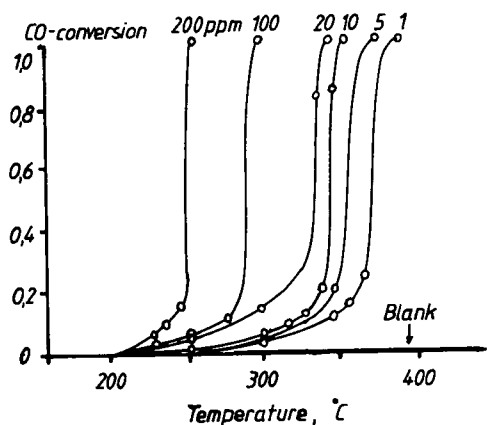


Fig. 2. Effect of platinum concentration

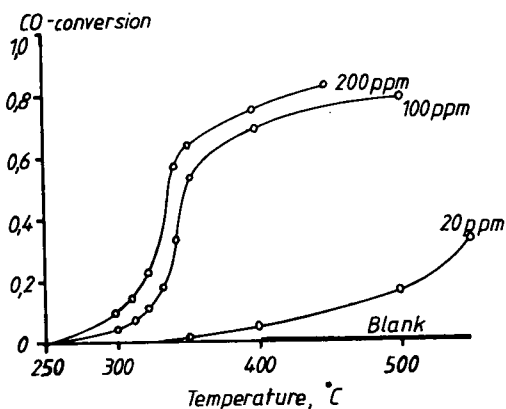


Fig. 3. Effect of palladium concentration

The same fluid cracking catalyst Al_F , when impregnated with solutions of palladium chloride according to the procedure previously described, behaved - compared to the platinum impregnated catalysts, as shown in Figure 3. - far less efficiently: e.g. to attain a carbon monoxide conversion of 0.5 about ten times as much of palladium was needed, as of platinum. Additionally, in the higher conversion range, curves flattened out, reaching total carbon monoxide conversion only at very high temperatures.

Preliminary experiments were run to find out if the conditions prevailing within the cracking/regeneration cycle influence the carbon monoxide oxidation activity of cracking catalysts. It has been found that thermal treatment in dry air modified only

slightly the carbon monoxide oxidation activity of the samples tested. high temperature hydrothermal treatment, however, brought about considerable changes.

Samples of catalyst Al_F impregnated with hexachloroplatinic acid solutions to 10 and 200 ppm platinum content, along with blank catalyst Al_F were subjected to hydrothermal treatment with steam at 750 deg. C for 6 hours, and subsequently tested for their carbon monoxide oxidation activity.

Results are shown in Figure 4. For comparative purposes, results obtained with the untreated catalysts are also shown. Whereas the oxidation activity of the blank Al_F catalyst increased slightly upon the hydrothermal treatment, catalyst samples containing platinum became less active than they were before hydrothermal treatment.

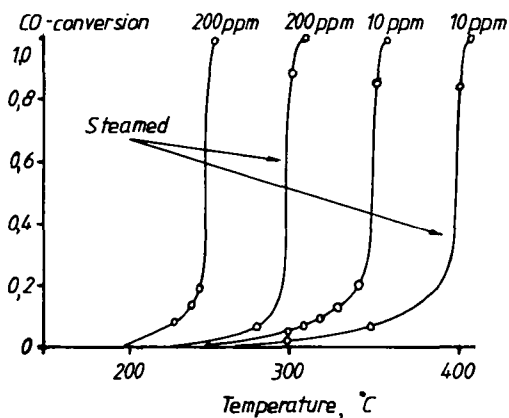


Fig. 4. Effect of hydrothermal treatment on platinum impregnated catalysts

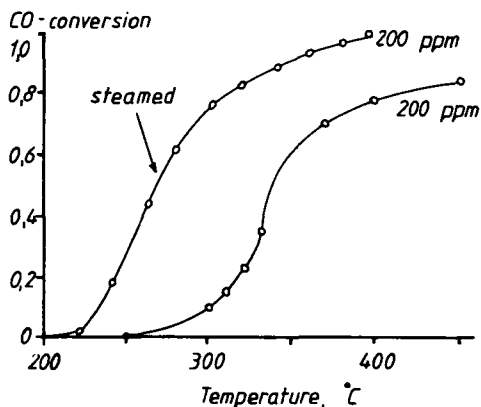


Fig. 5. Effect of hydrothermal treatment on palladium impregnated catalysts

Catalyst Al_F impregnated with palladium chloride solution to contain 200 ppm of palladium, was subjected to the same hydrothermal treatment. The carbon monoxide oxidation activity curve of the treated sample is shown in Figure 5, along with that of the untreated sample. Hydrothermal treatment increased the carbon monoxide oxidation activity of the palladium containing catalyst considerably: comparing this curve with the curve of hydrothermally treated catalyst containing 200 ppm of platinum on Figure 4, it can be seen that hydrothermal treatment brought the two catalysts to about the same oxidation activity level.

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