

Silicon Poisoning of Pt/Al₂O₃ Catalysts in Naphtha Reforming

M. O. G. Souza^a, P. Reyes^b and M. C. Rangel^c

^aDepartamento de Ciências Exatas e da Terra, Universidade do Estado da Bahia, Estrada das Barreiras s/n, Salvador, Bahia, Brazil

^bFacultad de Ciencias Químicas, Universidad de Concepcion, Casilla 3-C Concepción, Chile

^cInstituto de Química, Universidade Federal da Bahia, Campus Universitário de Ondina, Federação. 40170-280 Salvador, Bahia, Brazil

Abstract

The silicon poisoning of a Pt/Al₂O₃ catalyst was studied as a model system for industrial catalysts. Samples were contaminated using methyl- and phenyl-substituted polyoxysilane (MPSP) during the reforming of cyclohexane. It was found that silicon changes the chemisorption properties of platinum and does not affect its sinterization. However, coke has a more important effect in reducing the activity of the metallic function. On the other hand, silicon is harmful to the acid function, even in small amounts, suggesting that the poisoning is selective.

1. INTRODUCTION

Coke formation [1] and sulfur poisoning [2] usually deactivate naphtha-reforming catalysts. However, other poisons as nitrogen, arsenic, sodium, copper, mercury and lead compounds are also important deactivation agents. They can be irreversibly adsorbed, being accumulated over the active sites of the catalyst [2].

Although silicon has not been reported as a poison for reforming catalysts, a Pt-Re/Al₂O₃ catalyst became irreversibly poisoned in an industrial plant because of the presence of silicon compounds in the feed. This was attributed to the contamination of the naphtha feedstock during petroleum extraction in deep water, which requires a special technology. According to this technology silicone is injected in the well. As a consequence, small amounts of silicon from the feed (some ppb) were deposited over the catalyst, resulting in considerable amounts of this poison after some time. As silicon altered the operation cycle length of the catalyst, it is useful to study the poisoning of the reforming catalysts by silicon. With this goal in mind, the poisoning of a Pt/Al₂O₃ catalyst was studied, as a model system for industrial catalysts.

2. EXPERIMENTAL

The alumina (γ -Al₂O₃ Akzo Chemie Ketjen Catalyst CK 303, with a surface area of 184 m²/g and a pore volume of 0.49 cm³/g) was grounded and sieved to 40-80 mesh. Then, it was impregnated with a 0.0122M H₂PtCl₆ solution, using hydrochloric acid (0.5M) as a competing agent. After drying at 120°C for 6h, the catalyst was calcined in air (500°C, 4h) and reduced in hydrogen (500°C, 2h).

Samples were contaminated during the cyclohexane reforming in order to allow the competition for active sites between silicon compounds and coke precursors. A hydrogen stream was passed through two saturators, the first containing cyclohexane at 20°C and the other with methyl- and phenyl-substituted polyoxysilane (MPSP) at 230°C. This stream was fed to the reactor at 500°C, for 4 h (sample CS4). The procedure was repeated keeping the catalyst for 7h (CS7) and for 10h (CS10). These experiments were repeated using only MPSP to get samples without coke (S4, S7 and S10) and using only cyclohexane to get catalysts without silicon (C4, C7 and C10).

The chemical analysis was carried out by inductively coupled AR plasma (ICP/AES), in a ARL model 3410 equipment and by a Noran microprobe attached to a Jeol model JSM-T300 microscope. The surface area and the dispersion (hydrogen chemisorption) were measured in a Micromeritics model TPD/TPO 2900 equipment. The temperature programmed oxidation (TPO) profiles were got in the same equipment. Fourier transformed infrared spectroscopy (FTIR) was used by means of a Jasco model Valor-III equipment. The micrographs were obtained from extractive replica [3] in a Jeol model JEM-1200 EXII microscope. The metal function was evaluated in the cyclohexane dehydrogenation at 1 atm, 315°C, WHSV=30 h⁻¹ and hydrogen/ cyclohexane (molar)=7 [4]. The acid function was evaluated in the n-hexane isomerization at 1 atm, 420°C, WHSV=4.8h⁻¹ and hydrogen/hydrocarbon (molar)=7 [5].

3. RESULTS AND DISCUSSION

The presence of silicon in the contaminated solids was detected by FTIR. By ICP/AES, 1.2 % silicon was found in the sample CS10, while no silicon was detected in the other samples. No silicon was detected by microprobe, suggesting that its concentration on the surfaces remains in values lower than 1%.

Coke was not formed on samples contaminated for 4h. The TPO of the solids contaminated for 7h and 10h showed two peaks, due to coke deposited on the support (high temperature peak) and located on the metal (low temperature peak) [6]. In the first sample, the peaks are centered at 400 and 500°C while in the other they are centered at 450 and 540°C. The presence of silicon does not modify the TPO profiles. The highest amount of coke was shown by sample C10.

Silicon decreases the surface area of the sample S10 (Table 1), showing that it leads to a filling of the pores of alumina [7]; for shorter times under

Table 1
Surface area, dispersion and activity of the acid and metal functions of Pt/Al₂O₃

Sample	Sg (m ² /g)	H/Pt	Cyclohexane Conversion (%)	Hexane Conversion (%)	Selectivity to 2 MP (%)	Selectivity to 3 MP (%)
F	180	0.54	30	30	57	31
CS4	168	0.41	23	16	53	36
CS7	166	0.33	4	4	67	33
CS10	172	0.33	4	4	67	33
S4	178	0.49	28	16	48	22
S7	198	0.60	32	15	42	20
S10	155	0.19	7	4	67	33
C4	174	0.52	29	26	58	34
C7	177	0.38	6	3	64	32
C10	165	0.36	5	2	36	8

F= non-contaminated sample

2 MP= 2-methyl-pentane

3 MP= 3-methyl-pentane

contamination, the effect is not noticeable. In the presence of coke, no significant change was found. In the samples having only coke, a sharp decrease in surface area is detected only in the sample with the largest amount of coke (S10).

From the H/Pt ratio values (Table 1) we can see that low amounts of silicon do not alter significantly the chemisorption properties of platinum, in samples without coke (S4, S7 and CS4). At higher amounts of silicon or in the presence of coke (samples S10, CS7 and CS10), however, it leads to a large decrease of the H/Pt ratio. In the presence of coke alone, a large decrease of the H/Pt ratio is also noted (samples C7 and C10). Sample C4 has not coke or silicon and it behaves like the fresh catalyst. The large decrease detected in samples CS7 and CS10 seems to be more related with coke rather than with silicon. The minimum value of H/Pt is reached after 10 h, without coke formation (sample S10). These results indicate that the effect of silicon on the dispersion is related to the coke. From the TEM experiments it was also noted that platinum particle size remained in the range of 10-20 Å in all samples. Therefore, it seems that silicon causes a change in the chemisorption properties of platinum rather than in the platinum sinterization. In the coked samples, this is probably due to a blockage of the sites by the carbonaceous deposits. In the samples with silicon, however, an alloy between platinum and silicon could be formed [8].

The results of the cyclohexane conversion show that low amounts of silicon do not affect the activity of the metallic function but the activity is strongly reduced for higher amounts of silicon (sample S10). Coke has a more important effect in activity than silicon. These results are closely related to those of platinum dispersion.

From the hexane conversion it was noted that silicon is harmful even in small amounts, no detectable by analytical methods, in accordance with previous works about other poisons [9]. Samples CS4 and S4 showed a large decrease in the activity, indicating that the poisoning is selective. A further deactivation depends on the presence of coke; in its absence another decrease in activity is only detected after 10 h while in its presence a large decrease is noted after 7h. In the absence of coke, large amounts of silicon are required to produce deactivation. This poisoning is probably related with changes in the acid sites, because it does not seem to exist a relationship between the activity of the acid site and the sintering of alumina. These change should be related to silicon itself since the amount of chloride ($Cl/Al(\text{molar})= 0,017$) remains the same in all solids.

4. CONCLUSIONS

Silicon, added as MPSP, poisons both metallic and acid sites of Pt/Al_2O_3 catalysts during the reforming of cyclohexane, at 500°C . This poisoning occurs in the first hours of the reaction; after 7 h, coke starts to be formed and the highest deactivation is observed. Silicon changes the chemisorption properties of platinum and does not affect its sinterization. Coke has a more important effect than silicon in reducing the activity of the metallic function while silicon is harmful to the acid function, even in small amounts, due to a selective poisoning.

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