Regeneration and oxidation-reduction cycles of vapor phase and incipient wetness impregnation Pt/KL catalysts

Firoz Ghadiali, Gary Jacobs, Adriana Pisanu, Armando Borgna[1], Walter E. Alvarez, and Daniel E. Resasco*.

School of Chemical Engineering, University of Oklahoma, Norman, OK 73019, USA.
Phone: (405) 325-4370; Fax: (405) 325-5813; E-mail: resasco@ou.edu
[1] INCAPE, Santiago del Estero 2654(3000) Santa Fe, Argentina

The regeneration of three different Pt/KL catalysts has been studied after the n-hexane aromatization reaction in the presence of sulfur. It has been found that regeneration in air of poisoned catalysts does not result in recovery of the aromatization activity. After this regeneration, growth of Pt particles outside the channels of the zeolite is observed. By contrast, regeneration with addition of a halo-alcohol results in Pt redispersion and significant recovery of aromatization activity. The preparation method employed and the presence of Tm as a promoter plays an important role in the efficiency of the regeneration procedure.

1. INTRODUCTION

It is well known that Pt/KL catalysts have exceptionally high activity and selectivity for the aromatization of n-hexane to benzene. The principal drawback of these catalysts is their high sensitivity to the presence of sulfur even in very low amounts (e.g., ppb). Therefore, development of sulfur-resistant catalysts is a major goal in this area. At the same time, the understanding of the regeneration process is also an issue of great industrial relevance [1-3]. However, only a few papers in the open literature [4] have focused on the effect of different treatments after reaction under clean and sulfur-poisoning conditions. In a recent investigation [5], we have pointed out that by varying the preparation method of Pt/KL catalysts, one can greatly influence the size and morphology of the Pt particles inside the channels of the zeolite, and these morphological variations may have strong effects on the stability of the catalysts under both, sulfur-free and sulfur-containing feeds. The vapor-phase impregnation method (VPI) results in catalysts with smaller particles than those in the catalysts prepared by incipient wetness impregnation (IWI). The characteristic morphology produced by the VPI method was found to improve the performance of the catalyst under clean and sulfur poisoned conditions, enhancing the

catalyst's resistance to the formation of coke and decreasing the particle agglomeration rate. Similarly, we [6] and others [7-8] have observed that the addition of small amounts of thulium resulted in improved performance. We have demonstrated [6] that the addition of Tm (VPI) results in an improvement in metal dispersion. Also the Tm may act as a getter of sulfur, hence delaying the effects of sulfur poisoning on the Pt metal. In this contribution we have investigated different regeneration procedures on three Pt/KL samples, one prepared by IWI, one by VPI, and a third one prepared by VPI containing Tm.

2. EXPERIMENTAL

1 wt % Pt/KL catalysts were synthesized by incipient wetness impregnation (IWI) and vapor phase impregnation (VPI). The Tm-promoted catalyst was prepared by sequential vapor phase impregnation. This method has been described in detail elsewhere [6, 9]. Briefly, it consists of subliming acetyl-acetonates of Pt and/or Tm in the presence of dry KLTL zeolite in vacuum. Fresh and spent samples were characterized by EXAFS, TEM, and FTIR of adsorbed CO. EXAFS experiments on in-situ reduced samples were performed at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. EXAFS data were taken near the LIII-edge of Pt at liquid nitrogen temperature and the EXAFS signal was extracted from raw data by a conventional procedure[5]. The range in k-space utilized to do the analysis was 3.5-13.5$Å^{-1}$. The FEFFIT fitting routine[11] was employed to obtain the structural parameters of the Pt clusters after the various regeneration treatments. The Debye Waller factors for each bond type (σ), the edge energy difference (ΔE_o), the coordination number (N), and the difference in the bond distances (ΔR) with respect to the theoretical reference, were used as fitting parameters. The aromatization of n-hexane was studied in a pulse reactor in the temperature range of 400 °C to 500 °C, sending pulses containing around 6.57×10^{-7} moles of n-hexane in a H_2 carrier. The catalysts were studied in the freshly reduced state, after 9 h under steady state reaction, in the presence of 2 ppm S, and after regeneration. Regeneration procedures were carried out using oxidizing treatments with air and 1,3 dichloro-2-propanol. For both the regeneration treatments, the samples were reduced *in situ* under H_2 for 1 h at 500 °C. For the regeneration in air, the temperature was decreased to 400 °C and the sample was exposed to air for 1.5 h. For the halo-alcohol regeneration procedure, the sample was first treated with 5% O_2/He for 30 min at 400 °C. This was followed by an oxychlorination step to obtain the redispersion of Pt particles. The halo-alcohol was saturated with a continuos flow of He through a gas bubbler and then diluted with a stream of 5% O_2/He at 400 °C. Then, the sample was exposed to this mixture for 1.5 h. After that step, the halo-alcohol was switched off and the catalyst was allowed to oxidize under 5% O_2/He for another 30 min. The samples were then re-reduced at 500 °C for 1 h before the pulse experiments.

3. RESULTS

3.1. Catalytic Activity Measurements

The conversion of n-hexane was studied in the pulse reactor after the various pretreatments. Fig. 1 shows the benzene yields obtained on the three catalysts at 500 °C. In agreement with previous results [6], the fresh VPI and Tm-VPI catalysts exhibited somewhat higher activity and selectivity than the standard IWI Pt/KL catalyst. However, the greatest differences were observed on the samples aged under sulfur and those regenerated in air alone or with the addition of chloropropanol. In those samples, the VPI and particularly the Tm-VPI show much better performance than the standard IWI catalyst.

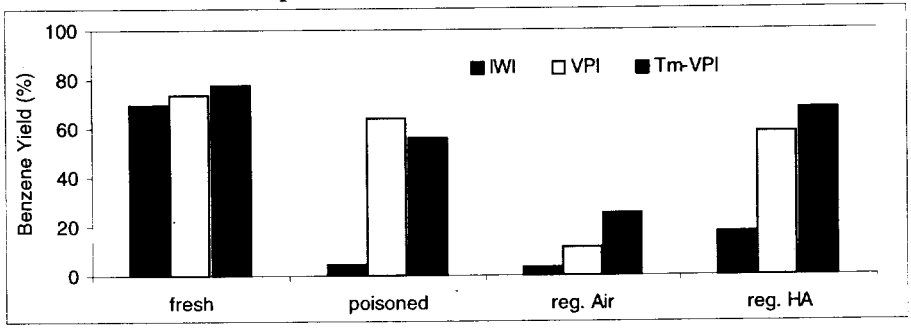

Fig. 1. Benzene yield for IWI, VPI and Tm-VPI catalysts at 500°C.

3.2. Catalyst Characterization

The characterization by EXAFS, TEM and H_2 chemisorption conducted over the three different catalysts indicate that the VPI method leads to the formation of Pt clusters inside the channels of the zeolite much smaller than those prepared by IWI. As summarized in Table 1, EXAFS shows lower Pt-Pt coordination numbers, confirming the presence of smaller clusters.

Table 1
Structural parameters determined from EXAFS analysis.

	Fresh			Poisoned			Reg-Air			Reg-Haloalcohol		
	Pt-Pt	Pt-O	R (Å)	Pt-Pt	Pt-O	R (Å)	Pt-Pt	Pt-O	R (Å)	Pt-Pt	Pt-O	R (Å)
IWI	7.6	--	2.74	8.2	--	2.75	8.7	--	2.74	3.1	--	2.66
	--	0.25	2.73	--	0.35	2.71	--	0.2	2.70	3.8	--	2.77
										--	0.40	2.68
VPI	2.1	--	2.81	3.1	--	2.77	5.8	--	2.74	2.8	--	2.78
	2.7	--	2.69	2.6	--	2.67	--	0.6	2.66	2.9	--	2.67
	--	0.6	2.67	--	0.5	2.67				--	0.6	2.66
Tm-VPI	2.2	--	2.74	1.9	--	2.8	1.9	--	2.8	2.5	--	2.78
	2.1	--	2.61	2.8	--	2.69	3.3	--	2.69	2.5	--	2.66
	--	1.1	2.39	--	0.95	2.67	--	0.9	2.69	--	0.9	2.64

At the same time, the coordination of Pt with the lattice oxygen of the zeolite was higher for the VPI catalyst than for the IWI, indicating a greater extent of interaction with the zeolite walls. Similarly, the addition of Tm as a promoter helps to obtain a higher dispersion of Pt, as reflected by lower coordination numbers on the freshly reduced catalyst.

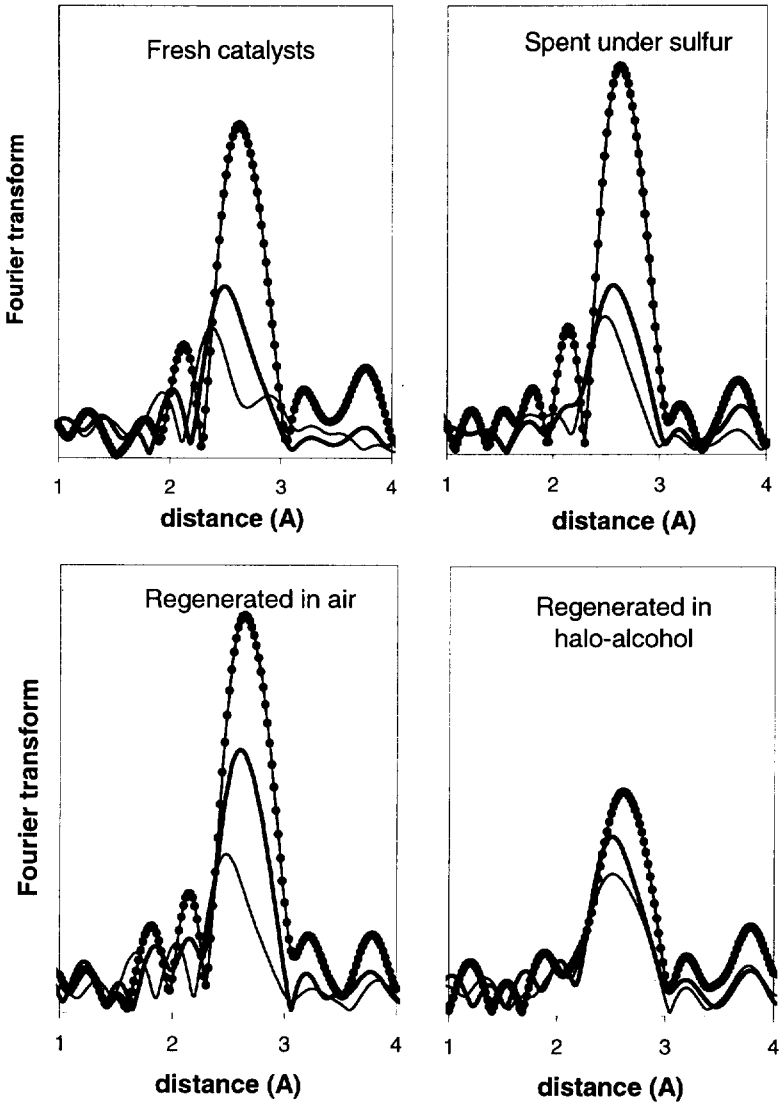

Fig. 2. Fourier Transform obtained from EXAFS data for fresh, spent and regenerated samples. (line with filled circles-IWI ; thick line-VPI ; thin line-Tm-VPI).

EXAFS has been used to investigate the changes in morphology of the Pt clusters on the three different catalysts after the various treatments. Fig. 2 includes the Fourier transforms of the EXAFS data obtained on the IWI, VPI, and Tm-VPI samples in the freshly reduced state, after reaction under sulfur (9 h, 2 ppm), after regeneration in air, and after regeneration with addition of chloropropanol. Interesting trends are observed. After reaction for 9 h in the presence of sulfur, a moderate increase in coordination number was observed for all three catalysts. However, it is important to note that, even after this growth, the particles in the VPI and Tm-VPI catalysts are still very small, as indicated by the low coordination numbers.

DRIFTS of adsorbed CO helps to further understand what happens with the catalysts after regeneration in air. The fresh catalyst exhibited the typical distribution of bands in the range 2080 to 1950 cm^{-1}. As discussed previously [5,10], the appearance of the low wavenumber bands are associated with the formation of Pt-carbonyl species, stabilized by the zeolite. Important differences were observed in the spectra of adsorbed CO after exposure to sulfur. While the spectra for the IWI catalyst showed a significant decrease in the region between 2014 and 1970 cm^{-1}, the spectra for the VPI catalyst only showed a modest change in this region. In addition, regeneration in air of the IWI catalyst caused the appearance of a shoulder at about 2084 cm^{-1} on the IWI catalyst that we attribute to large Pt particles that migrated to the outer surface of the zeolite. In contrast, after similar calcination at high temperature, the VPI and Tm-VPI catalysts did not exhibit that high wavenumber shoulder and showed lower decrease in hydrogen chemisorption in comparison with the IWI catalyst.

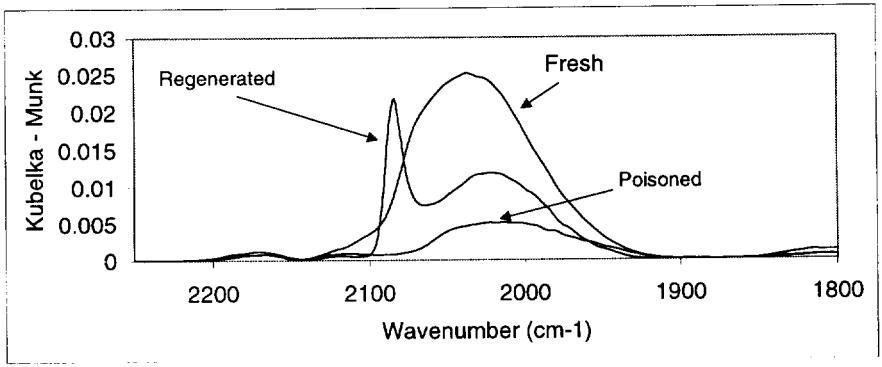

Fig. 3. DRIFTS spectra for fresh, spent(poisoned) and regenerated(air) IWI samples.

4. CONCLUSIONS

This study has demonstrated that both, the catalyst preparation method and the regeneration procedure have important effects on the activity of the catalyst samples. The VPI and the Tm-VPI catalysts have a better sulfur resistance than the IWI catalysts due to their initial small particle size. Therefore, channel blocking and Pt particle entrapment is delayed. Regeneration in air results in sintering of particles, which causes a drop in the activity of all the samples. The oxychlorination treatment of the poisoned samples result in better Pt dispersion and an increase in the aromatization activity. The increase in the aromatization activity for the IWI sample can be attributed to the redispersion of Pt particles as clearly indicated by EXAFS. For the VPI and Tm-VPI samples, the increase is mainly due to coke and sulfur removal. The addition of Tm as a promoter helps in maintaining the dispersion of Pt particles under the regeneration process.

5. ACKNOWLEDGMENTS

This work was supported by the Oklahoma Center for the Advancement of Science an Technology (OCAST). We acknowledge the Phillips Petroleum company for a scholarship (FG) and the National Science Foundation (NSF) for a GRT traineeship (GJ). We also acknowledge the personnel at NSLS, Brookhaven National Lab, for the EXAFS experiments. One of us (A.B.) is especially indebted to the Fundación Antorchas and the Fulbright Commission for financial support.

6. REFERENCES:

1. Burbridge W. B. and Rees D. M., US Patent No. 4 192 771 (1980).
2. Bernard J. R. and Breysse M., US Patent No. 4 493 901 (1985).
3. Fung S. C., Tauster S. J. and Koo J. Y., US Patent No. 5 726 112 (1998).
4. Sugimoto M., Katsuno, H., Hayasaka, T., Hirasawa, K. and Ishikawa, N., Appl. Catal. A: General, 106 (1993) 9-25.
5. Jacobs G., Ghadiali F., Pisanu A., Borgna A., Alvarez W. E. and Resasco D. E., Appl. Catal. A: General, 4749(1999)1-20.
6. Jacobs G., Ghadiali F., Pisanu A., Padro C., Borgna A., Alvarez W.E. and Resasco D. E., J. Catal. (in press).
7. Li F., Lu W., Wu G. and Li. J., J. Alloys and Comp., 207/208, 397(1994).
8. Fang X., Li F. And Luo L., Appl. Catal. A: General, 146, 297(1996).
9. Hong. S.B., Mielczarski E. and Davis M. E., J. Catal., 134, 349(1992).
10. Stakheev A.Y., Shpiro E.S., Jaegar N.I. and Schulz-Ekloff G., Catal. Lett. 34, 293(1995).
11. Mustre de Leon J., Rehr J. J., Zabinsky S. I., Albers R. C., Phys. Rev. B, 44 (1991) 4146.