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The Effect of Tin and Antimony Addition on the Performance of Dual Function Cracking Catalyst (DFCC) Mixtures

In 1976, the Phillips Petroleum Company successfully demonstrated in their Borger (Texas) refinery that the addition of certain organo-antimony compounds to a metal-contaminated heavy gas oil reduced the deleterious effects that metals such as Ni and V have on gasoline yields, coke, and hydrogen selectivities (*1–5*). Nickel has little effect on the activity of a fluidized cracking catalyst (FCC) but generates large amounts of gases, placing severe demands on capabilities of gas compressors. Marketed by Phillips Petroleum Company, Phil-Ad® CA antimony organics have been shown to reduce by 50% gas formation due to metal contaminants, especially nickel (*1–6*). However, Sb, when introduced into a fluidized cracking unit, could reduce and form SbH_3, stibine, that like arsine (AsH_3) is a highly toxic compound. Procedures for the safe usage of Sb in refining operations have been outlined; when used properly, Sb-containing passivating agents did not generate any detectable stibine (*7*). Today, after over 25 commercial trials, the use of metal passivation techniques has become an acceptable operating procedure by the oil refining industry (*7*).

Resistance to metal effects on an FCC can also be achieved by adding other materials such as Bi or Sn (*8–11*), which are believed to form inert residues on the catalyst surface (*1–4*). In contrast to Sb, Bi can passivate Ni without presenting the possibility of forming toxic compounds (*12*); however, Bi is not as effective as Sb (*7*).

Vanadium impurities affect the catalyst in a totally different manner, since catalyst activity appears to monotonically decrease with increasing vanadium levels due to zeolite destruction (11). Tin is known to passivate vanadium (*9*). The effects of Sn on V-contaminated model catalysts have been recently studied using luminescence experiments (*13*), Mössbauer spectroscopy (*14*), and electron paramagnetic resonance (EPR) measurements (*15*). It was found that luminescence experiments can provide useful information on the environment of the rare earth cations present in the zeolite and that they can be used to monitor V-migration between the zeolite and the catalyst matrix even in the presence of Sn (*13*). Tin-119 Mössbauer spectroscopy has indicated that Sn–V interactions take place only during steam-aging with formation of Sn^{4+}–O–V^{5+} complexes that are believed to minimize V–zeolite interactions, thus preserving zeolite crystallinity. The presence of excess tin minimizes oxidation to V^{+5} and promotes vanadate formation (*14*); thus, excess tin is to be avoided.

Recently, it has been reported that at microactivity test conditions, the additions of diluents (such as aluminas (*16*) and layered magnesium silicates (*17*)) capable of selectively sorbing metal contaminants from gas oils can form dual function cracking catalysts (DFCC) that retain most of their useful cracking activity even in the presence of as much as 1.0–1.5% V (*18–20*).

It is the purpose of this paper to report the stability of Sb- and Sn-loaded alumina particles and the effects that the addition of metal passivation compounds such as Sb and Sn have on the performance of DFCC mixtures.

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Analysis (TGA) was used for all high temperature reduction experiments; the balance sensitivity was ± 0.05 mg. Alumina was dried at 300°C for 10 h and then loaded with Sb (from antimony triphenyl) or Sn (from tin tetraphenyl), calcined in air at 540°C for 10 h, crushed to about 80–100 mesh, and then placed on the balance of the TGA. The sample was then heated at 5 K/min to 540°C in nitrogen and kept under nitrogen until a constant weight was attained. Once a constant weight was attained, the nitrogen flow was replaced with hydrogen and the sample weights monitored for 17 h (overnight), then purged in nitrogen, and finally oxidized in air for 1 h. Since only small amounts of catalyst were used, the only precaution taken for stibine (SbH_3) formation was the use of an exhaust line which led outside.

Intraparticle Sb (and Sn) was investigated by studying compositional changes in two DFCC mixtures, one containing 40% alumina (Catapal SB granules) have a surface area of 344 m^2/g and pore volume of 0.21 cm^3) loaded with 2% Sb (or 2% Sn) and 60% fresh FCC (*18*). The other mixture was prepared by combining the metal loaded FCC (with 2% Sb or 2% Sn) with 40% metal free alumina. The DFCC mixture was then placed in a reactor and exposed to H_2 (50 cm^3 H_2/h) at 540°C for 10 h.

Compositional information regarding Sb (or Sn) transport during reduction was obtained from electron microprobe analysis of the two DFCC mixtures. Samples were mounted on pre-carbon-coated glass slides using adhesive tabs. Excess sample was removed using a Freon duster. With the samples mounted, the slides were then carbon-coated again. Two types of analyses were run on each sample; *L*-value scans and antimony dot maps. Electron beam conditions for both were 15 kV and 10 nA. Antimony detection was achieved with a wavelength dispersive spectrometer (WDS) utilizing a pentaerythritol crystal. *L*-value scans from 112.0 to 108.0 mm were made, using a defocused beam, of one alumina granule and one catalyst microsphere per sample. This range encompasses the antimony peak, which occurs at approximately 110.16 mm. Scans were run with the strip chart recorder set at 20 mm/min, scan speed of 2 mm/min, and full scale equal to 100 X-ray counts. A secondary electron image and antimony, silicon, and aluminum dot maps at a magnification of 600× were also made. The purpose of the silicon and aluminum maps is to clearly identify which grains are alumina and which are catalyst, see Fig. 1. In Fig. 2, *L* is the distance between the X-ray generation source and the analyzing crystal.

Catalytic evaluation was performed using a microactivity test (MAT); the weight hourly space velocity was 15 with 80 s catalyst contact time at $T = 482°C$. Catalyst-to-oil ratio was 2.5; the feed API gravity was 27.9. Changestock was a 260–426°C boiling range gas oil. Prior to MAT testing, all microspheres were calcined at 350°C overnight and then steam deactivated for 10 h at 732°C under a 5.95% N_2–steam mixture. Vanadium and nickel naphthenates were used to load metal onto the fresh catalyst according to an established procedure (*21*).

MAT results from DFCC containing passivating agents are presented in Tables 1–3 (*22*). Table 1 shows that after diluting the

TABLE 1

Microactivity Data of a Dual Function Cracking Catalyst Containing ~60% GRZ-1 and 40% Al_2O_3 Promoted with Sb

	FCC	FCC + Al_2O_3	FCC + Al_2O_3 with	
			1% Sb	2% Sb
Conversion (V% FF)	81.4	76.1	73.4	74.5
Gasoline (V% FF)	52.4	53.5	53.8	52.9
LCGO (V% FF)	14.7	19.3	21.2	19.9
SO (V% FF)	3.9	4.6	5.5	5.5
Carbon (Wt%)	6.7	3.4	3.3	4.3
Hydrogen (Wt%)	0.04	0.05	0.04	0.05
Metals	0.0	0.0	0.0	0.0

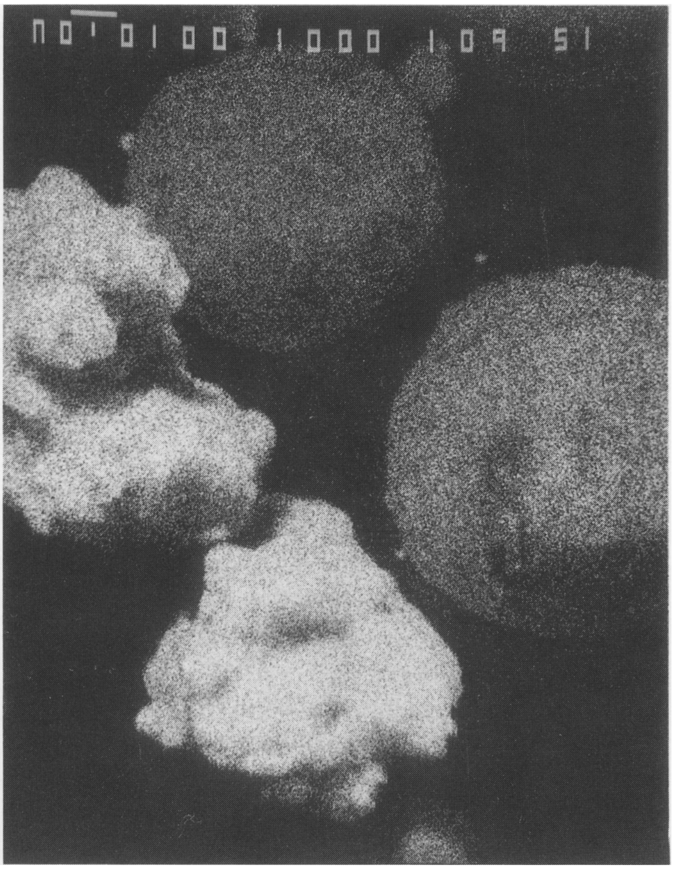

Fig. 1. X-ray map of Al distribution on a mixture of FCC microspheres and alumina granules.

parent catalyst (Davison's GRZ-1) with alumina, gas oil conversion decreased from 81.4 to 76.1%, whereas gasoline make increased slightly, indicating that at the MAT conditions used, the undiluted catalyst is overcracking. This is probably due to the high (35%) zeolite content of the catalyst. Antimony addition has negligible effect on the cracking properties of a metal-free DFCC. With 2% V, Davison GRZ-1 loses its useful cracking activity (*23*). Catastrophic losses in catalyst crystallinity and, therefore, cracking activity, can be prevented by the addition of a metal scavenger such as alumina, Table 2. Furthermore, by placing 1–2% Sb on the alumina surface, gasoline make, coke, and hydrogen selectivity can be improved significantly, Table 2. Similar selectivity effects have also been observed when, in addition to vanadium, nickel (5000 Ni-equivalents) is present on the DFCC surface, Table 3.

The improved selectivity properties of DFCC have been attributed to the ability of Sb (and Sn) to form inert metal compounds with Ni (and V) negating, in this way, the ability of these metal contaminants to affect catalyst properties and to catalyze the cracking of gasoline fractions with formation of high yields of light gases, coke, and hydrogen. High (1–2%) loadings of Sb (and Sn) were used to facilitate the study of these metals on alumina particles. In practice, Sb and Sn in the 0.2–0.6 wt% range will be employed since results similar to those in Tables 2 and 4 can be obtained with

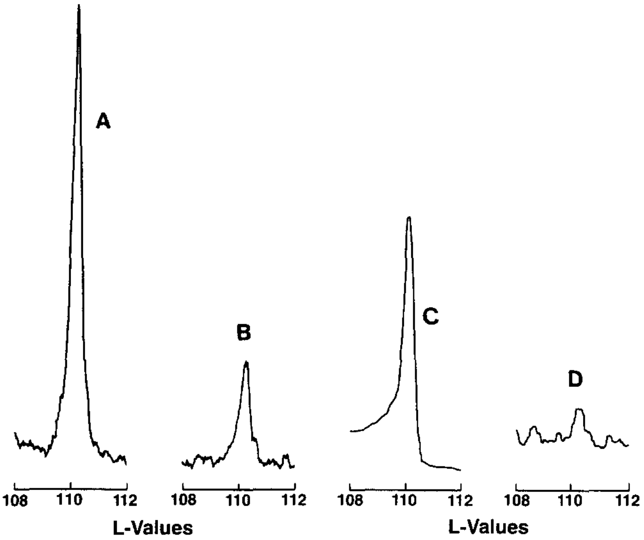

Fig. 2. X-ray scan over the Sb peak for a DFCC system containing 2% Sb on the host FCC (A). After exposure to flowing H_2 at 540°C, some Sb migrates to the alumina granules (B). When 2% Sb is placed on the alumina (C), Sb transport to the FCC microsphere is negligible (D).

only 0.4% Sb or 0.4% Sn on the diluent surface.

It has been shown that at the hydrothermal conditions at which cracking catalysts are deactivated, vanadium migrates from particle to particle, and that when it reaches the metal scavenger (alumina), it is trapped on its surface in the form of heat-stable vanadates (*18–20*). Nickel does not migrate and stays on the catalyst surface, where it acts as a hydrogenating center (*10*) or it can react with the metal scavenger and form Ni compounds (*18–20*). Antimony, when used to passivate nickel, could reduce and vaporize in the riser, causing metal losses and pollution problems. In fact, using the expression

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{\Delta H^\circ}{RT} + \frac{\Delta(nCp^o)}{R} (\ln T + C),$$

it can be shown that the reaction $Sb_2O_5 + 8H_2 = 2SbH_3 + 5H_2O$ has $\Delta G = -148$ Kcal/mole. In either case, the reduction of these oxides at high T (540°C) with stibine and water formation is thermodynamically favorable. In the above equation, K and ΔG° are the equilibrium constant and the free energy at the absolute temperature T; ΔH° and C are integration constants; R is the gas constant; ΔnCp^o is the molar summation of the heat capacity equation coefficients for the reactants and products of the examined reaction (*25*). Controlled release of Sb is necessary to passivate nickel deposits on the catalyst surface or in the gas phase. Sb-

TABLE 2

Vanadium Resistance of a Dual Function Cracking Catalyst Containing 40% Al_2O_3 Promoted with Sb

	FCC + Al_2O_3	FCC + Al_2O_3 with	
		1% Sb	2% Sb
Conversion (V% FF)	60.5	61.6	62.9
Gasoline (V% FF)	34.4	38.1	39.6
LCGO (V% FF)	29.7	29.3	28.5
SO (V% FF)	9.8	9.1	8.6
Carbon (Wt%)	6.9	5.4	5.6
Hydrogen (Wt%)	0.80	0.62	0.60
Metals (Wt%)	1.0	1.0	1.0

TABLE 3

Nickel and Vanadium Resistance of a Dual Function Cracking Catalyst Containing 40% Al_2O_3 Promoted with Sb

	FCC + Al_2O_3	FCC + Al_2O_3 with	
		1% Sb	2% Sb
Conversion (V% FF)	66.1	65.7	64.5
Gasoline (V% FF)	38.8	40.0	40.5
LCGO (V% FF)	26.0	26.7	26.7
SO (V% FF)	8.0	7.6	8.8
Carbon (Wt%)	7.8	5.7	6.0
Hydrogen (Wt%)	0.85	0.66	0.60
Metals (NiEq)	5000	5000	5000

loaded diluents (scavengers) could serve this purpose since, as shown below, they can slowly release Sb at a nearly constant rate.

Intraparticle Sb (and Sn) transport in H_2 was studied by analyzing alumina and FCC surfaces in several DFCC mixtures using wavelength dispersive X-ray measurements. This task was greatly facilitated by the different morphologies of the alumina and FCC particles, see Fig. 1. Probe analysis of two DFCC containing 2% Sb (or 2% Sn) alternatively on the FCC and on the alumina granules indicated that heating (540°C/10 h) in flowing air (~50 cm^3/h) did not include Sb (or Sn) migration. However, when the thermal treatment was repeated in the presence of flowing H_2, Sb was found capable of migrating from the FCC to the alumina surface, Figs. 2A and 2B. In contrast, when Sb is deposited on the alumina surface, it loses its mobility and migration of Sb from the alumina surface is either nonexistent or outside the limit of detection of the spectrometer used, Figs. 2C and 2D. Intraparticle Sn transport was not observed in any of the samples examined. Thus, when Sb loaded FCC microspheres are exposed to H_2 (at 540°C) lose Sb; metal mobility is greatly reduced when Sb is placed on the alumina surface. Possible metal losses from metal loaded alumina granules have been investigated using a microbalance with a sensitivity of ± 0.05 mg.

Microbalance reductions of alumina granules loaded with low levels of Sn and Sb were performed at 540°C in hydrogen in order to determine possible rates of conversion to metal and metal losses from the support. Weight losses for reduction of Sb loaded alumina are shown in Table 4. Weight losses were relatively rapid for the 17 hours of reduction. After that time, reoxidation in air brought the sample weight to within 1.8 mg of its original weight, which corresponds to a 38-wt% Sb loss over a 17-h period, for an average Sb loss of 0.0028 mg g^{-1} min^{-1}. Unsupported Sb_2O_5 loses Sb at a much faster rate (3.1 mg g^{-1} min^{-1}). Following a 2-h exposure to H_2, the Sb_2O_5 weight becomes invariant with time. After reoxidation in air, a 39% weight loss was observed.

Similar data for the Sn loaded alumina catalyst are shown in Table 5. In this case, weight losses were not as rapid nor as extensive; after 17 h in hydrogen, the average weight loss of Sn was 0.0017 mg g^{-1} min^{-1}. After reduction, a weight loss of 1.1 mg corresponding to a 63% reduction of SnO_2 to Sn was observed. However, upon reoxidation, the sample weight rose back to the original calcined weight, Table 5. Thus, in agreement with transport experiments, it

TABLE 4

Material Balances for the Reduction of 0.8% Sb/Alumina

(A)	Sample weight before TGA	=	693.8 mg
(B)	Initial sample weight	=	632.3 mg
	Sb Weight	=	4.8 mg
	Sb_2O_5 Weight	=	6.4 mg
	Sb_2O_3 Weight	=	5.8 mg
(C)	Reduced samples weight	=	629.1 mg
	Sb Weight	=	3.0 mg
	Sb_2O_5 Weight	=	4.0 mg
	Sb_2O_3 Weight	=	3.6 mg
(D)	Reoxidized sample weight	=	630.5 mg
	Sb Weight	=	3.0 mg
	Sb_2O_5 Weight	=	4.0 mg

TABLE 5

Material Balances for the Reduction of 0.3% Sn/Alumina

(A)	Sample weight before TGA	=	669.6 mg
(B)	Initial sample weight	=	642.7 mg
	Sn Weight	=	1.9 mg
	SnO_2 Weight	=	2.4 mg
(C)	Reduced sample weight	=	641.6 mg
(D)	Reoxidized sample weight	=	642.7 mg

can be concluded that losses from the Sn loaded alumina sample were negligible. It is not surprising that Sn is resistant to removal by reduction in hydrogen. This metal is a component of reforming catalysts which are routinely operated near 500°C for extended periods of time. Similar results and conclusions have been obtained also by reducing alumina granules loaded with higher (1–2%) Sb or Sn levels (*24*).

In summary, alumina promoted with metal passivating agents like Sb and Sn can improve a dual function cracking catalyst (DFCC) performance by decreasing carbon and hydrogen make while improving gasoline yields. Transport experiments have shown that when exposed to H_2 at 540°C, metal-loaded FCC microspheres lose Sb, and that Sb mobility is greatly reduced when this metal is placed on the alumina surface. Reduction measurements have shown that Sb loaded alumina samples lose Sb at a much slower rate than unsupported Sb_2O_3 powder. In contrast, losses of Sn were not observed after reducing Sn-loaded alumina in hydrogen at 540°C for 17 h. The reoxidation weight gain was equivalent to conversion of Sn to SnO_2 and restored the sample weight to its initial value, see Tables 4 and 5.

Results from this work indicate that a more universal DFCC should contain a diluent promoted with both Sb and Sn (*22*). Sn will remain on the diluent particle and passivate migrating vanadium. In addition to forming vanadates or heat stable V-compounds (*18*), the Sn promoted diluent can trap vanadium on its surface also as a Sn^{+4}–O–V^{+5} complex (*15*). Since nickel does not migrate, its effect would be moderated by the controlled (and slow) transfer of Sb from the scavenger surface to the host catalyst particle and to the gas phase. This suggests that of all possible ways of introducing Sb and Sn, the use of metal scavengers could be one of the preferred modes of metal passivator addition.

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REFERENCES

1. Dale, G. H., and McKay, D. L., *Hydrocarbon Process.* **56** (9), 97 (1977).
2. Dreiling, M. J., and Schaffer, A. M., *J. Catal.* **56,** 130 (1979).
3. McKay, D. L., and Bertus, B. J. Prepr., *Am. Chem. Soc. Div. Pet. Chem.* **24** (2), 645 (1979).
4. Merryfield, R., McDaniel, M., and Parks, G., *J. Catal.,* **77,** 348 (1982).
5. Parks, G. D., *Appl. Surf. Sci.* **5,** 92 (1980).
6. Gall, J. W., Nielsen, R. H., McKay, D. L., and Mitchell, N. W., "NPRA Annual Meeting," Vol. A82-50, p. 5 (1982).
7. Bohmer, R. W., McKay, D. L., and Knopp, K. G., *in* "NPRA Annual Meeting, March 19–21, 1989, San Francisco, CA" Vol. AM-89-51.
8. Readal, T. C., McKinney, J. D., and Titmus, R. A., U.S. Patent No. 3,477,963 (1976).
9. English, A. R., Kowalczyk, D. C., *Oil Gas J.* **127** (July 16, 1984).
10. Mitchell, B. R., and Swift, H. D., *in* U.S. Patent No. 4,101,417 (1978).
11. Ritter, R. E., Rheaume, L., Welsh, W. A., and Magee, J. S., *Oil Gas J.* **103** (July 1981).
12. Ramamoorthy, P., English, A. R., Kennedy, J. V., Lossens, L. W., and Krishna, A. S., *in* "NPRA Annual Meeting, March 20–22, 1988, San Antonio, TX," Vol. AM-88-50.
13. Anderson, M. W., Occelli, M. L., Suib, S. L., *J. Catal.* **118,** 31 (1989).
14. Anderson, M. W., Occelli, M. L., Suib, S. L., *J. Mol. Catal.* **61,** 295 (1990).
15. Anderson, M. W., Occelli, M. L., Suib, S. L., *J. Catal.* **112,** 2, 375 (1990).

16. Occelli, M. L., and Kennedy, J. V., *in* GB Patent No. 2,116,062A (1983).
17. Occelli, M. L., and Kennedy, J. V., *in* U.S. Patent No. 4,465,588 (1984).
18. Occelli, M. L., *in "Fluid Catalytic Cracking: Role in Modern Refining,"* p. 162, ACS Symposium Series, Vol. 375 (M. L. Occelli, Ed.), ACS, Washington, D.C. (1989).
19. Occelli, M. L., and Stencel, J. M., *in* "Zeolites as Catalysts, Sorbents and Detergent Builders" (H. G. Karge and J. Weitkamp, Eds.) p. 127. Elsevier, Amsterdam (1989).
20. Occelli, M. L. and Stencel, J. M., *in* "Proceedings 8th IZA Meeting, Amsterdam, The Netherlands," in press.
21. Mitchell, B. R., *Ind. Eng. Chem. Prod. Res. Dev.* **19,** 209 (1980).
22. Occelli, M. L., and Swift, H. E., U.S. Patent No. 4,466,884 (1984).
23. Occelli, M. L., Psaras, D., and Suib, S. L., *J. Catal.* **96,** 363 (1985).
24. Occelli, M. L., and K. L., Kibby, Gulf Research unpublished results (1984).
25. "Handbook of Chemistry and Physics," 48th ed, p. D-38. Chemical Rubber Co., Cleveland, 1967.

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