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LETTER TO THE EDITORS

Separate Determination of Pt and Re in Pt–Re–Al_2O_3 Reforming Catalyst

Chemisorption of hydrogen is almost routinely used in many catalysis laboratories for measurement of Pt dispersion in supported and unsupported Pt catalysts. Kubicka (*1*) and Yates and Sinfelt (*2*) have used hydrogen chemisorption for measurement of Re dispersion as well. The composite Pt–Re–Al_2O_3 catalyst has been one of the highlights of recent developments in catalytic reforming.

Buyanova *et al.* (*3*) have applied a pulse gas-chromatographic method for chemisorption of hydrogen and oxygen on supported Ni and Pt catalysts, enabling a rapid determination of metal dispersion. Recently Freel (*4*) has reported the use of this pulse method for gas titration of Pt surfaces; this is a quicker version of the Benson–Boudart (*5*) volumetric gas titration of Pt surfaces. We have been using this method for measurement of dispersion of Pt in Pt–Al_2O_3 and of Pt and Re separately in Pt–Re–Al_2O_3 catalysts (experimental samples). Some of our results are presented here.

The apparatus used by us is schematically shown in Fig. 1. Gas pulses (0.1–0.3 ml/pulse) could be sent into the carrier gas stream by a pneumatic device at preset time intervals. About 2 g of catalyst (extrudates of 1.5-mm diameter, broken into 1–2 mm length, calcined at 450°C for 1 hr in air) was taken in the reactor. The hydrogen flow was started and the catalyst was slowly heated to 450°C, kept at that temperature for 2 hr, and then cooled to room temperature in flowing hydrogen. The system was flushed with the carrier gas helium for 5 min. Oxygen pulsing was started with the catalyst at room temperature and continued until the oxygen peaks on the chromatograph were identical, indicating that no more oxygen was irreversibly adsorbed on the catalyst. Typical results of an oxygen-pulse experiment are shown in Fig. 2. Knowing the oxygen vol-

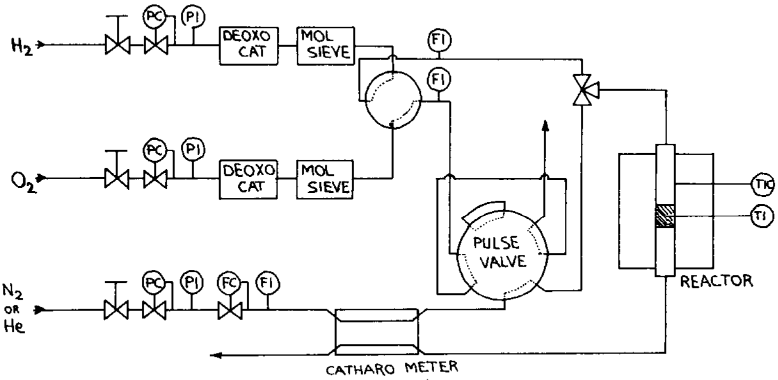

FIG. 1. Gas chromatographic set-up for gas titration of metal surfaces. PC, pressure control; FC, flow control; Fl, rotameter; Tl, thermocouple; TlC, temp. control. The automatic gas-pulsing device is not shown.

ume per pulse, the amount of oxygen chemisorbed can be readily calculated.

Preliminary experiments showed that, in contrast to Pt, the chemisorbed oxygen on Re could not be reduced by hydrogen at room temperature. Hence it was possible to determine oxygen chemisorption by Pt and Re separately in a Pt–Re–Al_2O_3 composite catalyst as follows (all at room temperature): (a) first oxygen pulsing gave chemisorption by Pt + Re; (b) subsequent reduction at 25°C converted Pt---O to Pt---H; (c) renewed oxygen pulsing gave chemisorption by Pt only; (d) the difference between (a) and (c) gave the chemisorption by Re only. In practice, reproducible results could be obtained for step (a) after a second reduction at 450°C, and for step (c) after 2 or 3 oxygen–hydrogen cycles at room temperature. The chemisorption of the two gases under the same conditions on the blank carrier alumina extrudates did not occur to any detectable extent; hence correction for the adsorption on the carrier, usual in volumetric methods, was unnecessary.

The dispersion of Pt on a commercial reforming catalyst (CK-306), made in our plant, measured by the present method is shown in Table 1. In the past, the Pt dispersion on this catalyst (not the same sample!) has been measured by (a) the standard volumetric method by Dr. M. S. Goldstein of American Cyanamid Company in 1964 and reported by Maat and Moscou (*6*), (b) the volumetric gas titration method by Boudart *et al.* (*7*) in Stanford University in 1968 on a sample of CK-306 supplied to them by Esso. These older data are also given in Table 1. The results are at least qualitatively comparable. Buyanova *et al.* (*3*) and Freel (*4*) have already shown that the simple and rapid gas-chromatographic technique can be applied for metal dispersion measurements without sacrificing much accuracy.

TABLE 1
Comparison of Pt Dispersion Values from Different Methods[a]

Method	Measured by	Gas adsorbed, ml STP/g cat.	Dispersion, %
A	Goldstein	0.282	82
B	Boudart *et al.*		73
C	This work	0.278	81
D	This work	0.271	79

[a] Methods: A, volumetric chemisorption; B, H_2-titration of Pt- - -O surface volumetrically; C, H_2-titration of Pt- - -O surface gas chromatographically; D, O_2-titration of Pt- - -H surface gas chromatographically. Note that the pretreatments of the catalyst in A and B were extensive and more severe than those in C and D. Catalyst: Cyanamid-Ketjen reforming catalyst CK-306

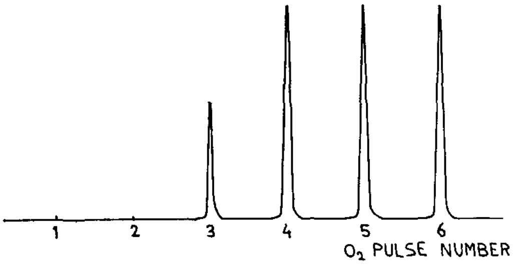

FIG. 2. Typical chromatogram for O_2-titration of a Pt- - -H surface.

Typical results for γ-Al_2O_3-supported Pt, Re and Pt–Re catalysts are given in Table 2. The pulse titer value is given as such in the Table; the chemisorbed amount on Pt (see Table 1 C,D) is obtained by multiplying the titer value by ⅔ as per the stoichiometry of the gas titration:

$$2\ \text{Pt---H} + 3/2\ O_2 \rightarrow 2\ \text{Pt---O} + H_2O.$$

TABLE 2
Oxygen Titration of Pt and Re in Pt–Re–Al_2O_3 Catalysts at 25°C[a]

Re Pt	0.0	0.1	0.3	0.6	1.0
0.0			(0.06)	(0.24)	
0.1	0.06	0.03 (0.07)			
0.3	0.19	0.18 (0.12)	0.18 (0.20)	0.18 (0.39)	0.23 (0.39)
0.6	0.39			0.30 (0.47)	

[a] Catalysts prepared by impregnation on γ-Al_2O_3. Metal contents in wt%. Titer values in ml STP/g catalyst Titer values for Re are shown in brackets.

It is not yet certain whether such an equation is also valid for the hydrogen–oxygen surface reaction on Re. The reproducibility of the titer value is ±5% for Pt and ±10% for Re. Taking the titer values as a measure for the dispersion of the metal, the dispersion of Pt is little altered in a composite Pt–Re catalyst compared to that in a Pt catalyst of the same metal content and prepared similarly; the dispersion of Re, however, seems to be considerably enhanced in the composite catalyst. This enhancement of O_2 chemisorption on Re can be explained by an improved reducibility of Re in the presence of Pt which may be an indication of Pt–Re alloy formation on the alumina surface, as originally proposed by Kluksdahl in his first Rheniforming patent (*8*).

REFERENCES

1. KUBICKA, H., *J. Catal.* **12,** 223 (1968); **20,** 163 (1971).
2. YATES, D. J. C., AND SINFELT, J. H., *J. Catal.* **14,** 182 (1969).
3. BUYANOVA, N. B., IBRAGIMOVA, N. B., AND KARNAUKHOV, A. P., *Kinet. Catal.* **10,** 322 (1969).
4. FREEL, J., *J. Catal.* **25,** 139 (1972).
5. BENSON, J. E., AND BOUDART, M., *J. Catal.* **4,** 704 (1965).
6. MAAT, H. J., AND MOSCOU, L., *Proc. Int. Congr. Catalysis, 3rd,* Amsterdam, Vol. 2, p. 1277, North-Holland, Amsterdam, 1965.
7. BOUDART, M., ALDAG, A. W., PTAK, L. D., AND BENSON, J. E., *J. Catal.* **11,** 35 (1968).
8. KLUKSDAHL, H. E., U. S. Patent 3,415,737 (1968).

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