

Short Communication

RAPID ACCURATE ANALYSIS OF METAL (OXIDE)-ON-SILICA CATALYSTS BY ATOMIC ABSORPTION SPECTROMETRY

B. A. H. G. JÜTTE, A. HEIKAMP and J. AGTERDENBOS*

Analytisch Chemisch Laboratorium der Rijksuniversiteit, Croesestraat 77 A, 3522 AD Utrecht (The Netherlands)

(Received 12th February 1979)

Summary. The catalysts, which contain 10–60% copper, chromium, nickel and silicon, are decomposed in sealed Teflon-lined vessels and analyzed by atomic absorption spectrometry. Matrix matching and bracketing standards are applied. The RSD of a single determination is about 1% for all components.

Studies of catalysts consisting of one or more metal oxides or hydroxides on silicon dioxide have recently been of interest; the metals applied are chromium, copper and nickel and the content of each metal generally lies within the range 10–40% [1]. These catalysts were originally analyzed by classical techniques involving NaOH fusion, gravimetry as SiO₂ and EDTA titration of the metals [1]. This procedure is laborious, requiring technical expertise, and EDTA titrations are not applicable for all the combinations of metals of interest. Faster methods were therefore sought. The procedure described below is rapid, simple enough to be applied by non-specialized workers, and applicable without much modification to catalysts made from silicon dioxide and a wide range of metals or combinations of metals. The compositions of some typical catalysts analyzed in this work are given in Table 1.

Experimental

Apparatus and reagents. Uniseal Teflon-lined decomposition vessels (capacity 23 ml) and an Instrumentation Laboratories Model 351 atomic absorption spectrometer equipped with the necessary hollow-cathode lamps were used. Volumetric apparatus was all made of polythene.

The acids used were of the highest purity available (Suprapur or analytical-reagent grade) and the water was twice-distilled from quartz apparatus. Silica (Akzo Chemie, Fluid silica F-2), nickel and chromium powder (Fluka reinst) and electrolytic copper wire were used in preparation of standards.

Matrix solution. A solution containing 6 g of boric acid and 8 ml of 40% hydrofluoric acid in 500 ml of water is needed to dilute standard solutions of the elements to be determined and as a blank in the atomic absorption spectrometric measurements. This solution is stored in polythene flasks.

TABLE 1

Percentage composition of some catalysts analyzed

Catalyst	Cu	Ni	Cr	Si
I	—	40.1	—	37.2
II	30.3	—	—	57.2
III	22.1	—	10.7	46.7
IV	—	38.2	—	39.0

Stock metal solutions. Dissolve 0.50 g of the metal in 25 ml of nitric acid (1 + 1) for Cu and Ni or of hydrochloric acid (1 + 1) for Cr, with gentle heating if necessary. After cooling to room temperature, add a solution of 6 g of boric acid in 75 ml of water. Transfer the solution to a 500-ml volumetric flask, add 8 ml of 40% hydrofluoric acid and dilute the solution to the mark with water.

Stock silicon solutions. Ignite silicon dioxide in a muffle furnace at 900°C and cool to room temperature over P₂O₅. Weigh ca. 0.50 g into the Uniseal Teflon beaker and wet it with 1 ml of acid mixture (1 part HNO₃ to 3 parts HCl). After addition of 4 ml of 40% hydrofluoric acid, close the vessel and heat for 60 min in an oven at 120°C. After cooling for 15 min in air and 60 min in an ice bath, open the vessel. Transfer the contents to a 250-ml volumetric flask with a solution of 3 g of boric acid in 75 ml of water, and dilute the solution to the mark with water.

Procedure for catalysts. Weigh about 0.15 g of catalyst (dried previously at 120°C and cooled for 1 h over P₂O₅) into the Uniseal Teflon beaker. Then follow the procedure described above for the stock silicon solution; this gives a sample stock solution. From this solution, prepare the final solutions for measurement by suitable dilution (if necessary) with the matrix solution. These final sample solutions should give absorbance values within the range 0.6–0.9 for the element to be determined (this may require preliminary measurements), corresponding to concentrations of about 50 mg Cr l⁻¹, 100 mg Ni l⁻¹ and 150 mg l⁻¹ for Si and Cu. These values may differ slightly depending on the apparatus and experimental conditions used (see below).

For standardization, prepare solutions of appropriate concentrations of the elements to be determined from the stock solutions by suitable mixing. These standards and the sample solutions must contain the same concentrations of boric acid and hydrofluoric acid. Matching is also required to within ± 20% in the sample and standard solutions for the other components in the sample solution that originate from the sample but are not measured; adequate matching of these concomitants is possible from a knowledge of the method of preparation of the catalyst.

Measurements. The instrumental settings are as follows: the spectral band-pass is 0.3 nm in all cases; the wavelengths used are 251.6 nm for Si, 425.4

nm for Cr, 222.6 nm for Cu and 351.5 nm for Ni; a nitrous oxide—acetylene flame is used for Si and Cr, and an air—acetylene flame for Cu and Ni, in accordance with the manufacturer's recommendations.

Each sample is bracketted between two standards (S1 and S2), the concentrations of which are selected empirically to give absorbances in the range 0.6—0.9 (see above). Readings are made in the order S1 (5X), sample (5X) and S2 (5X), each measurement requiring 15 readings. An integration time of 4 s is recommended.

Results and discussion

The concentration of the required element in the sample, c_s , is calculated by linear interpolation from the mean absorbance values A_1 , A_s and A_2 found for standard S1, sample and standard S2, respectively. The relative standard deviation (RSD) in c_s depends on the RSD of a single reading, RSD_r . Because five readings are made for each of the values A_1 , A_s and A_2 , the RSD in each of these values is $RSD_r/5^{1/2}$. The RSD in c_s is about $2^{1/2}$ times this value, i.e. about 0.6 RSD_r or 0.7 RSD_r .

Weighing errors and volumetric errors can be neglected. Experiments showed that errors arising from the chemical sample preparation are small enough to be neglected if the work is done carefully (see below, however). If the sample and standard solutions are matched as described above, any systematic error from differences in the matrices can also be neglected.

Calibration curves were found to be not exactly linear, and this feature introduces a (positive) systematic error in the value calculated for c_s . This error is at a maximum if c_s is midway between the concentrations of the two standards S1 and S2. With other factors kept constant, the error increases approximately by a factor p^2 if $(1 - R)$ increases by a factor p (R is the ratio of the concentrations of S1 and S2). Tests showed that the systematic errors introduced by the non-linearity of the calibration curve were well below 0.3% if $R > 0.6$ for Cu, $R > 0.7$ for Cr and Si, and $R > 0.9$ for Ni. Curvature may depend somewhat on the apparatus and experimental conditions, however, so that checking is advised.

Under the experimental conditions described above, the value of RSD_r within the absorbance region 0.6—0.9 was about 0.7%, so that the RSD in a c_s value should be about 0.5%. However, when a catalyst containing about 20% of copper was analyzed 36 times, the RSD was found to be about 1.2% (i.e., the absolute value of the standard deviation was about 0.25%). The discrepancy between the values 1.2% and 0.5% suggests that the fluctuations between measurements are much larger than the fluctuations during the period required for making one measurement (it must be recalled that each "measurement" consists of 15 readings as described under Experimental). It is suggested, therefore, that if high demands are placed on the accuracy of the final results, a sample solution should be measured several times. This is both more effective and less time-consuming than preparing several sample solutions. It is, however, advisable that the latter procedure be applied from

time to time as a check that the sample preparation step has been done with good precision.

The precision values given above were found for copper, but very similar results were obtained for other components, so that the same procedure can be recommended.

The authors thank Drs. J. M. Ravensberg for preliminary investigations and A. J. M. Glissenaar for technical assistance.

REFERENCE

- 1 A. J. van Dillen, J. W. Geus, L.A.M. Hermans and J. v.d. Meijden in G. C. Bond, P. B. Wells and F. C. Tompkins (Eds.), *Proc. Int. Congr. Catal.*, 6th 1976, Vol. 2, Chemical Society, London, 1977, pp. 677—685.