

The application of WD-XRF in determination of low sulfur contents in industrial catalysts

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Introduction

The role of catalysis in the modern chemical industry is well known. It is estimated that about 90% of the products of the modern chemical industry are obtained in catalytic processes, particularly with heterogeneous metal oxides or metallic systems. The catalysts can be utilized in the manufacture of products of a high economic importance such as ammonia, methanol, fuels and others. That is why there are high usage requirements for the catalysts [1, 2].

A typical industrial catalyst should be characterized by:

- high and stable activity and selectivity
- possibly highest geometric area per bed unit volume
- good and long-lasting mechanical strength.

The development of new types of catalysts that comply with these criteria usually requires time-consuming research studies on the formula optimization, preparation method and the evaluation of the most important kinetic features of the catalytic systems before and after their performance. What is extremely important in these research studies is the determination of the chemical composition, especially a content of the components, which are in a relatively low concentration, but greatly affect the catalytic performance. These are particularly the substances, which are promoters and poisons for a catalytically active species [3].

Catalytic systems are relatively sensitive to the presence of undesirable substances in a raw material, since they cause rapid, and usually irreversible loss of activity, what is shown in Figure 1 for a copper low temperature shift catalyst (LTS).

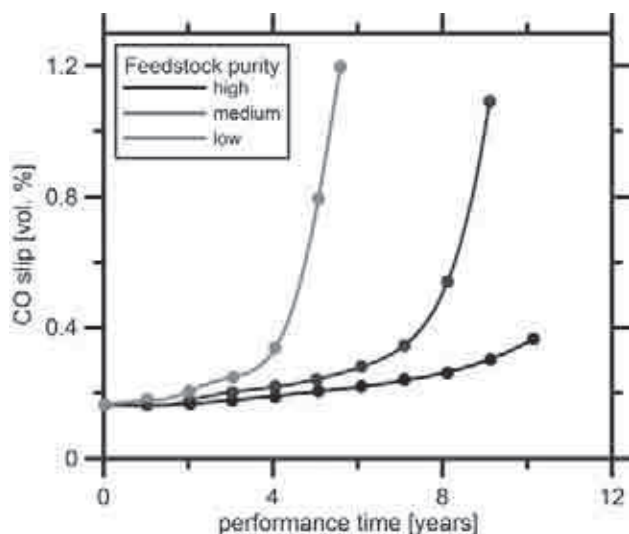


Fig. 1. Dependence of the performance time of the LTS copper catalyst on the process gas purity

One of the most harmful poisons to metallic catalysts are chlorine and sulfur compounds. Therefore, there is a need to control their concentration on the catalyst preparation step (analysis of raw materials, intermediates and final catalyst). This allows to provide the required

quality of the catalyst, leading to its high utility. The use of raw materials contaminated with sulfur compounds, or their accidental introduction at the stage of production makes the catalyst defective.

Another issue is the determination of the sulfur content in a catalyst during (if possible) and after its industrial performance. The analysis of the chemical composition of the catalysts after working in industrial reactors can provide the relevant information (sometimes impossible to be obtained in a laboratory) about the catalyst deactivation. Determination of the poisons content at different places of a catalytic bed allows to draw conclusions about the resistance to poisoning of the catalysts and then their differentiation in this respect. Figure 2 shows an example of an activity profile with the concentration distribution of sulfur in the copper catalyst bed, which shows the close relationship between these two parameters [2].

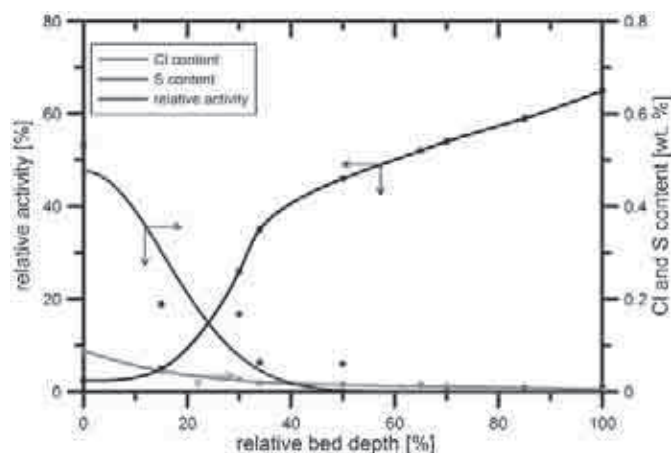


Fig. 2. Correlation between the poisons concentration profiles in the catalytic bed and the catalytic activity of the copper catalyst in the low temperature shift process (LTS)

This knowledge is a basis in order to know the mechanisms of the metallic catalysts deactivation, to find a dependence between the concentration of sulfur compounds in the reaction mixture and the catalyst activity and in next step also to work out the equations, describing the deactivation processes, allowing to simulate the lifetime of a catalytic bed under various operating conditions.

Determination of the relatively high concentrations of sulfur in the solid materials belongs to the "classics" of the analytical chemistry. The standard method for measuring sulfur in the form of sulfates is the gravimetric method. This method does not require any expensive or complex instruments, even though it is a subject to multiple interferences and is therefore difficult to conduct [4]. However, for the determination of low sulfur concentrations in a catalyst, e.g. on the level of dozens of ppm to several percent, this method is insufficient due to its low precision and a long analysis time. For this purpose, it is necessary to develop a new instrumental method with the desired precision in a wide range of concentrations.

A variety of methods have been used to determine the total sulfur in natural materials, but most of them are inconvenient and time-consuming [5]. One of the popular methods is ion-exchange chromatography (IC) [6, 7, 8]. For this determination a sample must be dissolved and this can be achieved by different means such as e.g. melting in the presence of Na_2O_2 at 800°C in a zirconium crucible, followed by dissolution in an acidic medium and the IC analysis of the liquid part. In another study [9], a sample is heated in an induction furnace and the combustion gases are collected in a solution that is subsequently analyzed by IC.

The sulfur content can also be determined during the combustion process of a sample by means of infrared spectroscopy (IR). This method can be used in the presence of various additives that accelerate the combustion process [10].

Spectroscopic methods of analysis are a very good tool for such applications. There are several literature data, where the sulfur has been determined using inductively coupled plasma mass spectrometry (ICP-MS) [11]. During the preparation a sample is dissolved in HF and aqua regia. Other studies describe the measurement of the sulfur content by inductively coupled plasma optical emission spectrometry (ICP-OES) [12, 13]. In these studies the ICP-OES method is compared with the traditional gravimetric one.

Fluorescent X-ray spectroscopy (WD-XRF) is another method useful in the analysis of the catalysts composition. It is a comparative method, the concentration of an element in a sample is determined by reference to the intensity of the characteristic radiation of a standard. An important advantage of the WD-XRF method for catalytic applications is the ability to fully analyze the sample composition in a single measurement, as well as its high sensitivity, accuracy and short analysis time. This method is a very convenient way of determining a small amount of catalyst components (e.g. poisons), since it does not require prior extraction of the analyte in the original sample and can be successfully used for catalysts in the oxide, pre-reduced or sulfided forms.

Due to its versatility the WD-XRF method is very useful for routine control of the catalysts composition. The limitation here may be the lack of reference materials and standards used for calibration and/or validation of the method. In the case of WD-XRF chemical and mineralogical composition of the samples must be as close as possible to that of reference materials [14, 15, 16].

Over the years the WD-XRF analysis has been used in INS, Puławy both in basic research at the stage of the preparation of model samples or industrial catalysts (fresh and used). This paper presents selected results of the analyses for a catalyst based on active alumina and for an iron catalyst for the high temperature shift (HTS).

Experimental

Instrumental

The WD-XRF analysis was carried out using a wavelength dispersive X-ray spectrometer (X'Unique II, Philips), equipped with a Sc-Mo X-ray tube and 3 kW excitation power. All measurements were performed under high vacuum with a use of a flow counter. A hydraulic press machine (TestChem) was used for the preparation of powder pellets. A planetary micro mill (Pulverisette 7, Fritsch) with an agate mixing bowl was utilized for homogenization after the addition of an aqueous reference solution to the base catalysts. The same equipment was used for pulverization of raw catalysts, and for homogenization with a binder.

Catalyst samples

The raw material for the preparation of calibration standards was taken from two batch productions of a catalyst. For analysis purpose two catalysts were tested. One of them was Fe-Cr-Cu catalyst manufactured by The Nitrogen Works in Tarnow and commercially applied during high-temperature water gas shift process.

The second one was an aluminum catalyst manufactured by the Fertilizer Research Institute in Puławy. After milling and homogenization of both catalysts using the planetary micro mill, the Fe-Cr-Cu catalyst was dried at 105°C whereas the aluminum catalyst was subjected to the calcination process at 550°C .

Chemicals

The reference solutions were prepared by dissolving relevant amounts of Na_2SO_4 (analytical grade, POCH) in demineralized water. In this event Na_2SO_4 required drying at 105°C to a constant mass of the weighed sample. For the Fe-Cr-Cu catalyst four reference aqueous solutions of Na_2SO_4 were prepared with the following sulfur concentration: 0.135, 0.312, 0.400, 1.173 mg S/ml. For the aluminum catalyst the reference aqueous solutions of Na_2SO_4 with the following sulfur concentrations: 0.090, 0.135, 0.225, 0.270 mg S/ml were utilized during impregnation of this alumina catalyst.

Standards preparation

The calibration standards were obtained by impregnation of each portion of a catalyst (mass of one catalyst portion 40g) with equal volume of relevant Na_2SO_4 reference aqueous solutions (50 ml). After the impregnation the Fe-Cr-Cu catalysts was dried at 105°C to obtain a constant mass. In case of the alumina catalyst the calcination process at 550°C for 5 hours was required. The samples prepared were milled using the planetary micro mill for 70 minutes to homogenize the samples. For WD-XRF analysis purpose the powder pellets were made by mixing 10 g of the prior prepared standards with 1 g of wax, followed by homogenization of these mixtures in the planetary micro mill for 20 minutes and finally by pressing them with the hydraulic press machine (pressure 80 kN, pressing time 10 seconds). Figure 3 shows the flowchart of standards preparation for each catalyst.

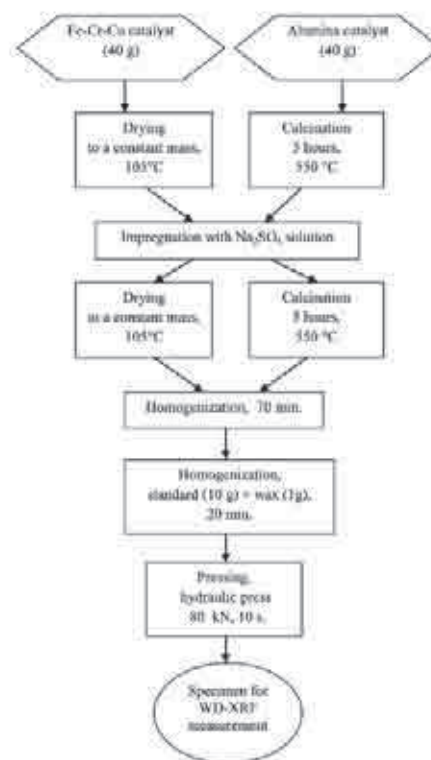


Fig. 3. Flowchart for the preparation of sulfur standards for Fe-Cr-Cu and alumina catalyst

Calibration curves

In practice, especially in case of routine analytical tests a calibration curve seems to be the most useful determination method, since the matrix remains the same for a sample tested as well as for a standard applied. However, the calibration curve method

has a specific disadvantage, namely the availability of commercial reference materials is firmly limited. In consequence, determination of sulfur content for Fe-Cr-Cu and alumina catalysts requires the preparation of own standards under laboratory conditions. The sulfur concentration for the base samples of both catalysts was determined by an internal standard method. For this purpose Na_2SO_4 was applied as the internal standard and Na_2SO_4 solutions were added into the samples via impregnation. Noteworthy, other analytical methods for the sulfur content determination in the catalysts did not provide satisfactory results. Upon impregnation of the raw catalyst sample with the Na_2SO_4 reference aqueous solutions, four Fe-Cr-Cu catalyst samples were obtained with various sulfur concentration. The sulfur content in these four Fe-Cr-Cu catalyst samples was 0.017, 0.039, 0.050 and 0.146 % (w/w), respectively. In case of the alumina catalyst five samples with the sulfur concentration of 0.011, 0.017, 0.022, 0.028 and 0.034 % (w/w) were obtained. All instrumental parameters applied during measurements of sulfur intensities in the standards obtained are shown in

Table I

Instrumental conditions of the WD-XRF analysis for the Fe-Cr-Cu and alumina catalysts samples

Spectral line:	K_{α}
Voltage:	40 kV
Current:	75 mA
Collimator:	coarse
Crystal:	Ge I I
2θ Angle:	110.729°
Detector:	FL

An original sulfur concentration for the base samples of both catalysts was obtained based on the analytical plot of dependence between the number of impulses recorded versus time and sulfur concentration expressed in % (w/w). The linear extrapolation was used by creating a tangent line at the end of the known experimental points and extending it beyond that limit to the intersection with the concentration axis. All the measurement results are shown in Figures 4 and 5.

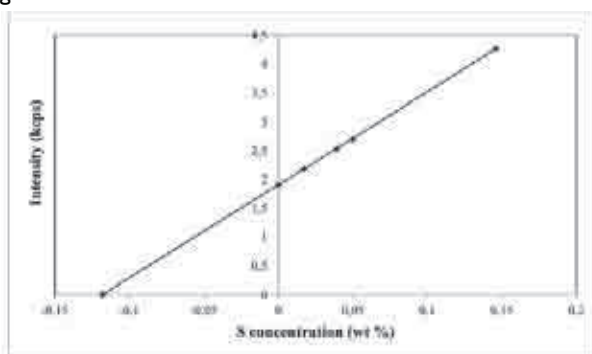


Fig. 4. Determination of sulfur in a raw Fe-Cr-Cu catalyst by an internal standard addition

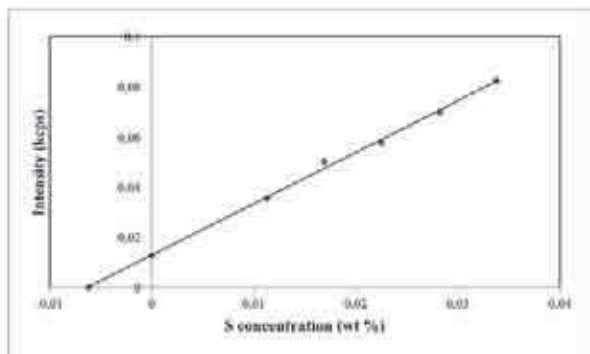


Fig.5. Determination of sulfur in a raw alumina catalyst by an internal standard addition

As a result of the extrapolation, the sulfur concentration in the base samples was found to be 0.118 % (w/w) for the Fe-Cr-Cu catalyst and 0.006 % (w/w) for the alumina catalyst. The correlation coefficients for these linear extrapolations were 0.999 and 0.998, respectively, for the Fe-Cr-Cu and alumina catalysts.

The sulfur contents for the reference standards were corrected by subtracting the sulfur concentrations obtained for the base samples of both catalysts. The sulfur concentration of each calibration standard (W1, W2, W3, W4, W5, W6, where W1 is the raw catalyst sample) are shown in Table 2. Based on that, the analytical curves for routine analytical tests of sulfur content in the mentioned catalysts were obtained.

Table 2

Sulfur concentration in calibration standards

Calibration standard	S concentration (% w/w)	
	Fe-Cr-Cu catalyst	Alumina catalyst
W1	0.118	0.006
W2	0.135	0.017
W3	0.157	0.023
W4	0.168	0.029
W5	0.264	0.034
W6	-	0.040

The experimental data were fitted for each calibration curve by minimizing the root mean square (RMS) value in accordance with the following equation:

$$RMS = \sqrt{\frac{\sum(C_{chem} - C_{calc})^2}{n - k}}$$

where,

C_{chem} – theoretical sulfur concentration,

C_{calc} – estimated sulfur concentration

n – number of reference samples

k – number of regression coefficients

Table 3

Comparison of sulfur content in the Fe-Cr-Cu and alumina catalyst samples determined with alternative analytical methods

Sample	S concentration (% w/w)			
	Fe-Cr-Cu catalyst		Alumina catalyst	
	standard addition method	gravimetric method	standard addition method	UniQuant method
1	0.039	0.040	0.007	0.009
2	0.024	0.025	0.038	0.042
3	0.051	0.060	0.032	0.034
4	0.040	0.050	0.027	0.025
5	0.014	0.018	0.011	0.014

The calibration of analytical curves was performed using a Philips regression model. For both catalysts linear characteristics were obtained. The values of root mean square (RMS) were 0.00056 for the Fe-Cr-Cu catalyst and 0.00075 for the alumina catalyst. In order

to evaluate the abovementioned analytical method for determination of sulfur content, a comparison of different analytical data obtained by different analytical methods was performed. For comparison, the sulfur content in several samples of the Fe-Cr-Cu catalyst was determined by gravimetric method with barium chloride. On the other hand, in case of the alumina catalyst the standard less WD-XRF method supported by UniQuant software was applied. All results obtained are shown in Table 3.

Conclusions

As demonstrated above, the presented method with the internal standard addition seems to be reliable enough for determination of small amounts of sulfur in commercially available catalysts. This method gave good results during analytical tests of the Fe-Cr-Cu catalyst samples, for which the sulfur content was in the range: 0.1 - 0.5 % (w/w). In case of the alumina catalyst this method also provides reliable results and, additionally, much smaller amounts of sulfur can be confirmed applying this procedure (approximately 10 times less). Moreover, this method is characterized by good accordance with other alternative methods and, thus, it proves that the standard samples preparation method and the way of determination of sulfur content in the initial catalyst samples were chosen correctly. However, the main advantage of the presented method compared with others is that this procedure requires much less labor and chemicals consumption and also the preparation of tested samples is easy (reduced number of the required operations). In consequence, this procedure seems to be attractive for the chemical industry, especially in case of the high scale production.

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