Stoichiography as applied to studying composition and real structure of catalysts

V.V. Malakhov

Boreskov Institute of Catalysis, Novosibirsk, 630090, Russia

Abstract

The general principles of a new concept of chemical analysis, called stoichiography, are represented. Stoichiography allows the reference-free analyzing of the molecular and phase composition of complex substances. The differential dissolving technique as a new stoichiography method was developed to characterize in detail the phase composition of heterogeneous catalysts and to identify known and absolutely unknown phases composing the catalyst. The analyzed phases may be in crystalline or amorphous state, which is of no importance for the analysis performance. Such phase analysis is performed with a high sensitivity and very fast. Equipment, developed specially for this analysis, is called stoichiograph. The advantages of differential dissolving in studying the phase composition of catalysts are demonstrated through many particular examples. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Physical methods are known to dominate in studying modern catalysts. This paper, however, describes a new chemical method for determining the composition and in some cases the real structure of catalysts. This method belongs to the family of new methods called stoichiography. The idea of stoichiography was suggested about fifteen years ago [1,2]. At present we know hundred publications focusing on the development of this scientific method and its applications. This paper discusses the main concept of stoichiography as well as what it is able to do, and what specific results for catalysts it may provide.

2. Stoichiography and its methods

Stoichiography is a family of new methods for molecular and phase analysis related to the stoichiometry of non-steady processes, which are used in chemistry and in analytical chemistry to separate complex mixtures into individual components. The nature of such processes may vary a lot (see Table 1). The stoichiography methods comprise a combination of two procedures: separation of mixtures and on line registering of the stoichiometry of the elemental composition flow. Special equipment for such analysis is called stoichiograph and is discussed below (see also Ref. [3]). At present stoichiographs for dissolving and for ionic chromatography are already manufactured.

Table 1
Separation methods promising for stoichiography

Level of separation	Methods of separation	Types of separtaion
Atom.–molec. level	Chromatography	Heterophase processes
	Ionic exchange	
	Electrolysis	
	Dissolution	
	Distillation	
	Extraction	
	Diffusion	Homophase processes
	Electromigration	
	Magnetic mass-separations	
Macro-level	Gravitational field	Processes without phase transitions
	Magnetic field	
	Electrical field	

The problem how to analyze mixtures consisting of several unknown compounds is as old as chemistry itself. It also remains actual for catalysts, since as a rule catalysts are the compositions of known and absolutely unknown compounds. Stoichiography allows one to solve many problems very efficiently with the elucidation of catalysts composition. Most physical methods are known to operate with various spectra, while stoichiography uses patterns called stoichiograms. Stoichiograms are the time functions of ratio of the molar rates for chemical element mass transfer from the sample to be analyzed and undergoing a separation. The time profile of stoichiograms is governed by two main rules: (i) stoichiograms remain constant, if the flow is formed by a single compound, and their values equal to the stoichiometry coefficients in the formula of this compound; (ii) stoichiograms are variable, if the flow is formed by several compounds. Thus, the time profile of stoichiograms directly indicates, whether the mixture is really separated into individual compounds or not.

What particular result may be obtained with stoichiography methods, regarding many other existing methods for molecular and phase analysis? It is possible to determine the quantity and stoichiometry of all prior known and absolutely unknown compounds composing a multiphase solid, not using some standard reference materials for these compounds. Stoichiography methods are conceptually reference-free, and require no necessity to have in the pure state compounds to be identified. Fig. 1 demonstrates how two compounds of a model mixture may be separated by means of their differential dissolving. Stoichiograph determines the elements of compounds present in the flow, and records a set of kinetic curves for these elements (Fig. 1a). This is a starting information from which a set of stoichiograms may be derived (Fig. 1b). Basing on stoichiograms one may determine chemical formula for each compound. When the formulas are known, there is no problem to transform the kinetic curves of elements into the kinetic curves of the individual compounds, and this transformation is performed using common stoichiometry calculations. The area under the compound kinetic curve (see Fig. 1c) is equal to the quantity of this compound. Note that the stoichiometry coefficients and, thus, the linear parts of the stoichiograms, can not depend and do not depend indeed on the separation parameters, such as solvent concentration, temperature, hydrodynamic conditions, etc. It means, that the stoichiograms for an individual compound are invariant to all these mass transfer process parameters. All advances of the stoichiography methods application to the separation of the multiphase solids come through these fundamental properties.

3. The method of differential dissolution

Differential dissolving (DD) may be considered as a particular stoichiography method for the phase analysis of solid substances. Fig. 2 schematically shows a stoichiograph as a device for the DD method. Catalyst sample with a weight of $\geq 10^{-6}$ g (lower threshold) is loaded into a reactor (7). The solvent flow (HCl, HNO_3, HF acids or mixture there of (1,2)) passes
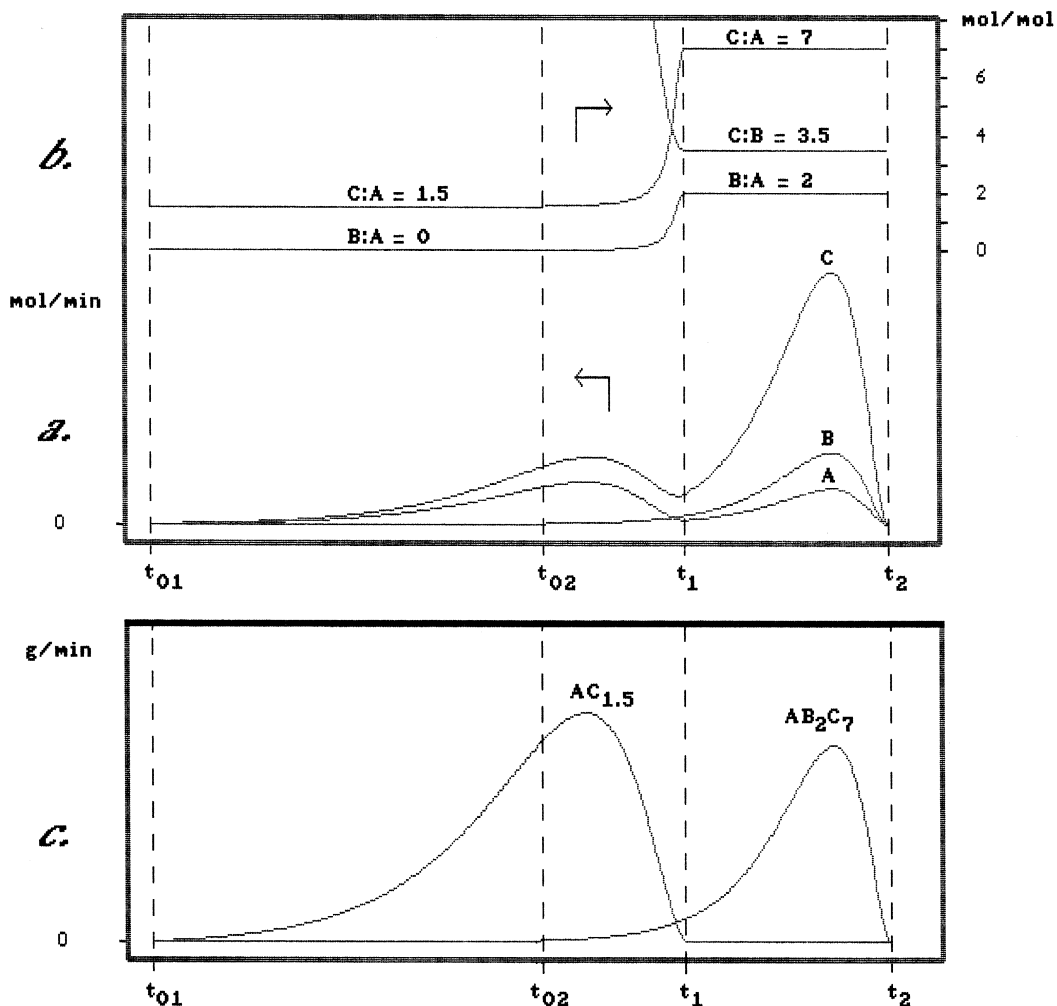
Fig. 1. Kinetic curves of dissolution: (a) starting kinetic data for elements and stoichiograms (b) calculated from (a) kinetic curves of phases dissolution; (c) the total DD picture for dissolving the model mixture consisting from two phases of $AC_{1.5}$ and AB_2C_7 composition.

through the reactor with a velocity of 3 ml per minute. Two peristaltic pumps (4,5), controlled by electronic system (3) through special computer program, provide the desired solvent concentration in the flow. Thus, a constant velocity of the flow with the intentionally increasing concentration of, e.g., an acid is provided. The flow from the reactor is directed to the multi-element detector-analyzer ICP AES with 38 channels (8). It allows one to record a set of dissolution kinetic curves of all elements composing the sample. The stoichiography calcula-tions of the composition and quantity of individ-ual phases are performed with special computer program (9). As the solvent temperature and/or concentration grow, the solution chemical po-tential also increases. The dissolving process is arranged so that its dynamic regime [6] allows different phases to dissolve sequentially rather than simultaneously. The DD method looks like the well-known electrochemical methods such as voltametry and polarography, and the kinetic curves for the elements and phases dissolving are similar to the volt–ampere curves.
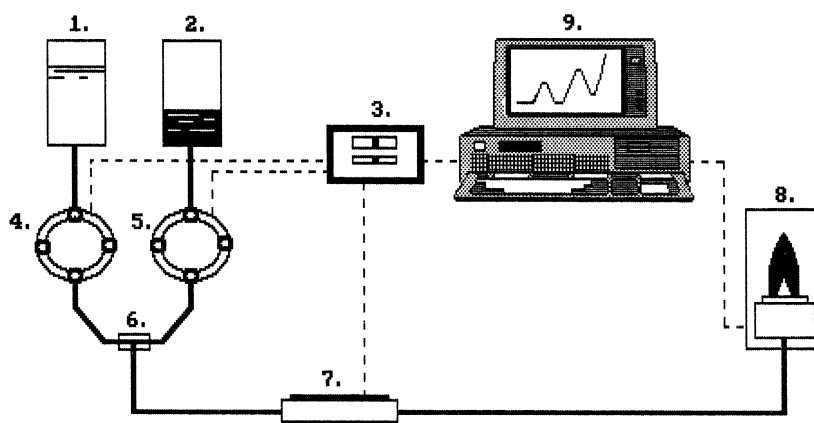
Fig. 2. Schematic diagram of stoichiograph: (1, 2) capacities with solvent components, (3) electron device regulating flows, (4, 5) peristaltic pumps, (6) mixer, (7) reactor, (8) detector analyser as ICP AES, (9) computer.

Usually, 1–30 mg of a solid sample dissolve during 3–30 min, which is rather fast. There are other advantages as well. Elements may be determined with a high sensitivity, and there are no special requirements to sampling (assorted shape, size, surface state, and structural perfection). To date, the DD method has been successfully used for determining the stoichiometry and content of the main and impurity phases, crystalline or amorphous, for recognizing the phases of constant or variable composition, and for controlling the spatial distribution of the phases over the sample. By now, many different type catalysts were analyzed by the DD method. More than sixty elements of the Mendeleev Periodic Table, composing these catalysts, are well controlled during the dissolving procedures. Table 2 lists solvents suitable for catalysts dissolving.

4. The DD analysis results

In this section, we present some examples of the DD method application for phase analysis, for surface composition analysis, for the prepar-

Table 2
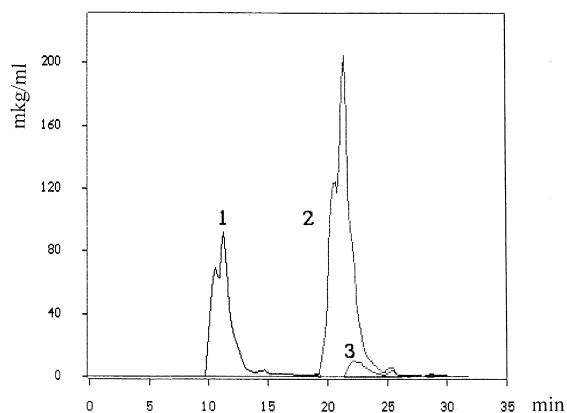Heterogeneous catalysts phases and conditions of the DD analysis

Fig. 3. The phase composition of the $CuAl_2O_4$ catalyst for hydrogen reduction reaction (270°C). Total DD picture: (1) Cu^0, (2) $Cu_{0.12}Al_2O_{3.12}$, (3) $CuAl_2O_4$.

Table 3
Phase composition of initial and H_2-reduced samples of copper aluminate (phases and amount, mass%)

Sample	X-ray	DD method				
		CuO	Al_2O_3	Spinel $CuAl_2O_4$	Cu^0	Non-stoichiometric spinel
Initial	Spinel	1.20	3.30	95.5	Not detec.	Not detec.
Reduced at 270°C	Spinel + Cu^0	Not detec.	Not detec.	4.40	20.8	$Cu_{0.34}Al_2O_{3.34} \cdot 74.8$
Reduced at 400°C	Spinel + Cu^0	Not detec.	Not detec.	3.00	29.1	$Cu_{0.12}Al_2O_{3.12} \cdot 67.9$
Reduced at 700°C	Spinel + Cu^0	Not detec.	Not detec.	2.20	30.4	$Cu_{0.10}Al_2O_{3.10} \cdot 67.4$

ative and synthetic chemistry and as an efficient procedure of physical and chemical studies. The phase analysis, applied to studying a family of Cu–Al–O spinels reduced by H_2 is shown in Fig. 3 and Table 3. Apparently, the DD method gives more information than the X-ray analysis. The DD method detects still further the impurity phases in the initial sample, gives the amounts of the main and impurity phases in the reduced samples, and identifies a non-stoichiometry spinel, present along with the stoichiometry one. Such information can hardly be obtained with other phase analysis methods. Fig. 4 shows the phase analysis of a very thin $YBa_2Cu_3O_x$ (YBC) film, which is an oxidation catalyst. Applying the DD method for studying these films, weighting only few micrograms, several impurity phases were observed and their amounts were determined along with that of the main YBC-phases. Such quantitative information could not be obtained with other known physical methods.

Catalyst surface composition can be determined, when only the surface portion of the catalyst is dissolved, and then dissolving is stopped before the support itself starts to dissolve. The DD picture of a silver catalyst for ethylene epoxidation is given in Fig. 4. Silver is found to be located on the corundum surface, and a very small quantity of an easily soluble aluminium oxide phase is also detected on the carrier surface.

The significant contribution of the DD method to physico-chemical studies has also been demonstrated for the Ca–Ti–O system [4]. In
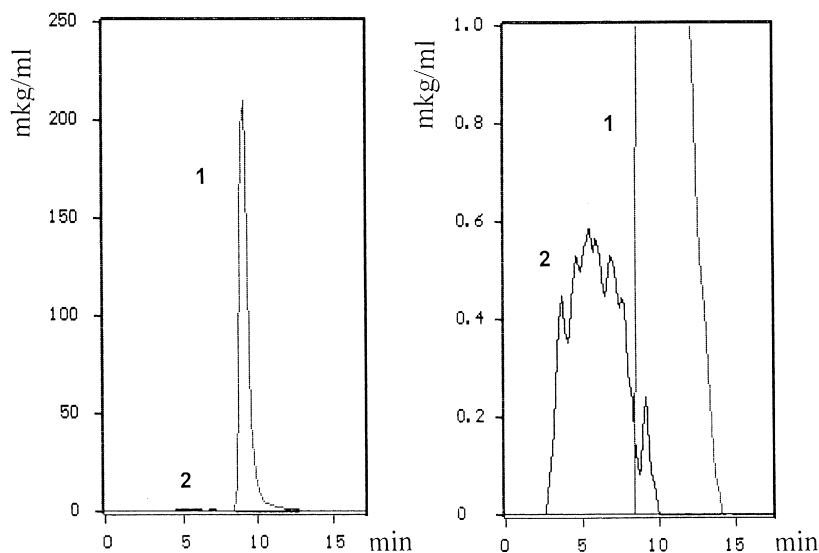
Fig. 4. The composition of the silver catalyst for ethylene epoxidation (10% Ag/α-Al_2O_3). Total DD picture: (1) Ag, (2) Al of soluble form.

this case it characterizes the reactivity of compounds with identical composition but with different structure, providing useful data on the kinetics and mechanism of the solid–solid transformation. The interesting fact is that calcium titanate begins to form after some induction period during which an activated form of titanium oxide is accumulated. The important information was obtained only due to the DD method, though this process was previously studied by many other physical methods.

The DD method may be a good help in preparative chemistry, especially when spectra, which characterize the phases, composing sample, overlap. In this case, it is difficult to identify these phases by the X-ray diffraction or the Raman spectroscopy methods. The DD method can gradually dissolve such phases one by one, reduce the number of phases in the mixture, alleviating the problem of phases identification with physical methods. In Ref. [5], one may find the X-ray powder diagrams for the multiphase oxide ceramics before and after each procedure of phase removal. The further identification of the phases has become simple after these procedures.

The DD method finds its application not only in the analysis of heterogeneous catalysts [6–8]. Other materials, such as high-temperature superconductors (ceramic, crystals, films) [5,9,10], luminophorms [11], inorganic pigments [12] were also successfully studied by the DD method. And in all these cases, unique results, revealing the stoichiometry and amount of phases in many-element multiphase solids, were

obtained. Therefore, the DD method plays a significant role in the development of informative methods for studying various materials.

Acknowledgements

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