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Editorial

General introduction: origins and objectives of the study

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1. History

Fundamental research in heterogeneous catalysis in most academic or industrial laboratories is usually performed on catalysts prepared on a very small scale. This has several disadvantages, such as the difficulty of preparing homogeneous materials on the scale of a few grams, and of exactly repeating preparations. Moreover with such a small amount of material its characterisation is often limited, particularly if one wishes to return to study it in later years, when new techniques and concepts may have arisen. Also you cannot share the materials with your friends and colleagues who may wish to check your findings or enlarge the scope of your study. It also often happens that differences in findings published in the literature are explained by hypothetical differences in the material, which cannot obviously be checked. It therefore appeared in the early 1970s that there existed an urgent need for *standard or reference catalysts* to be available to the world catalysis community.

Such standard catalysts were envisaged to be of great value in a number of ways. First, it would be useful to test the practical skills of new research workers and to calibrate newly constructed equipment, since the results could be predicted. Secondly, it could be of value in assessing the validity of new and as yet unproven methods of characterisation. Thirdly, its widespread use for a variety of reactions would lead to a corpus of coherent and comparable information, which would contrast with what is so frequently seen in the literature. Finally, it could be possible to use it as a base catalyst to which alterations and modifications might be made, without changing its essential physical structure.

At this time a group of European scientists under the chairmanship of Professor E.G. Derouane from the University of Namur (B) formed in 1975 a Research Group on Catalysis as part of the Group on Surface Chemistry and Colloids of the Council of Europe. This body received financial support from the Council of Europe for travelling to meetings and for administrative expenses, and reported to the Council's Committee on Science and Technology. During the Sixth International Congress on Catalysis, held in London in July 1976, the group decided to embark on a collaborative programme on characterisation of supported metals to compare experimental procedures, and to interpret the results, using the blossoming new physical techniques available in the 25 European laboratories of the Group. They first commissioned the preparation by Johnson Matthey of a large quantity (6 kg) of a Pt/SiO_2 catalyst, designated EUROPT-1, and so to characterise it that it could come to be regarded as a primary standard for the measurement of chemisorption capacity and catalytic activity. An extensive work was then devoted to the study of the catalyst by the Group and their assistants and students over almost

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one decade. The results of the study as they concerned chemical composition, physical structure, chemisorptive behaviour and catalytic properties were published in a series of papers in Applied Catalysis [1–6]. The same approach was also followed for the more industrially realistic Pt/Al_2O_3 and $Pt–Re/Al_2O_3$ catalysts, designated EUROPT-2 and -3 with low precious metal loadings (0.3 wt.% Pt and 0.3 wt.% Re) but the success in physical characterisation was limited due to the low metal loadings. In parallel, similar works were devoted to Ni/SiO_2 catalysts, designated EURONI-1 and -2 and were also published in Applied Catalysis [7,8].

This work by the Group was not the only one. Japanese scientists launched a similarly-conceived but more broadly-based programme and have published some of their results [9]. Further on, detailed studies of the preparation procedures and characterisation of a 13 wt.% MoO_3/Al_2O_3 catalyst have been performed in Japan under the programme of "Standardisation of Catalyst Preparation by Use of JRC-Reference Catalysts" financed by the Ministry of Education, Science, Sports and Culture. The work was published recently in Applied Catalysis A: General [10]. A group of scientists in the USA has also conducted extensive research on a number of well characterised supported metals [11] and has made samples widely available. A programme on reference catalysts was also launched in Russia [12]. A comprehensive review of all catalyst standardisation programmes has been published in the "Handbook of Heterogeneous Catalysts" [13].

The Research Group was in due course incorporated under Belgian law as a charitable body called European Association of Catalysis (EUROCAT). Support from the Council of Europe has terminated, and the last few years have not been easy for the Association. A realisation grew that it was too narrowly based, and its sphere of activity too restricted. Additional programmes on catalyst characterisation were started, on metals, zeolites, sulfides and oxides. The works of these four sub-groups have been hindered by our failure to persuade major funding agencies, such as the European Commission and the European Science Foundation, to support them. Nevertheless, and in the absence of any funding, the EUROCAT oxide group has produced a first work on V_2O_5/TiO_2 catalysts, used industrially for *o*-xylene oxidation to phthalic anhydride, which was published as a special issue of Catalysis Today [14] in 1994.

At present the EUROCAT oxide group is part of the activities of the European Federation of Catalysis Societies. This Federation was created in 1993 following the recommendations of a working party composed of representatives of National Catalysis Societies in Europe, supported by EUROCAT, and who met in Paris on 13 June 1990 under the initiative of the Catalysis Division (Professor M. Che, President) of the French Society of Chemistry and at Brunel University (Uxbridge, UK) on 6 December 1990.

2. Selective catalytic reduction of NO_x

The use of catalytic systems for pollution abatement has grown tremendously in the last decades from virtually nothing to a multi-billion euro worth world wide business, due to more and more restrictive environmental regulations for mobile and stationary sources. In the case of stationary sources the most important applications consist of VOC abatement from chemical processing plants and manufacturing processes, and $DeNO_x$ processes.

The selective catalytic reduction (SCR) of NO_x by NH_3 represents an important catalytic process that was introduced in the late 1970s for the control of NO_x emissions in stack gases from power plants and other industrial facilities [15–17]. SCR systems are currently operating in Europe, the Far East and Japan for a total capacity of ca. 150 000 MWe. This technology presently accounts for more than 90–95% of total $DeNO_x$ flue gas treatments in Europe and Japan. Although the potential market for SCR in the USA amounts to a few hundred thousand MWe, SCR applications in the USA are still essentially confined to gas turbines having a capacity of ca. 5000 MWe and primarily located in California. This is because current Federal NO_x emission limits are designed to be met essentially by combustion modifications. In addition to the most common power plant applications, the SCR technology has been proved and applied for the treatment of waste gases of industrial and municipal incinerators, of chemical (e.g. nitric acid plants, catalytic cracking units), glass, steel and cement industries. The SCR technology is also used for the combined removal of NO_x and SO_x in thermal power plants and industrial boilers and for the abatement of NO_x and dioxins in incinerators.

The SCR process is based on the reduction of NO_x with NH_3 into water and nitrogen according to the reaction

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

If SO_2 is present in the combustion gas, it can be oxidised to SO_3, over the catalyst, according to the reaction

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$$

Even very small SO_2 conversions to SO_3 are highly undesirable because they cause deposition and accumulation of ammonium sulfate salts over the catalyst (if the temperature is not high enough) and on the pre-heater downstream from the catalytic reactor.

The $DeNO_x$ reaction is operated industrially over catalysts made of homogeneous mixtures of TiO_2, WO_3 (or MoO_3) and V_2O_5 [18]. TiO_2 in anatase form is used as high surface area support for the active components. V_2O_5 is responsible for the activity for both SCR of NO_x and, unfortunately, SO_2 oxidation reactions. Accordingly, its content is kept low and even below 1 wt.% in high sulfur applications. WO_3 (or MoO_3) contents are much larger (10 or 6 wt.%, respectively): WO_3 or MoO_3 act as “chemical” and “structural” promoters by enlarging the temperature window of the SCR reaction, limiting SO_2 oxidation and improving structural and morphological properties of the catalysts. Silico-aluminates and fibreglass are used as ceramic additives to improve catalyst strength. The commercial SCR catalysts are employed in the form of honeycomb monoliths or plates for the following reasons:

- lower pressure drop by two or three orders of magnitude than in packed beds;
- comparable geometric surface areas per unit volume of catalytic reactor, which has to be maximised since the reaction is controlled by gas–solid diffusion limitations;
- superior attrition resistance and lower tendency to fly-ash plugging.

The most important and critical requirement for commercial catalysts is to combine high activity in the $DeNO_x$ reaction and very low (negligible) activity for SO_2 oxidation. The former activity is known to be proportional to V_2O_5 content, whereas the latter one increases much more with V_2O_5 content. Active sites for SO_2 oxidation have been suggested to be dimeric (or polymeric) vanadyl sulfates, in line with those suggested for commercial sulfuric acid catalysts [19]. Active sites for $DeNO_x$ reaction have been suggested to be isolated vanadyl species, identified by FTIR and Laser Raman spectroscopies. However such suggestions are still controversial.

3. Objectives

Our objectives for this exercise were similar to those followed previously for EUROPT, EURONI and EUROCAT oxide V_2O_5/TiO_2 catalysts, the philosophy of which was recalled above. For oxide catalysts more specific objectives were described in Ref. [13], pp. 3–5. In addition, it was quite important and novel to characterise not only the catalyst as manufactured but also after it has been running for a long time in an industrial unit. After a general inquiry to the participants in the previous exercise (13), our choice went to V_2O_5–WO_3/TiO_2 catalyst at a meeting, which was held during EUROPACAT II in Maastricht (NL) on 6 September 1995. Professor J.A. Lercher of the University of Twente in Enschede (NL) (he moved recently to München in Germany) informed us that an Austrian company “Austrian Energy and Environment” could provide us with a fresh and used V_2O_5–WO_3/TiO_2 catalysts at no cost, while Dr. B. Grzybowska from the Institute of Catalysis in Krakow (PL) proposed that a Polish company “Kedzierzyn Kozle” (Nitrogen Chemicals Works) could prepare for us a V_2O_5/TiO_2 catalyst on a ceramic support for US $ 2000. Dr. B. Wichterlova from the J. Heyrovsky Institute in Praha (CZ) proposed also a Czech company “MCHZ ostrava”, which had expertise in $DeNO_x$ technology and could make the samples for US $ 2000, as long as we could provide precisely the preparation and testing conditions.

The Austrian company was finally chosen with Professor J.A. Lercher as our correspondent. The Austrian Energy and Environment Company has supplied us in February 1996 with large batches of honeycomb monoliths of the starting support of WO_3/TiO_2, of the fresh material V_2O_5–WO_3/TiO_2 and of the same batch having been used in a power plant for 9000 h. One hundred grams of each were sent in May 1996 to all contributors. More details about the materials were provided by Austrian Energy and Environment Technology Company and are given in Chapter 1.

4. How the present work was conducted

When the new programme was agreed in 1995, some 46 different laboratories in Europe showed enthusiastic interest for the new round-robin exercise. Unfortunately six of them in CZ, D, F, I, NL and S had to quit for lack of time, money, students or interest. After a wide inquiry about every laboratory's possibilities and expertises, tasks were allotted and readily accepted. J.C. Védrine accepted to continue to coordinate the work of the group up to its end. Ten main characterisation fields were defined and one responsible person was designated for each. It was then up to the person to define more precisely the experimental conditions for the given techniques within a general frame defined in a meeting of all participants. As the samples were provided in an honeycomb monolith form, it was decided to study them as such, if the technique permitted, or after gentle grinding for techniques using only powders. About 100 g of each sample were provided to all participants in the Spring of 1996. Several meetings were organised to follow the work, while preliminary reports were distributed. We met in Baltimore during the 11th ICC on 3 July 1996 and in Krakow during EUROPACAT III on 2 September 1997. The final meeting, devoted to a deep scientific and very exciting and lively discussion on all the available experimental results was held in Lyon on 15–16 May 1998 with 20 participants who came for this unique purpose.

Our colleagues in this odyssey have brought to bear most of the commonly used methods for catalyst characterisation. Every chapter contains contributions from several laboratories, so that it is possible to see what measure of agreement can be obtained with each technique. Some chapters offer recommendations for best obtaining or recording the data, and thus constitute a mine of useful information for supported oxide systems. Some techniques could not arrive at an ambiguous interpretation or description of the material, while another technique has permitted the ambiguity to be removed.

Finally, a word of explanation concerning the way in which credit is to be assigned to those who have helped the project to progress and to be completed. For each experimental or group of experimental techniques, one person accepted the responsibility of coordinating the work and of writing the final document alone or with some help. His/her (their) name(s) appears directly after the title with the designation: *"compiler(s)"*. All other scientists who have contributed in an academic sense are listed as *"contributors"*; they include those who have done the experimental work and those who have helped to interpret it.

A list of addresses and other useful coordinates (telephone, fac similé, e-mail) are given in the Appendix at the end of this issue.

Samples of the materials can be obtained free of charge from Mr. V. Martin at IRC in Villeurbanne (Laboratory F-1).

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