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A modified robotic system for catalyst preparation by wet or dry impregnation

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Abstract

A modified robotic workstation has been developed which is able to reproduce a conventional catalyst preparation method used routinely in our laboratory, thereby increasing significantly the number of catalysts that can be prepared at once. This paper describes some of the features of this modified system and outlines some of the difficulties encountered in transferring from manual to automatic operation. Some catalytic test results are given for the selective oxidation of propane over a catalyst consisting of Mo-V-Nb-W oxides supported on alumina which illustrate good reproducibility of data for samples prepared with the robotic system and a close similarity with data obtained with equivalent manually prepared materials.

Keywords: Selective oxidation catalysts; Mo-V-Nb-W-O/Al_2O_3; Robotic preparation method

1. Introduction

The combinatorial approach to catalyst screening has come to the fore over the last few years [1–3] and much attention has been given to the development of automated (robotic) catalyst preparation systems and to high throughput screening (HTS) reactor systems. The work described in this paper has been carried out within the framework of a larger EU-funded programme aimed at the development of novel high throughput screening methods for a variety of types of reaction, including gas–liquid–solid processes. The aim of the work is to develop robotic preparation methods for the preparation of a range of supported multi-component transition metal oxides of a type developed previously in our laboratory for the selective oxidation of propane (typically Mo-V-Nb-W oxides supported on alumina), to demonstrate that the robotic method produces materials equivalent to those prepared manually, and then to produce libraries of catalysts based on this type of system to be tested and optimised using the high throughput screening reactors developed within the programme. This paper describes the robotic workstation developed for the preparation of multi-component samples using either wet or dry impregnation methods and also gives the results of preliminary experiments on the selective oxidation of propane which illustrate the reproducibility of samples prepared using the system.

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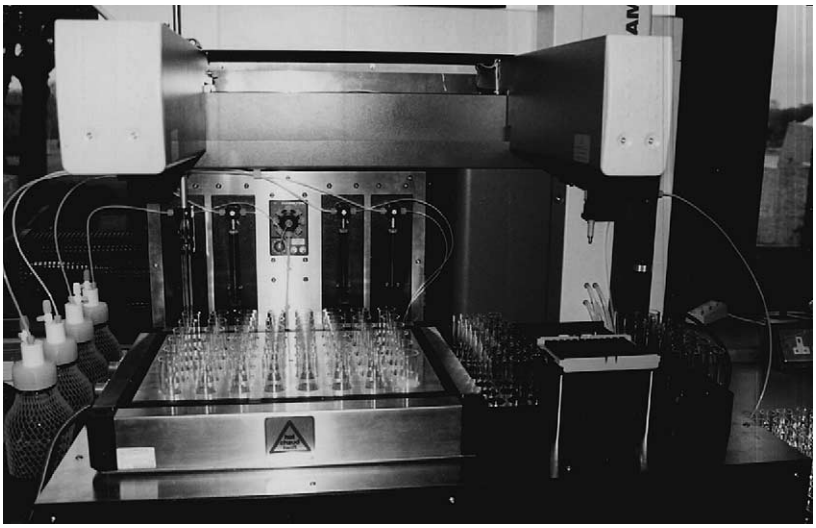

Fig. 1. Photo of the robot.

2. Experimental

2.1. The robotic workstation

Fig. 1 shows a photograph of the robotic workstation developed in this work and Fig. 2 shows the layout schematically. The workstation is based on a Hamilton Microlab Duo system with a two-arm arrangement: a single *needle arm* on one side (left-hand side) and a *D-Head* connected to an internal syringe on the other (right-hand side), the use of two arms offering a greater flexibility in the number of unit operations that can be performed than would be possible with a single-arm system.

The *needle arm* (see Fig. 2) was modified to support a five-needle arrangement. Four of these needles are connected to syringe drivers and hence to reservoirs containing the appropriate reagent solutions while the fifth needle is connected to a nine-port valve modular valve positioner (MVP). In the arrangement illustrated in Fig. 2, the MVP can introduce either water (e.g. to permit dilution of the reagents added) or a gas (e.g. to allow operation under a controlled atmosphere). The needle arm may be used to deliver predetermined volumes of each of the four separate solutions simultaneously or successively either to one of the 48 vessels containing catalyst support placed in the primary *heating/stirring block* (for 'wet impregnation') or to intermediate vessels placed in the *secondary rack* the use of which is described further below. A *wash station* on the right of the main block is used to wash the needle assembly between injections.

Further modification of the original Hamilton system includes the introduction of an integral *heating/stirring block* (*H&P Labortechnik*) on the left-hand side of the deck. This block, which can be heated to 200 °C, contains 48 quartz vessels (25 mm diameter), each of which can be magnetically stirred (at a variable speed, from 100 to 2000 rpm); the vessels can be either flat-bottomed or round-bottomed. We have investigated the use of both types of vessel and are currently using the flat-bottomed vessels for dry impregnation and the round-bottomed vessels for wet impregnation. In the selection of the hardware to be used, we performed an extensive investigation on the influence of stirring on the process of catalyst preparation and the final choice of stirrer geometry (cross-shaped for the flat-bottomed vessels and rugby-ball shaped for the round-bottomed vessels) was made on the basis of the observation that the best mixing, while avoiding excessive fragmentation of the catalyst support, was achieved with these combinations. A programmable *H&P Control Station* is

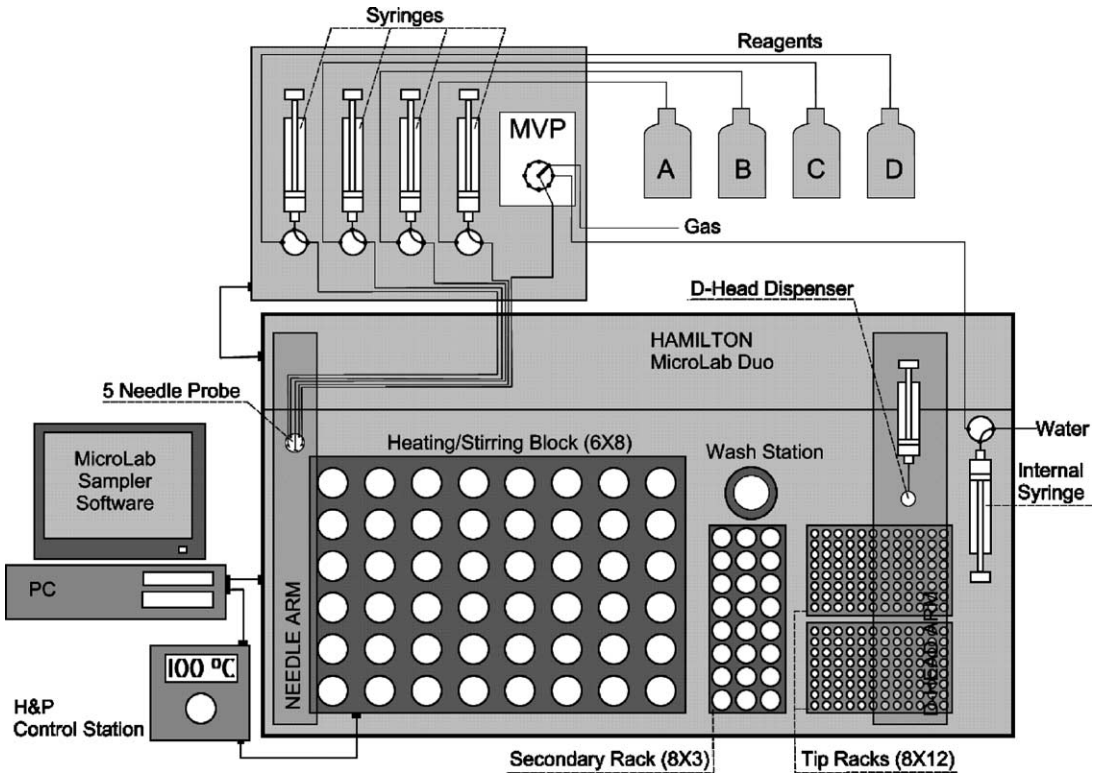

Fig. 2. Scheme of the robot.

used to give independent control of both the heating rate applied to the primary block and the stirring speed.

The *secondary rack* (24 vessels) is used to allow solutions of salts to be premixed for use in the dry impregnation method; in that case, the five-needle probe of the workstation can be used to make up the solutions just prior to use. (This rack can be exchanged for another containing 12 vessels of 32 mm diameter for use in situations needing a larger volume of solution.) The syringe mounted on the *D-Head arm* supports can be used to transfer solutions made up in the intermediate vessels of the *secondary rack* to 24 of the 48 vessels (i.e. those on the right-hand side) of the primary *heating/stirring block*. The syringe of the *D-Head arm* uses disposable tips (to avoid cross-contamination) and these are stored in the *tip rack*. This syringe may be used to dispense solutions drop by drop and, more importantly, to do this in a circular motion around the circumferences of each vessel instead of only at the centre, thus enabling 'dry impregnation' to be carried out in a homogeneous fashion.

As indicated above, the *five-needle assembly* has access to both the primary and secondary racks. A filter may be fitted next to each of the storage vessels to avoid any clogging of the syringes by undissolved solids. The syringes are located behind the *heating and stirring block* and they are easily replaced with others of different capacities to offer the necessary precision for dispensing (±1% of total syringe volume).

The original software supplied by Hamilton (Microlab sampler) was modified by Hamilton Bonaduz, Switzerland to a newer version (Version 1.5) able to operate all aspects of the new modified workstation.

An important feature with the new version of the software is its capability of controlling any additional third-party hardware, in this case the H&P Control Station. Commands are transmitted to the H&P Control Station via a serial port, thus allowing catalyst preparation sequences to run to completion without manual intervention.

2.2. Standard manual catalyst preparation

A series of Mo-V-Nb-W-O/Al_2O_3 catalysts for use for the selective oxidation of propane was prepared manually using wet impregnation method described previously [4,5]. The alumina support used was crushed, sieved (particle size = 212–425 μm) and calcined at 1150 °C and it was then placed in a round-bottomed vessel. Solutions each containing different metal species (ammonium molybdate, AnalaR; ammonium metavanadate, AnalaR; niobium oxalate, CBMM; ammonium metatungstate hydrate, Aldrich) were fed sequentially to the vessel and the resultant mixture was equilibrated for a period of 12 h. Drying was then carried out using a Rotavapor system and the resultant solid was calcined for 6 h at 650 °C.

2.3. Catalyst preparation by robotic system

2.3.1. Standard wet impregnation

The aim was to reproduce the original method of wet impregnation described above using the robotic system before doing exploratory work on new catalyst formulations. The initial experiments for which results are described in this paper involved the preparation of identical formulations of the $Mo_xV_yNb_wW_z$/alumina material in all 48 vessels, the aim being to demonstrate the reproducibility of the system.

For each set of preparations by the wet impregnation method, a sample of the powder was weighed carefully (±0.1 mg) into each vessel. The appropriate quantity of each of the four mother liquors was added to each vessel without stirring and these were then allowed to stand at room temperature for 12 h. The theoretical composition of the resultant materials, assuming that all the added salts were taken up by the support, was in each case $Mo_6V_{0.4}Nb_1W_1$, concentration of metals being expressed as weight percent of metal per gram of alumina. The solvent (water in all cases in the experiments carried out to date) was removed by evaporation by heating the heating/stirring block to 120 °C for 2 h, stirring being carried out for 1 min in every 10 min. After drying, half of the samples of catalyst were calcined at 650 °C and the other half at 700 °C.

Preliminary experiments showed that an issue that has to be controlled very carefully is the possibility that the support particles are crushed to a powder form during the drying step and that layers of powder may then form on the walls of the vessels. This has been minimised by careful selection of the geometries of the vessel and the stirrer and, also, increasing the temperature of drying and reducing time and speed of stirring. In fact, sieving the catalysts after the preliminary test and the last one we found that the percentage of crushed powder (below 212 μm) decreased from 60 to 30%.

2.3.2. Dry impregnation

A procedure to enable this method to be carried out has been established and a number of tests have been carried out. This procedure can be used to carry out both sequential impregnation (adding each solution, followed by drying, before the addition of the next) and simultaneous impregnation (premixing all the solutions in the secondary rack before impregnation). In both cases, the D-Head probe is used to feed the appropriate solution, drop by drop, into the centre and then round the circumference of each of the 24 vessel on the right-hand side of the primary block, this procedure ensuring a homogeneous distribution of the solutions over the support. The results of experiments carried out using catalysts prepared using this procedure will be described elsewhere.

3. Results of for catalysts prepared using the robotic system by wet impregnation: the selective oxidation of propane over Mo-V-Nb-W oxides supported on α-alumina

We report here the results of a series of catalytic experiments carried out with a batch of catalysts designed to have exactly the same composition which were prepared with the robotic system and we compare these results with data obtained with a roughly equivalent sample prepared manually. The object of these experiments was to show the reproducibility of the method rather than to optimise the catalyst composition. The results of catalyst optimisation experiments will be reported elsewhere. We discuss here also some experimental limitations, which must be overcome in order to achieve reproducibility.

The catalytic tests were carried out in a standard microreactor using a quartz tubular reactor of 4 mm internal diameter. The total flow rate was

40 $cm^3\,min^{-1}$ and the catalyst weight used for each test was 300 mg; in each case, the sample was diluted with 100 mg of quartz (GHSV = 5300 h^{-1}). The composition of the flow used (using mass-flow controllers) was: $C_3H_8/O_2/H_2O$ = 15%/15%/10%, He being used to make up the balance to 100%. The water was introduced to the reaction stream through a stainless steel saturator and its partial pressure was controlled by heating the saturator to the appropriate temperature (measured by a thermocouple system). Analysis of the gas stream was carried out by on-line gas chromatography using a Varian 3400CX GC system. This is equipped with both thermal conductivity (TCD) and flame ionisation (FID) detectors. The TCD was used to measure permanent gases and the FID was used for an accurate evaluation of the concentrations of organic compounds. A methanation column was inserted between the two detectors to convert the CO and CO_2 of the product stream to CH_4, detectable by FID. The carrier gas used for the GC was helium (13 $cm^3\,min^{-1}$). Two GC columns in series were used for separation of the components: a 10 m Molsieve 5 A to separate the permanent gases and a 10 m Poraplot Q for the separation of the hydrocarbons and oxygenated compounds. A 10-way gas-sampling valve was used for gas sampling, using a 50 μl loop and, also, to avoid the contamination of Molsieve 5 A column by CO_2, C_2 and C_3 compounds.

Six catalysts were tested and compared: five made by the robot and one, with approximately the same composition, prepared manually. The catalysts prepared by the robot (A5, A16, A18, A29, A40) were chosen randomly from half the batch of 48 identically prepared samples, that which had been calcined at 650 °C (see Section 2.3.1 above). Fig. 3 shows the results of the experiments carried out with these

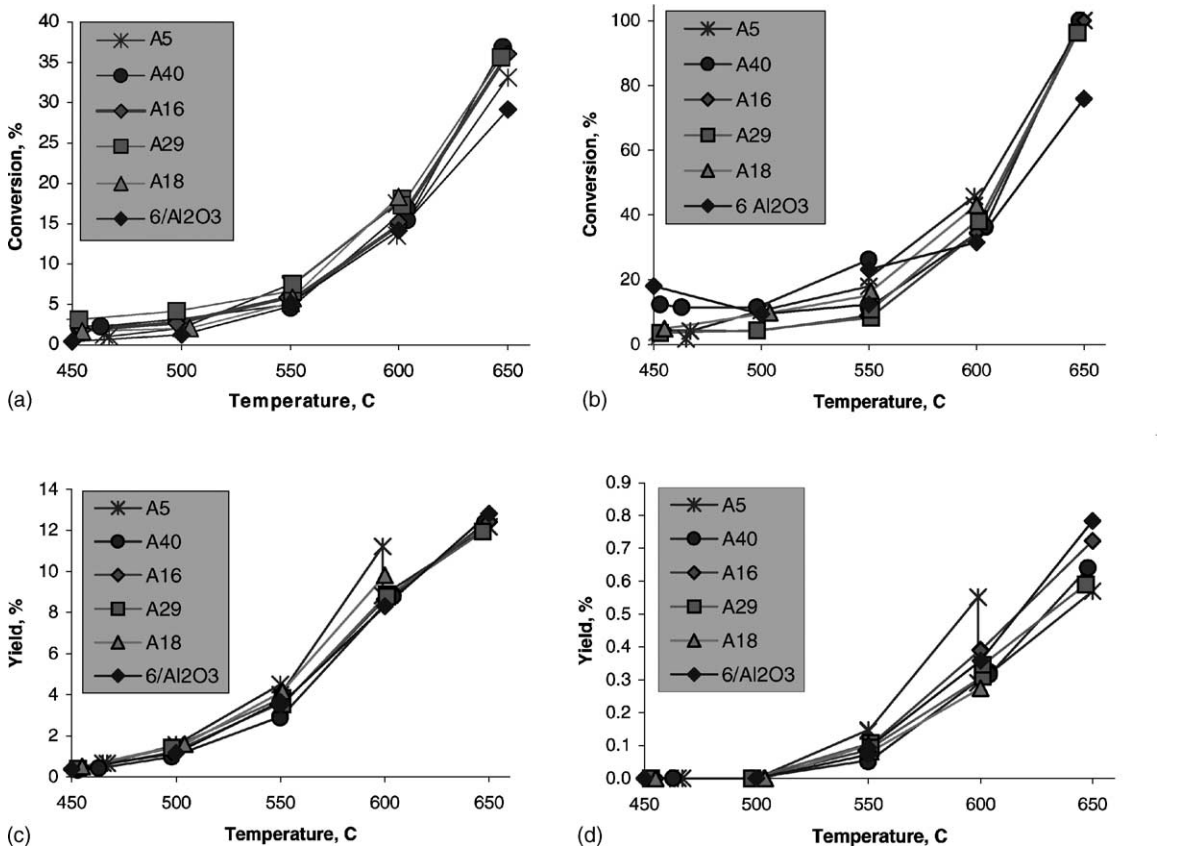

Fig. 3. Comparison between catalysts A5, A16, A18, A29, A40 (robotic preparation) and 6/Al_2O_3 (manual preparation): (a) propane conversion, (b) oxygen conversion, (c) yield of propane, (d) yield of acrolein.

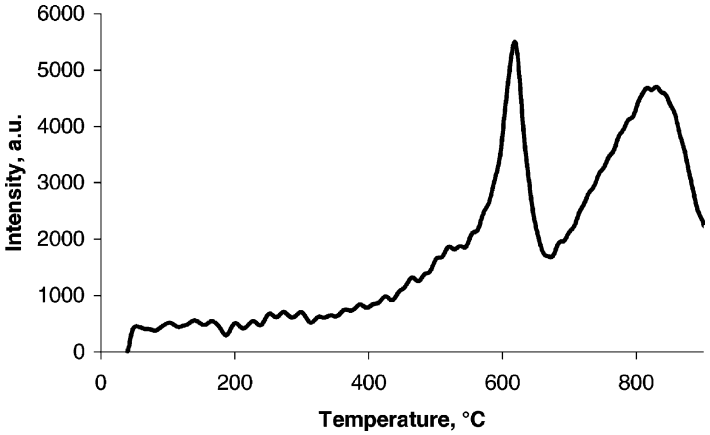

Fig. 4. TPR of the catalyst A40. Experimental conditions: catalyst weight = 100 mg; flow = 50 $cm^3\,min^{-1}$, 3% H_2 in Ar; temperature ramp = RT to 900 °C at 10 °C/min.

samples. The conversions of propane as a function of reaction temperature are shown in Fig. 3a and the equivalent oxygen conversions and the propene and acrolein yields are shown in Fig. 3b–d respectively. (Other trace products were also obtained but these are not shown, as they do not contribute significantly to the product yields.) The results for all the robotically prepared samples (A5, A16, A18, A29, A40) show very good reproducibility in terms of both the propane and oxygen conversions, although there are small differences in the propene and acrolein yields. The data are similar to those obtained with the manually prepared material ($6/Al_2O_3$) but this material was less active at all temperatures; this sample contained slightly less vanadium that those prepared robotically and it will be shown elsewhere that increasing vanadium concentrations gives increased propane conversions and associated shifts downward in the temperature distribution of products.

An interesting observation made during these experiments was that there are time-dependent changes, which occur at a temperature of around 600 °C. This phenomenon is dramatically shown by the behaviour of yield of propene and acrolein of catalyst 5 A, which changes over the period of 45 min, represented by the subsequent points on the graph 3c–d. The phenomenon is reflected also by temperature programmed reduction (TPR) experiments carried out with all the samples tested here (an example of such an experiment being given in Fig. 4), which show a significative reduction peak occurring in the same temperature range of the catalytic experiments.

We will report elsewhere the results of experiments which show additional data on the time-dependent effects occurring at and around 600 °C, particularly on the effects of the water partial pressure on these changes.

4. Conclusions

A robotic catalyst preparation system has been developed which is able to prepare simultaneously 48 catalysts by wet impregnation or 24 catalysts by dry impregnation. In either case, addition of solutions can be performed either sequentially or simultaneously. These batches of catalysts can be prepared in a time comparable with that necessary for the manual preparation of a single sample. The results obtained using samples selected at random from a series with the same nominal compositions showed very satisfactory reproducibility.

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