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QUALITATIVE SPECIATION OF SULFONIC GROUPS OF FRESH CATION EXCHANGER CATALYSTS

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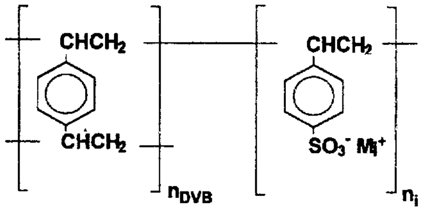
Abstract

On the basis of the thermogravimetric data, the procedure to perform the qualitative speciation of sulfonic groups of the cation exchanger in the mono- or bi-ionic form is proposed.

Keywords: cation exchanger catalyst, speciation analysis, sulfonic cation exchanger, thermogravimetry

Introduction

Within the synthetic cation exchange resins, only sulfonic cation exchangers are used as heterogeneous acidic catalysts for liquid phase commercial organic syntheses. From the chemical point of view, sulfonic cation exchange resins are sulfonated styrene-divinylbenzene (DVB) copolymers, where the latter is the cross-linking agent:



where M_i^+ denotes counter-ions of sulfonic groups in the above formula. These counter-ions may be: hydrogen, metal(s) as well as ammonium (optionally substituted) cations. If only one type of counter-ions is present, the cation exchanger is said to be in the mono-ionic form (e.g. H-form, Na-form). When two types of couriter-ions are present, the exchanger is in the bi-ionic form, and when more than two counter-ion types are used – it is in the poly-ionic form.

Generally, cation exchangers in the hydrogen form are used as catalysts. However, in the case of syntheses of bisphenols, some part of hydrogen counter-ions is frequently replaced with mercaptoamines. This replacement has some promoting action and it is supposed to increase the reaction rate [1]. As a result,

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the cation exchanger in the {hydrogen, ammonium} bi-ionic form is obtained then. If the commercial cation exchange resin is delivered in the sodium form, it must be activated before it can be used as a catalyst. This is done by means of ion exchange with a mineral acid. If the activation is not complete, the cation exchanger in the {hydrogen, sodium} bi-ionic form is obtained. For this reason (and also for some other reasons), the cation exchange resin prepared to act as a catalyst should in general be, or it may be, in the bi-ionic (or even in the poly-ionic) form.

The cation exchangers delivered or prepared to be used as catalysts should undergo quality control. For this purpose a procedure is needed which makes it possible to perform the speciation of the sulfonic groups. The qualitative speciation analysis of the sulfonic groups must be performed at first. This qualitative analysis of the sulfonic groups must recognise whether hydrogen and/or metals and/or substituted ammonium cations are the counter-ions of the cation exchanger sulfonic groups. In other words, it must be determined what form(s) of the cation exchanger is/are present: hydrogen and/or metal(s) and/or ammonium form(s).

In the present paper the applicable procedure is presented and discussed. This is based on thermogravimetry and makes it possible to perform such a qualitative speciation analysis.

Experimental

The Amberlyst-31 sulfonic cation exchanger in the hydrogen form was delivered by Rohm & Haas Company. The samples of this cation exchanger in the sodium form and in the {hydrogen, sodium} as well as {hydrogen, cysteamine} bi-ionic forms were prepared by total or partial neutralisation of their sulfonic acid groups. Sodium chloride or cysteamine hydrochloride solutions were used for this purpose, respectively. All the cation exchanger samples were dried at room temperature to achieve the air-dry state.

20 mg samples of air-dry cation exchanger were used in tests. The samples were weighed in platinum pans and were heated in the dynamic air from ambient temperature to 950°C, at the heating rate $\beta=12°\text{C min}^{-1}$. The Mettler TG-50 thermobalance in the Mettler TA-4000 Thermal Analysis System was used.

Results and discussion

According to author's experience, the collected cation exchanger samples:

- in the hydrogen form,
- in the sodium form,
- in the {hydrogen, sodium} bi-ionic form,
- in the {hydrogen, cysteamine} bi-ionic form

are model materials for the basic states of fresh cation exchangers which can exist at the catalyst preparation stage. TG and DTG curves of these cation exchanger samples are shown in Figs 1–4.

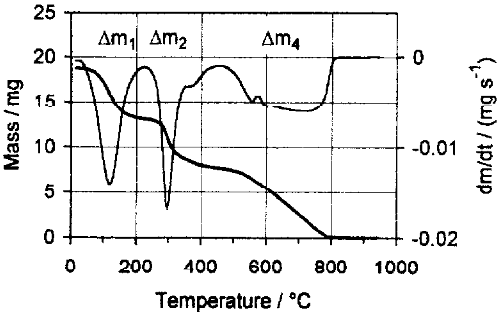

Fig. 1 TG and DTG curves of a fresh sulfonic cation exchanger in the H$^+$ form

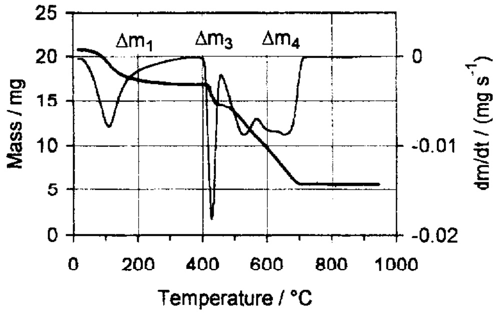

Fig. 2 TG and DTG curves of a fresh sulfonic cation exchanger in the Na$^+$ form

As can be seen, in the case of a fresh mono-ionic cation exchanger (which is free of any contamination) only basically three consecutive mass loss steps are observed (Figs 1 and 2).

They result from the following processes: thermal dehydration (Δm_1), thermal desulfonation (Δm_2 or Δm_3) and thermal oxidative decomposition of the cation exchanger polymer matrix (Δm_4), respectively. What is noticeable, the temperature of the desulfonation step depends on the type of the counter-ions of the sulfonic groups. This temperature is lower for hydrogen, and higher for the other counter-ions. In the case of a fresh cation exchangers in the bi-ionic form, the desulfonation process proceeds in two steps, and four steps of mass loss are observed (Figs 3 and 4). The sample mass after the dehydration step is assumed to be the dry matter of the cation exchanger. The solid residue in temperature ~900°C is assumed to be the ash. The ash is formed quantitatively from the metal form(s) of the cation exchanger. It is the sulfate type one.

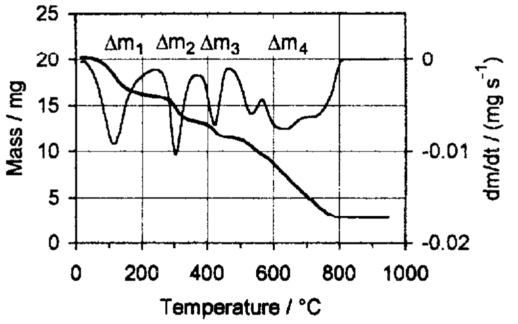

Fig. 3 TG and DTG curves of a sulfonic cation exchanger in the $\{H^+, Na^+\}$ bi-ionic form

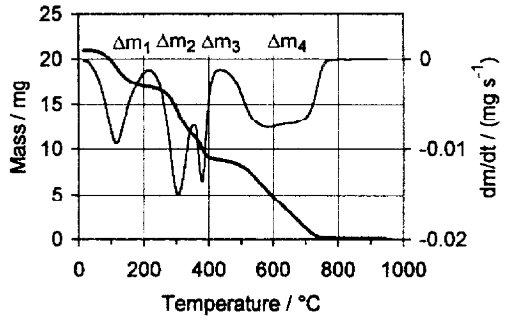

Fig. 4 TG and DTG curves of a sulfonic cation exchanger in the $\{H^+, HN^+H_2CH_2CH_2SH\}$ bi-ionic form

On the basis of the above interpretation of the steps of mass loss, the TG data may be used for the qualitative speciation of cation exchanger sulfonic groups. The analysis of the TG data and arriving at the conclusions as to the qualitative composition of the cation exchanger follow the procedure presented as a logical diagram in Fig. 5. The information on the mass losses Δm_1, Δm_2 and Δm_3 as well as on the ash content are always considered and utilised. The information on nitrogen content (from complementary determination) is only used if necessary.

The Δm_1 step must always be observed because of solvating properties of cation exchangers. Its value is used in the quantitative analysis of cation exchangers. If the Δm_2 step is observed, it makes the evidence for the H-form present in the cation exchanger sample. The Δm_3 step is connected with the content of ionic forms other then the hydrogen one. They may be metal and/or ammonium forms. These forms can be differentiated on the basis of the information on the ash content (and nitrogen content, if necessary). If the ash content is greater then zero, the presence of metal(s) forms can be expected. If the nitrogen content is (also) greater then zero, then ammonium form is (also) present in the cation exchanger sample. The simplest situation is for the cation exchanger resins in the mono-

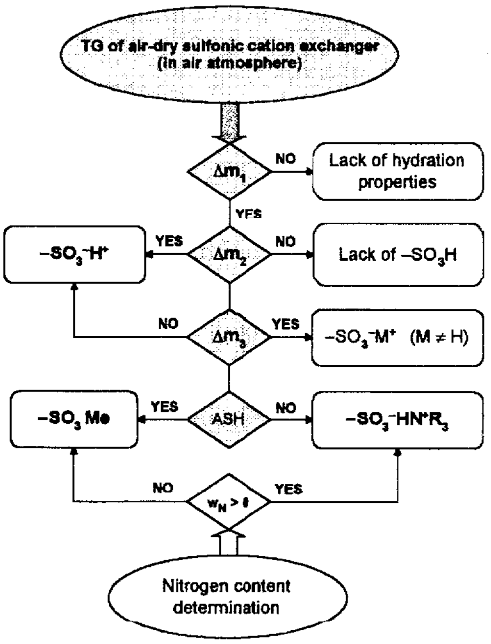

Fig. 5 Logical diagram for the qualitative speciation of sulfonic groups of a fresh cation exchanger

ionic form. The TG curve shows only three mass loss steps then. And the TG data is satisfactory to differentiate between the cation exchanger in the hydrogen and metal form(s). When the TG curve shows four mass loss steps, this suggests that the cation exchanger is (at least) in the bi-ionic form. An additional information about the nitrogen content is then needed to specify all the ionic forms present in the cation exchanger sample.

Conclusions

1. The presented procedure for the qualitative speciation of sulfonic groups is applicable to gel-type and to macroporous-type sulfonic cation exchangers as well.

2. The quantitative speciation of the sulfonic groups may be carried out with the use of conventional standard test methods [2]. The special method, applicable particularly in the case of a fresh cation exchanger in the bi-ionic form, when one of these forms is the hydrogen form, was described earlier [3]. This method employs the principle of ion exchange and consists of two consecutive determinations of the hydrogen form content for the same analytical sample: the first determination covers the original sample, and then the sample completely con-

verted into the hydrogen form is analysed. The difference between the results obtained describes the total content of the form(s) other than the hydrogen one.

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