

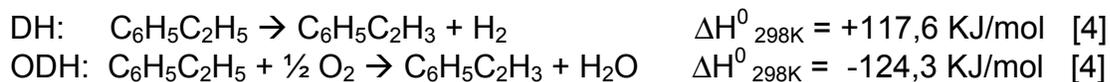
# RELEVANCE OF THE SURFACE OXYGEN GROUPS ON THE PRODUCTION OF STYRENE OVER ACTIVATED CARBON FIBRES

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## Introduction

Styrene is one of the most important raw materials in the petrochemical industry. It is widely used to prepare commercially important polymers such as polystyrene, SBR, ABS resins and polyesters. For this reason, styrene production is subject of great interest and studies [1-3]. This compound is mainly obtained by dehydrogenation (DH) of ethylbenzene over potassium-promoted iron oxides. The oxidative dehydrogenation (ODH) procedure has two important advantages. Thus the dehydrogenation is an endothermic process, whereas the oxidative dehydrogenation is exothermic, consequently, lower temperature is needed since the hydrogen oxidation generates the necessary energy for the endothermic dehydrogenation; additionally, the hydrogen is removed from the reaction and the styrene yield increases.



In one of the first papers published about oxidative dehydrogenation [5], the authors used an industrial alumina as catalyst. Nevertheless, carbon materials are the most used in the oxidative dehydrogenation due to their good catalytic activity and low reaction temperature (300-350°C) [6-13].

A large variety of carbon forms have been studied in the literature for this purpose, including activated carbons [6-13], graphites [10,14], carbon blacks [14,15], activated carbon fibres [16,17], carbon nanofilaments [14], nanotubes [18] and onion like carbons [19]. When carbon materials are used for the oxidative dehydrogenation, the porosity of the carbon is a parameter which has influence on the catalytic activity [7] but it has been speculated that oxygen functional groups of the carbonyl and quinone type, are the active phase [11,20,21]. In order to improve the catalytic activity, it is crucial, for a given porosity, to prove that the surface oxygen groups are the active phase. In the present work, the surface chemistry and porosity of different treated activated carbon fibres (ACF) samples were analyzed and used to interpret the ethylbenzene conversion and styrene production.

## Experimental

### - Samples studied.

A commercial activated carbon fibre (ACF) from coal tar pitch was used (A20, Osaka Gas). The commercial sample was heat treated in oxidizing and inert atmospheres. Nitric acid (69%), hydrogen peroxide (33%) and 20% of O<sub>2</sub> in helium at 400°C, were employed as oxidizing agents and helium has been used as inert atmosphere at different temperatures (620, 900, 1200°C). The nomenclature of the samples used in the present work is described in Table 1. It must be noted that the sample A20 will be named as A in this work.

Table 1. Treated samples.

| Sample   | Treatment                                      |
|----------|--|
| A        | None   |
| AHN69    | HNO <sub>3</sub> (69%), 25°C, 13h              |
| AHP33    | H <sub>2</sub> O <sub>2</sub> (33%), 25°C, 48h |
| A400C19h | 20% O <sub>2</sub> in He, 400°C, 10°C/min, 19h |
| A620C0h  | He, 620°C, 20°C/min, 0h                        |
| A900C0h  | He, 900°C, 20°C/min, 0h                        |
| A1200C0h | He, 1200°C, 5°C/min, 0h                        |

### - Characterisation of porosity.

The characterisation of the porosity of the activated materials was done using physical adsorption of N<sub>2</sub> at -196°C (Quantachrome, Autosorb-6B). The samples were outgassed at 250°C under vacuum for 4 hours. Nitrogen adsorption results were used to determine BET surface area values and DRN<sub>2</sub> micropore volumes (i.e., Dubinin-Radushkevich micropore values).

### - TPD experiments.

The temperature programmed desorption experiments were carried out in a quadrupole mass spectrometer GSD300T3, Thermo Star (Balzers) coupled to a SDT 2960 Simultaneous DSC-TGA (TA instruments). The amount of sample used was around 20 mg and the total flow of helium was 100ml/min. Heating rate and final temperature were 20°C/min and 950°C respectively.

### - Oxidative dehydrogenation of ethylbenzene.

The experiments were carried out in a quadrupole mass spectrometer MSC 200, MS-Cube (Balzers), coupled to a BTRS-Jr reactor (Autoclave Engineers). The amount of sample used was around 100mg. The composition of the carrier gas was 20% O<sub>2</sub> and 80% He and the total flow was 40ml/min. The carrier gas passes through a saturator with liquid ethylbenzene; in this way 1.2 % (v/v) of vapour ethylbenzene is obtained. The chosen temperature to carry out the reaction was 350°C.

## Results and Discussion

- Characterisation of porosity.

The nitrogen isotherms (Figure 1) indicate that the samples are essentially microporous (i.e. isotherms of type I). Samples A, AHN69, AHP33 and A1200C0h have a wide micropore size distribution as the wide knee in the nitrogen isotherm indicates. The treatment at 1200°C increases the porosity (Table 2), whereas the treatment with HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> reduces slightly the porosity to the same extent in both cases (Table 2). Finally, the oxidation with O<sub>2</sub> reduces significantly the porosity due to ACF burning and oxygen chemisorption at 400°C.

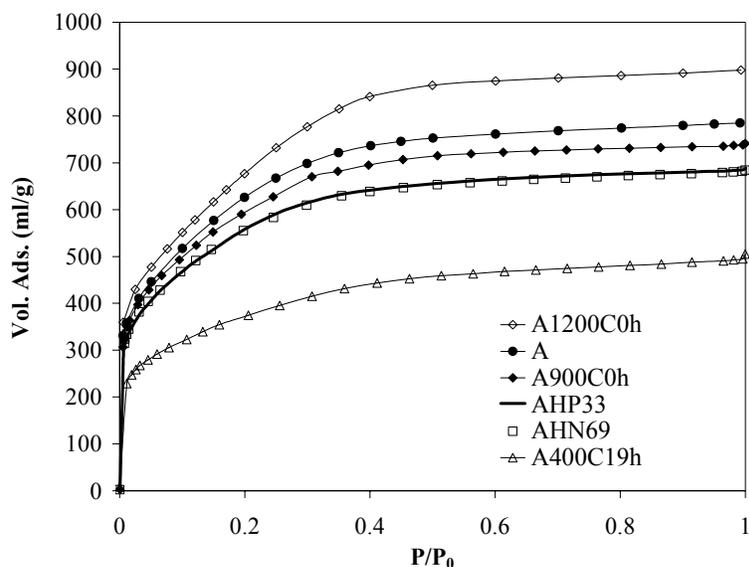


Figure 1. Nitrogen isotherms of the treated samples

Table 2. Porosity of the samples.

| Sample   | B.E.T. Surface<br>(m <sup>2</sup> /g) | Vol. D.R.<br>N <sub>2</sub> (cm <sup>3</sup> /g) |
|----------|---------------------------------------|--|
| A        | 2272                                  | 0.78   |
| AHN69    | 2024                                  | 0.74   |
| AHP33    | 2031                                  | 0.72   |
| A400C19h | 1351                                  | 0.52   |
| A900C0h  | 2168                                  | 0.78   |
| A1200C0h | 2615                                  | 0.87   |

- TPD experiments.

Figure 2 shows the TPD profiles for the different samples and Table 3 summarizes the TPD quantification. Sample treated in O<sub>2</sub> (20%) exhibits the highest content of surface oxygen groups, most of which decompose at temperatures higher than 400°C, and being most of them of CO type. ACF treated at 900°C and 1200°C show small desorption in the temperature range studied. AHN69, AHP33 and A400C19h have a similar content of oxygen groups desorbed as CO<sub>2</sub> (Table 3). Finally, sample AHN69 presents a desorption for m/e=30 (Figure 3), related to nitro groups (NO<sub>2</sub>) decomposition formed by HNO<sub>3</sub> treatment [22,23].

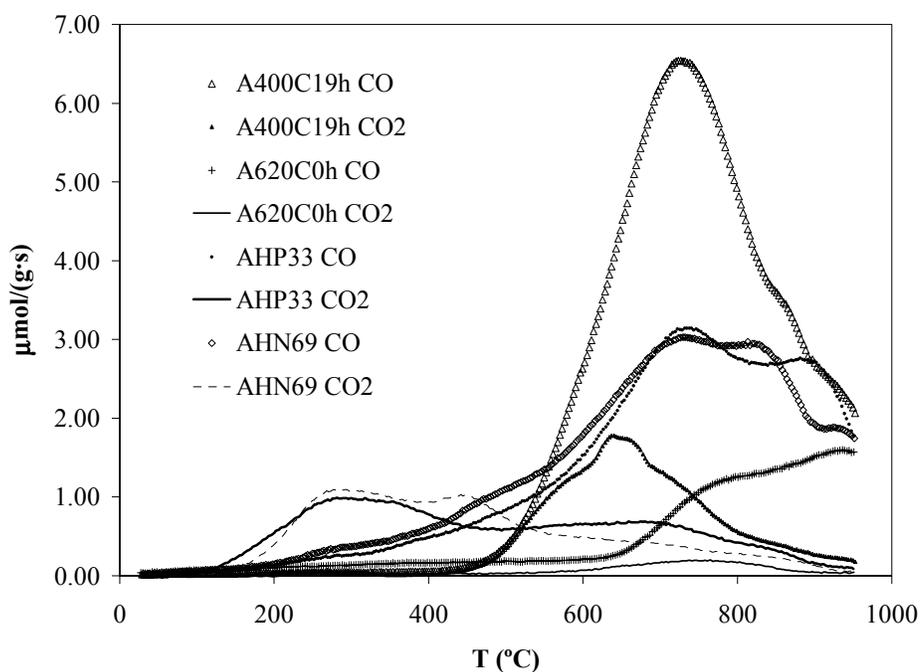


Figure 2. TPD profiles.

Table 3. TPD quantification of the treated samples.

| Sample   | CO (μmol/g) | CO <sub>2</sub> (μmol/g) |
|----------|-------------|--------------------------|
| A        | 1337        | 363                      |
| AHN69    | 3625        | 1373                     |
| AHP33    | 3496        | 1467                     |
| A400C19h | 5151        | 1255                     |
| A620C0h  | 1303        | 166                      |
| A900C0h  | 392         | 127                      |
| A1200C0h | 38          | 347                      |

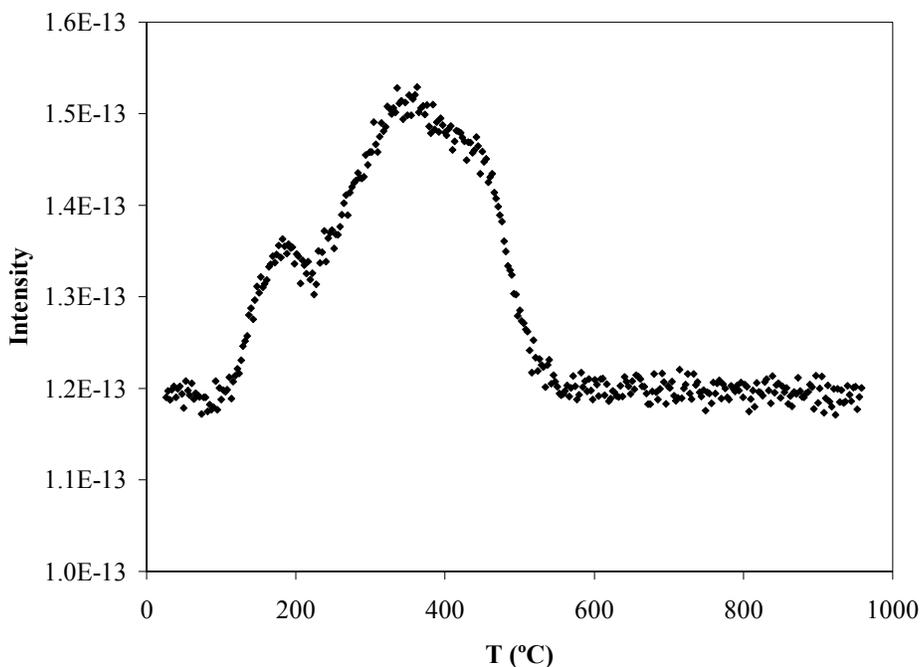


Figure 3. TPD of the sample A20HN69, desorption of the  $m/e=30$ .

In summary, the samples available have, essentially important differences in surface chemistry and porosity, what makes them useful to study the effect of these parameters on ODH of ethylbenzene.

- Oxidative dehydrogenation of ethylbenzene reaction.

During the oxidative dehydrogenation of ethylbenzene catalyzed by carbon, a continuous Polymer Organic Deposit (POD) takes place [24]. There is an important initial deactivation of the catalysts due to the carbonaceous deposit which partially blocks the porosity. This continuous deposit reduces the porosity of the sample and the active sites accessible to ethylbenzene. Moreover, this POD is known to be also active and its presence increases the catalytic activity of some catalysts, for instance  $Al_2O_3$  [4,20]. Since its formation is time dependent, a steady state is never reached.

In Figures 4 and 5, the ethylbenzene conversion and styrene production are respectively shown. Table 3 contains some data deduced from these experiments. The treated samples AHN69, AHP33 and A400C19h have the highest conversion of ethylbenzene and styrene production. This behaviour is due to a high content of surface groups (especially of CO type) which are present at the former samples and also due to nitrogen-containing groups in the sample AHN69. In spite of the fact that sample A400C19h has lower porosity than sample A, its activity per surface area unit is the highest (1.27 versus 0.68 nmol Styrene/( $m^2 \cdot s$ ) for sample A) what has to be related to

the highest content of surface groups of CO type. This fact, demonstrates the strong influence that surface chemistry has on the catalytic activity. AHN69 and AHP33 have similar porosities, CO<sub>2</sub> and CO groups (Figure 2 and Table 3); in spite of this, the activity for sample AHN69 is higher, what suggests that the presence of nitrogen-containing groups increases the styrene production (Table 4). NO<sub>2</sub> groups remain on the sample until 500°C (Figure 3), therefore during reaction at 350°C some of these groups are still present on the sample. It must be pointed out the high activity showed by AHN69, which is even higher than that reported for treated activated carbons [11]. Samples with low amount of surface groups (A900C0h and A1200C0h) have a poor catalytic activity. Consequently, there exists a relationship between the surface chemistry and the activity of the ACF. Figures 6 and 7 plot, respectively, the ethylbenzene conversion per surface area unit and the styrene production per surface area unit versus the CO-type groups. The figures show that there are clear correlations between these parameters.

When the contact time is decreased by increasing the flow (Sample A 100ml/min), the conversion decreases considerably but the selectivity towards styrene increases. The increase in the styrene production can be associated with a higher flow, in spite of the lower conversion of ethylbenzene. The decrease in the conversion is related to a lower oxidation of the ethylbenzene to CO and CO<sub>2</sub>, which is higher for longer contact times (i.e. low flows).

In all the cases, the styrene selectivity (considering only benzene and toluene as secondary products) was between 73% (A1200C0h) and 84% (A 100ml/min).

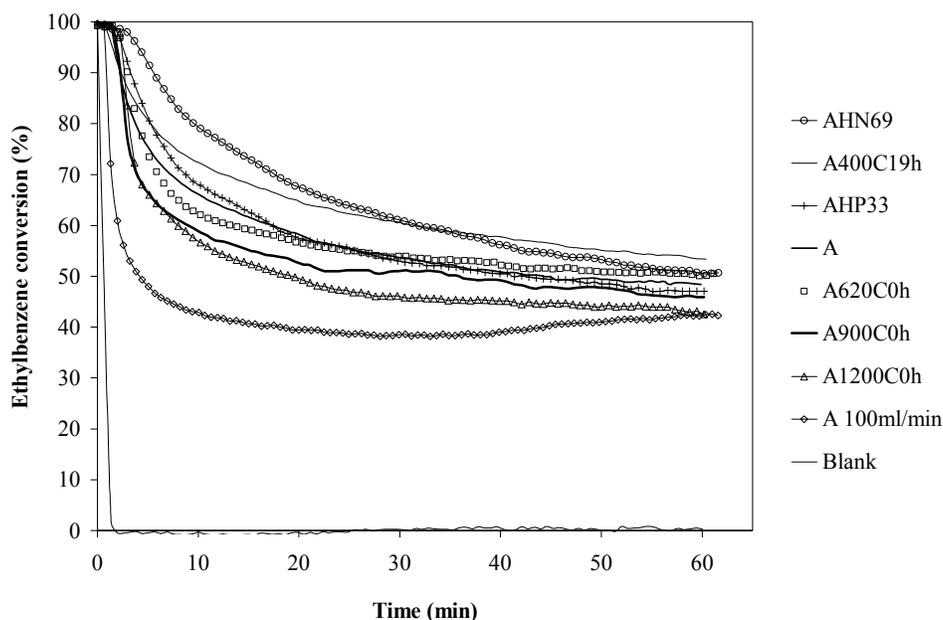


Figure 4. Ethylbenzene conversion.

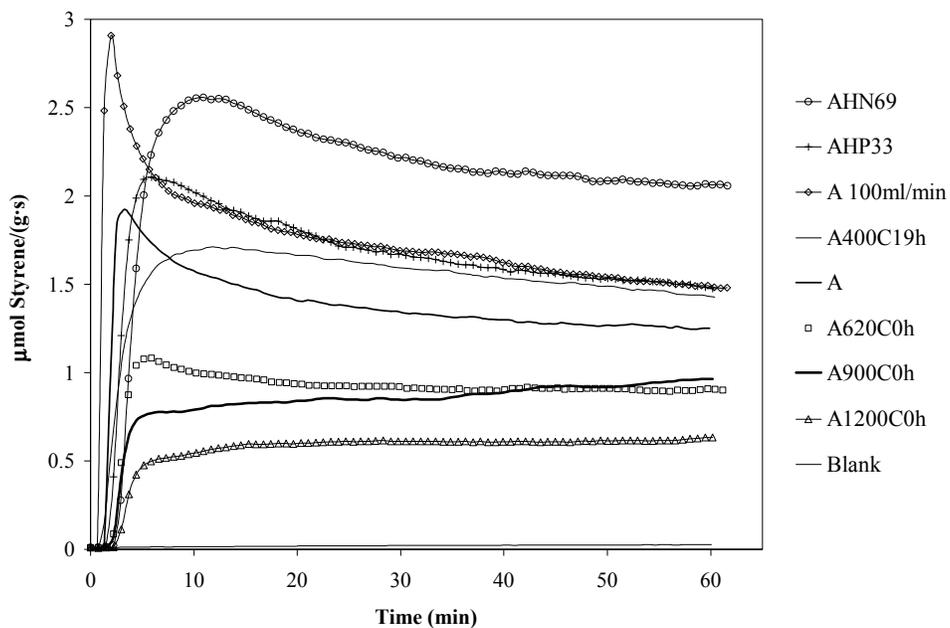


Figure 5. Styrene production.

Table 4. Ethylbenzene conversion and styrene production for 10 and 60 min.

| Sample      | Ethylbenzene conversion (%)<br>10 min | Ethylbenzene conversion (%)<br>60 min | Styrene prod. ( $\mu\text{mol}/(\text{g}\cdot\text{s})$ )<br>10min | Styrene prod. ( $\mu\text{mol}/(\text{g}\cdot\text{s})$ )<br>60min |
|-------------|---------------------------------------|---------------------------------------|--|--|
| A           | 66.16                                 | 48.37                                 | 1.58   | 1.25   |
| AHN69       | 79.02                                 | 50.52                                 | 2.55   | 2.06   |
| AHP33       | 67.85                                 | 47.08                                 | 2.02   | 1.48   |
| A400C19h    | 72.39                                 | 53.32                                 | 1.69   | 1.43   |
| A620C0h     | 62.10                                 | 50.08                                 | 1.00   | 0.91   |
| A900C0h     | 58.62                                 | 45.93                                 | 0.79   | 0.96   |
| A1200C0h    | 56.63                                 | 42.50                                 | 0.55   | 0.63   |
| A 100ml/min | 42.85                                 | 42.46                                 | 1.96   | 1.48   |

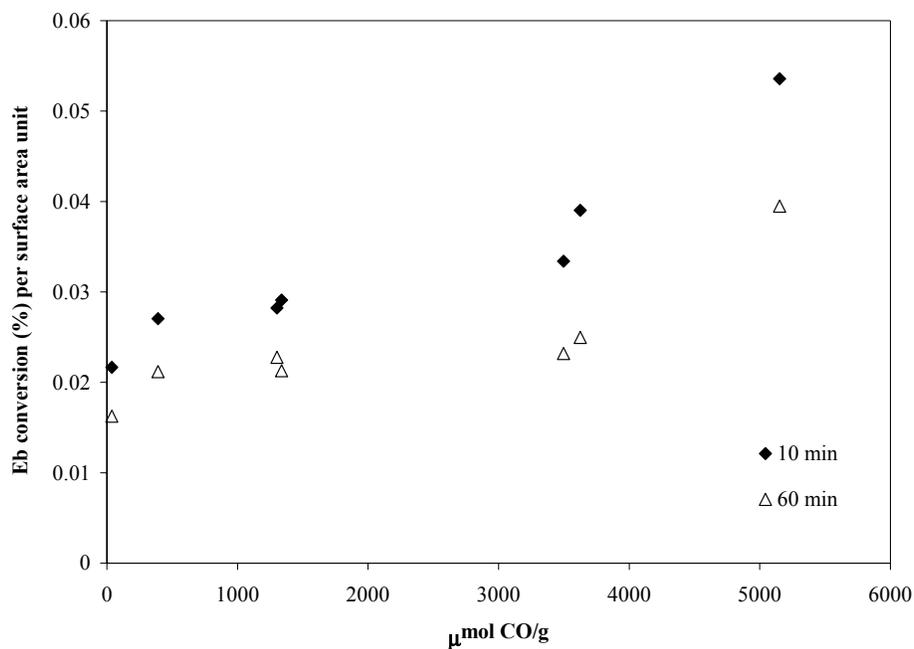


Figure 6. Correlation between ethylbenzene conversion (per surface area unit) at 10 and 60 min and surface groups of CO type.

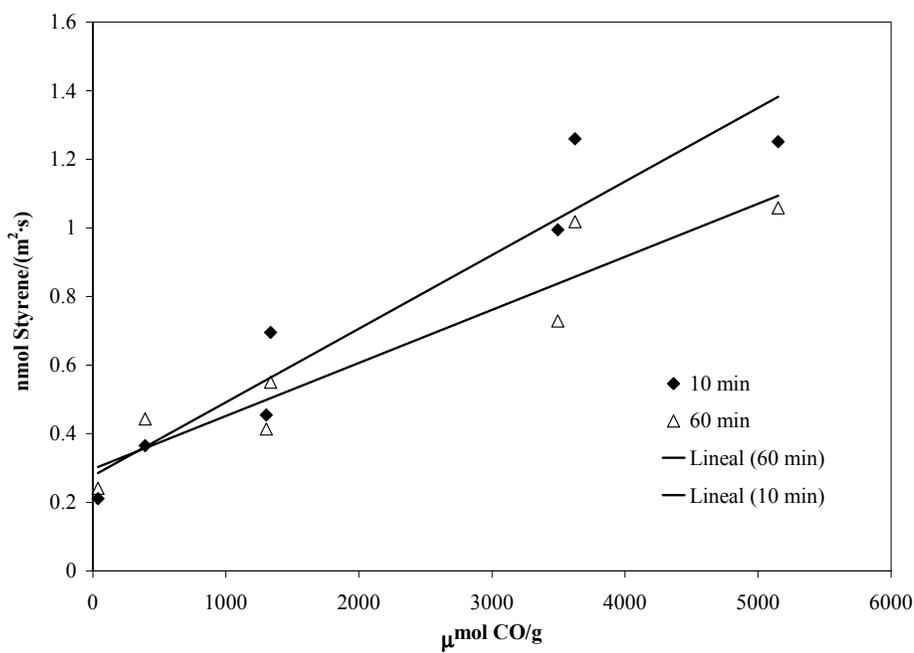


Figure 7. Correlation between styrene production (per surface area unit) at 10 and 60 min and surface groups of CO type.

## Conclusions

Samples with high content of oxygen functional groups, specifically of CO type, show higher ethylbenzene conversion and styrene production than samples containing low amount of those groups. Sample treated in O<sub>2</sub> exhibits the highest styrene production per unit of surface area because it has the highest content of oxygen functional groups. Moreover, the sample oxidized with nitric acid presents the highest styrene production per gram of sample, compared to other samples with similar porosity and oxygen functional groups, what indicates that, nitrogen-containing chemical groups are also involved in the reaction. Although both porosity and surface chemistry of the ACF determine the catalytic activity of the sample, surface chemistry has a much stronger influence than porosity.

## Acknowledgements

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