

## **THERMOSTABLE SULPHOCATIONITES - CATALYSTS OF PETROCHEMICAL PROCESSES**

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The results of tests on new thermostable sulphopolymer-based and aluminosilicate carrier-supported sulphocationites with conjugated bond systems, prepared in The Crude Oil and Gas Institute in Moscow, are presented. Their operating temperature is 280-350°C and they exhibit high catalytic activity in various petrochemical processes.

Specific properties of polymers with conjugated bond, e.g. their paramagnetism (an unpaired electron concentration of  $10^{18}$ - $10^{20}$  spin/g), photoconductivity ( $10^2$ - $10^{-11}$  cm<sup>-1</sup>ohm<sup>-1</sup>), high thermal resistance (600-700°) and mechanical strength, have led to their wide use in the production of thermostable plastics, organic semiconductors, elastic electrodes, etc. [1].

Particular interest is attached to the catalytic activity of polymers with conjugated bonds, and the possibilities of modifying them by the introduction of groups or elements with donor-acceptor character [2]. Thus, polyphenylketone, produced by the thermal polymerization of phthalic anhydride [3], is an active catalyst for the dehydrogenation of alcohols and the hydrogenation of acetaldehyde. Both reactions were carried out in a continuous flow reactor over a stationary catalyst bed at temperatures of 350 and 330°.

Studies on the mechanism of dehydrogenation of deuterium labelled ethanol showed that, as in the case of inorganic catalysts, the limiting stage of alcohol dehydrogenation is the removal of a hydrogen in the alpha position.

Introduction of the sulphone group into the polyphenylketone matrix [4] allowed the production of a thermostable sulphocationite (> 280°) with a static exchange capacity of 2.95 mg-equiv/g. The presence of conjugated bonds in the sulphocationite chain was confirmed by the IR spectra, with

bands at  $1610\text{ cm}^{-1}$ , and by the concentration of unpaired electrons  $(1.24\text{-}6.43) \cdot 10^{18}\text{ spin/g}$ .

The thermostability and catalytic activity of sulphopolyphenylketone (SPF) were confirmed in the esterification of methacrylic acid with methanol [5] and butanol [6], where the catalyst was used at  $100\text{-}160^\circ$  during one year without loss in activity and with 100% selectivity.

SPF also exhibited high catalytic activity and thermal stability in the alkylation of benzene with propylene [7]: the temperature was  $160^\circ$ , the pressure was 30 MPa, the benzene:propylene ratio was 1:1, and the productivity of the catalyst was  $4038\text{ kg of isopropylbenzene/m}^3$  of catalyst per hour. During a 500 h run under optimal conditions ( $148\text{-}160^\circ$ , 20-30 MPa), no changes in catalytic activity of SPF were observed. The conversion of propylene was 94-99%.

The small particle size of the cationite (0.25-05 mm) and its not appropriately high mechanical strength did not allow the wide application of SPF in high-capacity continuous reactors.

In order to attain a catalyst satisfying the requirements of the petrochemical industry, the polymer was applied as a coating on a porous, inorganic support with subsequent sulphonization [8]. The resulting sulphocationite has the mechanical resistance (stability) of the support and a particle size depending on the support particle size distribution.

The sulphocationite on the inorganic support has a high specific area ( $217\text{-}321\text{ m}^2/\text{g}$ ). The particle size is (2-8 mm) [9]. The exchange capacity (0.16-0.22 mg-equiv/g) depends on the support coating procedure and the degree of polymer sulphonation. The thermostability, as indicated by the maximum operating temperature, is  $280\text{-}350^\circ$ . The high activity of aluminosilicate-supported sulphocationite in the alkylation of isobutylene with methanol [9] is probably determined by the high total acidity (0.423 mmol/kg, determined by the thermal desorption of ammonia), the large surface area and the high concentration of unpaired electrons: at  $90^\circ$ , in the liquid phase, with a small surplus of methanol it is possible to separate isobutylene from the C<sub>4</sub> fraction with 100% conversion and high selectivity.

Polisorb SI sulphocationite, with a specific surface area of  $321.9\text{ m}^2/\text{g}$ , and pore radii of  $17.7\text{-}110.0\text{ \AA}$  (93%) and  $110.4\text{-}8080.4\text{ \AA}$  (7%), displayed a high catalytic activity in the oligomerization of isobutylene.

The particle size of the tested catalyst was  $3\text{-}5 \cdot 10^{-3}\text{ m}$ , its press crushing strength was 50-70-130 N/m<sup>2</sup>, its free fall density was  $568.3\text{ kg/m}^3$ , the operating temperature was  $280^\circ$  and the maximum static exchange capacity was 0.22 mg-equiv/g.

Isobutylene oligomerization was carried out in a continuous reactor over a stationary catalyst bed, in both the liquid and gas phases, on the C<sub>4</sub> fraction with various contents of isobutylene (between 89.04% and 2%).

The catalyst was found to be active in the oligomerization of isobutylene at a temperature as low as 20°, where the conversion of isobutylene was 12.2%. Increase of the temperature to 150° enhanced the conversion 7-fold while preserving the high ratio of dimers to trimers at 41.2:1. Doubling the feeding rate led to the exclusive production of isooctenes.

At 200°, a 15-20% decline in the isobutylene conversion and an increase in the content of dimers in the product were observed.

Recovery of isobutylene from the C<sub>4</sub> fraction in the gas phase was carried out over 100 g of the cationite in a metallic reactor. The temperature varied from 20 to 110°, and the feeding rate (mass) from 0.5 h<sup>-1</sup> to 3 h<sup>-1</sup>. 100% isobutylene conversion for the FCC isobutylene fraction was reached at 90°. During a 588.6 h run, the activity of Polisorb remained constant, but its selectivity for dimer production after 360 hours of operation had increased by 20%.

The process was optimized after the experimental data processing and handling. Figure 1 shows the optimal region for isobutylene conversion versus the process temperature and the content of isobutylene in the C<sub>4</sub> fraction.

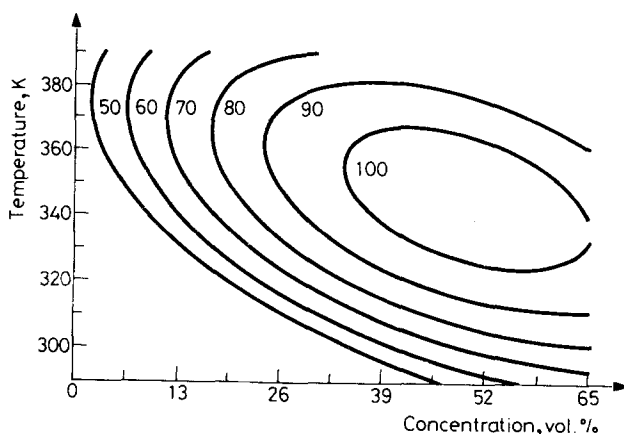


Fig. 1 Dependence of isobutylene conversion on process temperature and isobutylene concentration at constant mass velocity, h<sup>-1</sup>

The oligomerizate produced has a high octane number (104), and satisfies the spec values (except for the induction period) for gasoline. After the oligomerization process, the polisorb SI catalyst has a higher free fall density ( $666.3 \text{ kg/m}^3$ ), and a decreased total exchange capacity (from 2.44 to 1.68 mg-equiv/g), with the static exchange capacity and thermostability preserved at the initial levels.

The presented data confirm that during operation for 600 hours at  $90^\circ$ , sulphocationite was not subject to desulphonation in the reaction environment.

The presence of Fe ions in the  $C_4$  raffinate fraction (residual) after MTBE production had no effect on the sulphone group activity. Another interesting finding was that the nonsulphonated polymer coating on the aluminosilicate support is also active in the oligomerization of isobutylene, the conversion reaching 70%.

## Conclusion

1. The thermostable polymer polyphenylketone, which is catalytically active in the dehydrogenation of alcohols, the hydrogenation of acetaldehyde, and the alkylation and oligomerization of isobutylene, is a suitable matrix for the introduction of sulphone groups. This permits the production of thermostable sulphocationite at a temperature above  $150^\circ$  with a catalytic activity comparable with that of sulphuric acid, active in various processes of acidic catalysis.

2. Polisorb catalyst, sulphopolyphenylketone on an aluminosilicate support, has several advantages over industrial sulphocationites, the most important being its high thermal resistance and mechanical strength, large particle size, low swelling (8-15% vol), and high catalytic activity. The presence of the conjugated bond system in the polymer chain is probably the factor responsible for these properties, inhibition of the removal of sulphone groups by the delocalized  $\pi$ -electron system and by the local activation of reagents ensuring the high catalytic activity.

## References

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**Zusammenfassung** — Es wird über die Untersuchungsergebnisse von neuen hitzebeständigen Sulphokationiten mit konjugierten Bindungssystemen auf Sulphopolymerbasis und auf Aluminiumsilikat-Trägermaterial berichtet, die im Moskauer Institut für Rohöl und Erdgas hergestellt wurden. Wie festgestellt, weisen sie in verschiedenen petrochemischen Prozessen eine hochkatalytische Wirkung auf, ihre Funktionstemperatur liegt bei 280-350C.