CATALYTIC BEHAVIOUR OF Mo-BASED CATALYSTS IN LIQUID PHASE EPOXIDATION OF PROPYLENE BY HYDROPEROXIDES

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The activity of different Mo-based catalysts in propylene epoxidation by t-BuO₂H was investigated. MoO₂(C₁₃H₁₀O₂N)₂ and MoO₂(oxine)₂ gave quantitative yields in propylene oxide; other compounds were inactive and MoO₂(acac)₂ was less active and selective.

The different catalytic behaviour of these catalysts is attributed to the different strength of Mo-ligand bonds.

INTRODUCTION

The oxidation of propylene by hydroperoxides is an attractive method of obtaining propylene oxide from both technological and economic points of view.

Several molybdenum compounds have been patented as active catalysts in the epoxidation of olefins by hydroperoxides /1/.

The aim of the present work was (a) to carry out a preliminary investigation on some Mo-based catalysts in the epoxidation of propylene by t-BuO₂H, and (b) to point out the role of the ligand in determining the catalytic behaviour of molybdenum in epoxidation reactions.

EXPERIMENTAL

A - Preparation of the catalysts

The catalysts investigated were:

MoO₂(oxine)₂ /2/, MoO₂(C₁₃H₁₀O₂N)₂ /3/, MoO₂(acac)₂ /4/, MoO₂(dien) /5/, and Na₄(Mo₂O₈(EDTA)). 8H₂O /6/.
They were prepared according to reported procedures, calcined at 200°C for 2 hrs and characterized by X-ray and IR analyses.

B - Reagents

- propylene: 99.99% by volume
- t-BuO₂H: Schuchardt Reagent (79.5% by volume)
- n-heptane: Carlo Erba RPE Reagent

C - Activity Measurements

Propylene was oxidized in the liquid phase with t-BuO₂H using n-heptane as solvent, according to the following scheme:

\[
\text{CH}_2=\text{CH}-\text{CH}_3 + \text{t-BuO}_2\text{H} \xrightarrow{\text{cat}} \text{CH}_2=\text{CH}-\text{CH}_3 + \text{t-BuOH}
\]

The activity runs were carried out in a stainless steel reactor of the complete mixing batch type, equipped with a magnetic stirrer and a heat exchange apparatus in order to provide temperature control.

The amounts of reagents employed were: n-heptane, 50 ml; t-BuO₂H, ranging from 1 to 2 ml; propylene, ranging from 14 to 25 g; the amount of the catalyst used was within the range of 1x10⁻² - 2x10⁻² g.at. of Mo per mol of hydroperoxide.

The activity runs were carried out according to the following procedure.

The catalyst – n-heptane – t-BuO₂H mixture is stirred at 80°C for 1 hour and then charged into the reactor. Thereafter, air from the reactor is pumped off, while the reactor is kept in an acetone-dry ice bath at -70°C in order to avoid losses from the liquid reaction mixture.

Propylene is then added (t=0 in Table 1) and the reaction temperature is brought to the desired level (ranging from 80°C to 95°C). The reaction is carried out under pressure and the amount of propylene charged has to be such as to ensure the presence of liquid propylene under the experimental conditions.

After completion of the reaction the reactor is placed into an acetone-dry ice bath with a temperature of -60°C; thereafter, the product mixture is withdrawn into a glass tube equipped with a magnetic stirrer and rubber stoppers for drawing samples for gas-chromatographic analyses.

Propylene is flushed with N₂ as carrier gas (waste current), while two acetone-dry ice traps, at t = -30°C and t = -50°C, respectively, prevent the loss of