

# PARTIAL OXIDATION OF AROMATIC COMPOUNDS WITH NITROUS OXIDE UNDER SUPERCRITICAL CONDITIONS

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## Introduction

One of the modern approaches in the catalysis is based on running the catalytic reactions under supercritical conditions. Performing the processes in the supercritical fluids provides considerable advantages in comparison with the traditional techniques of carrying out the processes in liquid or gaseous phases. The supercritical fluids possess the higher density, dissolving capacity and heat conductivity compared with gases, and they are marked by a higher diffusion rate of dissolved substances compared with the liquid state. Therefore supercritical fluids combine the advantages of both liquid and gas states: higher concentrations of reactants in a unit volume, excellent heat and mass transfer, high extent of miscibility of substances, which beneficially influences the heterogeneous catalytic processes.

These advantages allow one to enhance the efficiency and ecological safety of catalytic processes. Furthermore, supercritical media significantly influence both the activity and selectivity of the processes as well as the kinetics of deactivation processes. Under conventional conditions of hydrocarbon conversion (vapor, liquid), the catalysts tend to be deactivated by the condensation and tar products. Usually the regeneration of catalysts requires a periodical high-temperature oxidative or reductive treatment.

Running the catalytic reaction in a supercritical medium helps to remove the heavy products from the catalyst surface due to dissolution and leaching of these side products by the supercritical fluid, which thereby results in the increase of the catalyst lifetime. One more advantage of the catalytic reactions in supercritical fluids is the possibility to increase (10-30 times) the space-time yield by increasing the space velocity.

For instance, the process of benzene oxidation into corresponding phenols is the unique alternative for the outdated methods of phenols production. Modern phenol production capacities reach 6 million tons per year. The main method of phenol production is the cumene-based technology which accounts for about 90% of the world phenol market. The bottleneck of the cumene process is the problem of acetone overproduction, which does not find an adequate demand. Excellent results were obtained when ZSM-5 zeolites are used as catalysts in the direct oxidation (hydroxylation of benzene with  $N_2O$ ). The gas-phase oxidation of benzene in excess of  $N_2O$  at 380-420°C in the presence of the high-silica zeolites leads to the phenol selectivity of 90%. However the gas-phase oxidation of benzene in high-temperature conditions is accompanied by the formation of tars and coke leading to deactivation of the zeolite catalyst. Therefore new efficient methods of performing such conversion allowing one to increase the

catalyst life time before deactivation is of great importance. The direct oxidation of benzene into phenol under supercritical conditions would probably solve the problems.

## Experimental

Partial benzene oxidation was carried out in a U-shape flow reactor in the temperature range from 350 to 425 °C and the pressure range of 60–180 atm. The high-silica zeolite HZSM-5 was used as catalyst.

## Results

Figure 1 shows the curves for the catalytic oxidation of benzene to phenol by  $N_2O$  in supercritical conditions. The reaction is characterized by the selectivity to phenol over 95%. Using high pressures, we can reach high degrees of conversion and higher stability as compared to the reaction in the gas phase. This figure shows that under supercritical conditions, the catalysts preserve their activity at the constant level compared with the gas phase process when the catalyst works only for half an hour.

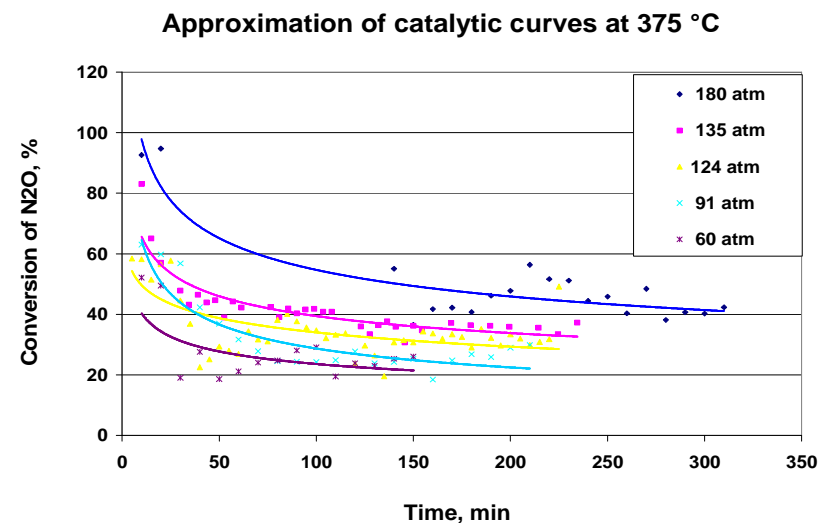


Figure 1. Partial benzene oxidation on HZSM5 catalyst under supercritical conditions.

## References

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