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Oxidation of toluene with N_2O on ZSM-5 zeolite under supercritical conditions

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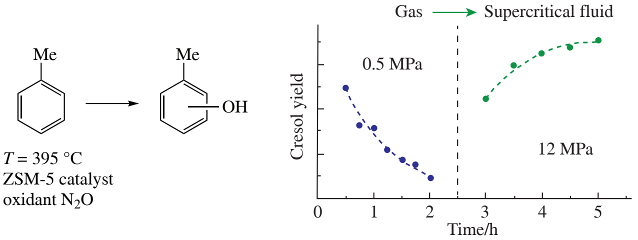
The direct oxidation of toluene to cresols with nitrous oxide as the oxidant was carried out over a ZSM-5 zeolite catalyst under gaseous and supercritical conditions (395 °C and 0.5, 7, 12 MPa; 420 °C and 15 MPa). The supercritical oxidation is characterized by a significantly greater productivity as compared to the gas-phase process. Successful *in situ* regeneration of the deactivated catalyst during the transition from the gas-phase to the supercritical process has been demonstrated.



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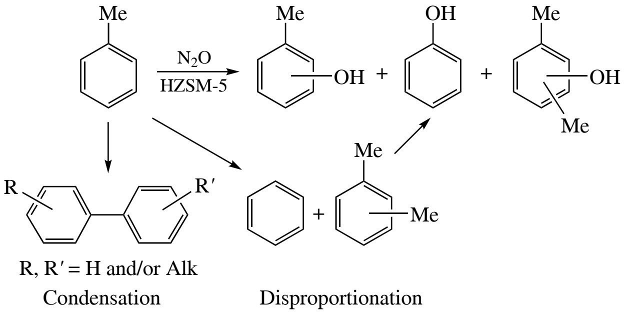
Aromatics contribute a significant fraction to organic compounds in the troposphere and are mainly emitted by anthropogenic activities and biomass burning. Emissions of aromatics are primarily anthropogenic, related to fuel combustion and leakage from fuels and solvents. Toluene emission into the atmosphere is 5.89 Tg (on carbon) per year, of which 82% is attributed to anthropogenic factors.[1] Several solutions are proposed to mitigate this pollutant. Toluene can be oxidized to benzaldehyde[2–6] or to cresols,[7–11] and then to CO_2 and H_2O.[4,6,11] Cresols are of interest as organic solvents and as precursors in organic synthesis. The following methods are used to obtain cresols from toluene: photooxidation,[7] electrooxidation[8] in H_2–O_2 fuel cell, and catalytic oxidation with hydrogen peroxide[9] or nitrous oxide[10] as oxidants. The microbiological oxidation of toluene to cresol has also been the subject of research.[12,13] There have also been theoretical studies[14–16] of the oxidation pathways of toluene.

Direct oxidation of aromatic compounds to phenols with nitrous oxide in the presence of ZSM-5 zeolite[10,11,17–23] has a significant shortcoming that this process involves severe deactivation of the catalyst by the condensation products.[17,20,22,23] A possible solution to this problem is carrying out the reaction under supercritical conditions, since processes in supercritical fluids largely eliminate the heat- and mass-transfer restrictions.[24,25] Furthermore, unlimited mutual miscibility of the reagents and reaction products in the supercritical state can promote dissolution and removal of the coke precursors from the surface, thus prolonging the catalyst lifetime. Advantages of carrying out organic reactions in supercritical conditions compared to gas phase reactions were shown,[26,27] in particular, for the oxidation of benzene.[28] Catalytic reactions in supercritical substrates, which are both a reagent and a supercritical medium, have been successfully carried out.[29–32] However, despite the considerable interest in the application of supercritical fluids, the number of such studies is limited.

This work is focused on juxtaposition of the direct oxidation of toluene to cresols with nitrous oxide as the oxidising agent on the ZSM-5 catalyst under a gas-phase and supercritical state of the reagents. The effect of transitions from gas-phase to supercritical conditions on the *in situ* regeneration of the ZSM-5 catalyst has been examined. The reaction pathways for the process of toluene oxidation are shown in Scheme 1.

The XRD characterisation of the parent ZSM-5 and the zeolite sample subjected to high-temperature activation (see Online Supplementary Materials, Figure S3) demonstrates that the degree of crystallinity and phase composition of the activated zeolite do not differ significantly from the original material. At the same time, the *in situ* FTIR data, obtained using pyridine as a probe molecule, reveal that the concentration of the Brønsted acid sites considerably decreases and the concentration of the Lewis acid sites increases following the high-temperature treatment (Figures S4 and S5).

In the direct catalytic oxidation of toluene using N_2O (395 °C, activated ZSM-5) under traditional gas-phase conditions the catalyst productivity for cresols drops notably (see Online Supplementary Materials, Table S2), probably following the



Scheme 1

Table 1 Experimental data for the partial oxidation of toluene with N_2O on ZSM-5 zeolite under supercritical conditions.

T/°C	P/MPa	Toluene conversion (%)	N_2O conversion (%)	Cresol productivity/ g g_{cat}^{-1} h^{-1}	Selectivity (%)				
					Cresols	Phenol	Disproportionation products	Condensation products	Complete oxidation
395	7	10	7	0.33	32	2	47	18	1
395	12	14	11	0.36	25	5	44	24	2
420	15	22	92	0.12	5	3	64	16	12

formation of condensation products blocking the zeolite pores and the external surface. In order to enhance both the activity and stability of the catalyst, the oxidation has been carried out under supercritical conditions. The pseudo-critical parameters of the reagent mixture are 178 °C and 4.9 MPa (the calculation is given in Online Supplementary Materials).

The results obtained for the partial oxidation of toluene with nitrous oxide on ZSM-5 zeolite (Table 1) demonstrate that at moderate temperature and pressure (395 °C and 7 MPa), the selectivity to cresols is 32%, and there also occurs the formation of by-products such as benzene, xylenes, biphenyl and polyphenyls, resulting from condensation and disproportionation reactions. Some of these species give rise to the coke precursors, which are difficult to remove under the conventional gas-phase reaction conditions. At higher temperature and pressure (420 °C and 15 MPa), while the N_2O conversion rises sharply to over 90%, the selectivity to cresols falls as side reactions and complete oxidation to CO_2 dominate. Hence, the reaction temperatures should not be higher than 400 °C.

In agreement with the previous reports,[11,28] our data confirm that direct catalytic oxidation of toluene on dehydroxylated high-silica ZSM-5 zeolites can be performed both under the gas-phase and supercritical conditions. However, under the more common gas-phase reaction conditions, a considerable deactivation of the catalyst occurs within 2 h with the cresols productivity falling by over 80%, from ~0.30 g g_{cat}^{-1} h^{-1} to 0.05 g g_{cat}^{-1} h^{-1} (Figure 1). A reaction test with a changeover from the gas-phase to supercritical conditions has been carried out, whereby the transition to supercritical conditions occurs as the pressure is increased from 0.5 to 12.0 MPa (see Figure 1).

The data obtained show that as the reaction pressure increases from 0.5 to 12 MPa, a significant increase in the catalyst productivity is observed, reaching up to 0.43 g g_{cat}^{-1} h^{-1}, thus exceeding its initial value. The time dependence of toluene conversion (Figure S6) and full catalytic data for this experiment (Table S2) are given in Online Supplementary Materials. In other words, a catalyst that has been almost completely deactivated under the gas-phase conditions is regenerated upon transition to the supercritical region. The observation that the ZSM-5 catalyst can be ‘revitalised’ under the supercritical reaction conditions indicates that its deactivation under the gas-phase conditions is not likely to have resulted from irreversible structural degradation or the loss of active sites. We have previously shown that deactivation of the ZSM-5 catalyst in benzene oxidation with nitrous oxide in the gas phase occurs as a result of catalyst coking,[28] which has been confirmed by *ex situ* catalyst characterisation following the oxidation reaction. Additionally, a decrease in coking of the zeolite catalyst has been observed under supercritical conditions. Similar reaction conditions and the nature of the substrate (benzene *vs.* toluene) in our studies are indicative of the same reason for deactivation of the ZSM-5 catalyst during partial oxidation of aromatic compounds with nitrous oxide in the gas phase, namely, surface coking with subsequent blocking of the active sites. Whereas under supercritical conditions, the removal of coke precursors from the zeolite surface takes place, which results in a stable operation of the catalysts.

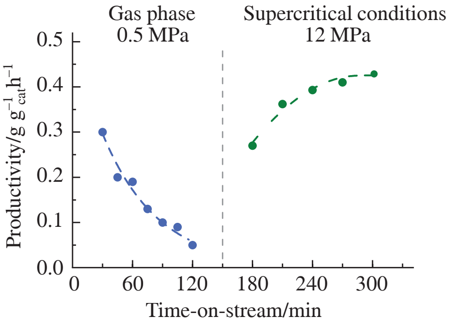


Figure 1 Comparison of productivity for cresols in a reaction test involving a changeover from the gas phase conditions to the supercritical region carried out at 395 °C.

In conclusion, the catalytic oxidation of toluene with nitrous oxide over ZSM-5 zeolite has been carried out in a continuous-flow reactor under supercritical conditions and compared with the results of the gas-phase reaction. Under the gas-phase conditions, the catalyst is almost completely deactivated within several hours of the reaction. In contrast, during the supercritical oxidation of toluene into cresols, the aromatic substrate and nitrous oxide act as both the reagents and a supercritical medium, which leads to a significantly enhanced productivity as compared to the gas-phase process owing to the limited deactivation of the zeolite catalyst under supercritical conditions. The effect is attributed to partial dissolution and removal of the condensed coke precursors from the catalyst by the supercritical reaction medium. These findings are also confirmed by the successfully carried out *in situ* regeneration of the deactivated zeolite catalyst during the transition from gas-phase reaction conditions to supercritical conditions in a single experiment.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7626.

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