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

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Experimental

Materials and chemicals. Toluene (99.9%), pyridine (Acros Organics, 99.5%), nitrous oxide (high purity grade 99.9999 vol. %), and ZSM-5 zeolite (Zeolyst, Si/Al = 15) were used as received. The original NH_4-ZSM-5 zeolite was pressed into tablets, crushed, and a fraction of 0.25–0.50 mm was selected. It was activated in a quartz reactor by heating to 500 °C in an air flow at 5 $K \cdot min^{-1}$, kept at this temperature for 4 hours and then heated at 900 °C for 5 hours. Prior to catalytic experiments, the prepared catalysts were activated in a stream of air at 700 °C for 5 hours.

Catalytic tests. Catalytic experiments were carried out in a flow-through U-shaped stainless steel reactor at a temperature of 395 and 420 °C and a pressure of 7, 12 and 15 MPa. The volume of the loaded catalyst was 2 cm^3 (about 1 g). The pressure in the system was created by supplying reagents with liquid pumps and was maintained using a back-pressure regulator. The temperature control thermocouple was located in a metal pocket in the middle of the catalyst layer. The temperature change in the reactor along the catalyst bed did not exceed 2 °C. In the calibration experiments without a catalyst with a thermocouple inside the reactor, it was found that the difference between the temperature values inside and outside the reactor did not exceed several degrees. The catalyst was heated to the reaction temperature in a flow of toluene supplied by a Knauer piston pump. N_2O was then added using high-pressure syringe pumps. The supply of reagents was 12 $cm^3 \cdot h^{-1}$ of toluene and 6 $cm^3 \cdot h^{-1}$ of N_2O (liquid). The molar ratio of toluene to nitrous oxide is given in Table S1.

Table S1. Reagent feed rates and molar ratio of toluene oxide to nitrous oxide.

Reagent	*P*, MPa	Density, $g \cdot cm^{-3}$ *	Feed rate		Toluene/N_2O molar ratio
			$ml \cdot h^{-1}$	$mol \cdot h^{-1}$	
Toluene	0.1–15 **	0.87	12	0.113	
N_2O (liquid)	7	0.78	6	0.106	1.1
N_2O (liquid)	12	0.84	6	0.115	1.0
N_2O (liquid)	15	0.87	6	0.119	1.0

* Calculated using NIST Chemistry Webbook (https://webbook.nist.gov).

** To calculate the ratio, we assume that the density of toluene is independent of pressure.

The conversion of toluene was determined from the ratio of its concentrations before (c_f) and after (c_{init}) the reaction:

$$X_{tol} = (c_{init} - c_f) / c_{init} \cdot 100\%.$$

The conversion of nitrous oxide (X_{N2O}) was determined from the ratio of the peak areas in the chromatograms after and before the conversion, and was also controlled by the amount of nitrogen formed. The selectivity (S) of the formation of reaction products was calculated for several groups: cresols (*ortho*-, *para*-, and *meta*-isomers), phenol, disproportionation products (benzene, xylenes, ethyl- and ethylmethylbenzenes), and biphenyls (biphenyl and alkylbiphenyls).

$$S_i = \sum c_i / \sum c_k \cdot 100\%,$$

$\sum c_i$ and $\sum c_k$ – the sums of the concentrations of the products of only one group (or the concentration of a single product in the case of phenol) and all reaction products, respectively. The selectivity for complete oxidation was determined from the amount of the CO_2 formed. The data presented in Table 1 correspond to the values of conversion and product selectivities at time-on-stream of 90 min. The productivity for cresols [$g \cdot g_{cat}^{-1} \cdot h^{-1}$] was calculated as cresols yield ($X_{tol} \cdot S_{cr}$), multiplied by the feed rate of toluene (V_w) and normalized to the catalyst mass (m_{cat}):

$$P = X_{tol} \cdot S_{cr} \cdot V_w^{-1} \cdot m_{cat}^{-1}.$$

The reaction test with a transition from gas-phase to supercritical conditions was conducted at 395 °C. Under the gas-phase conditions, toluene was supplied by Knauer liquid pump and gaseous N_2O was dosed by Bronkhorst mass-flow controller. The transition to supercritical conditions occurred as the pressure increased from 0.5 to 12.0 MPa.

The product analysis was carried out using gas chromatography. Gaseous products were analysed on-line during the experiments on an LCM-80 GC equipped with a Porapak Q packed column (3 m × 3 mm) and a zeolite CaA packed column (3 m × 3 mm) with a thermal conductivity detector, and a Varian GC with a flame induction detector and an OV-101 capillary column (100 m). Identification of components was carried out using a GC-MS Thermo Focus-GC-DSQ II GC-MS instrument with Thermo TR-5ms capillary column (30 m).

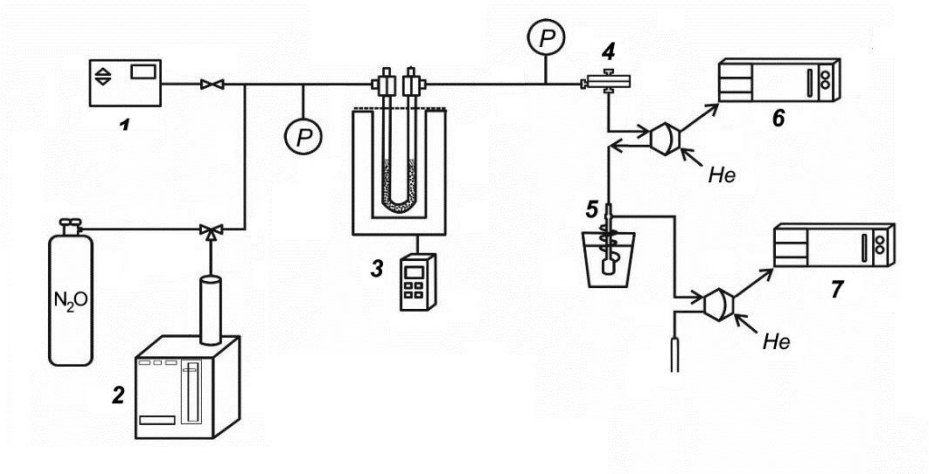

Figure S1. Schematics of a catalytic unit for the oxidation of aromatic substrates. *1* – liquid pump, *2* – syringe pumps for N_2O supply, *3* – oven, *4* – back-pressure regulator, *5* – products receiver, *6* – chromatograph (FID), *7* – chromatograph (TCD).

Pseudocritical properties of a mixture of toluene and N_2O. Calculation of pseudo-critical properties (critical properties of a mixture obtained from the critical constants of pure components and their mole fractions) of mixtures of toluene (T_c = 318.7 °C, P_c = 4.1 MPa) and nitrous oxide (T_c = 36.6 °C, P_c = 7.2 MPa) was performed using the empirical rules of Kay and Prausnitz–Gunn [B.E. Poling, J.M. Prausnitz, J.P. O'Connell, *The property of gases and liquids, Fifth Edition*, McGraw-Hill, New York, 2001], according to which the pseudo-critical temperature (T_{cm}) and pressure (P_{cm}) are calculated with satisfactory accuracy using the following equations:

$$T_{cm} = \sum y_i T_i$$

$$P_{cm} = \frac{R(\sum y_i Z_{ci}) T_{cm}}{\sum y_i V_{ci}}$$

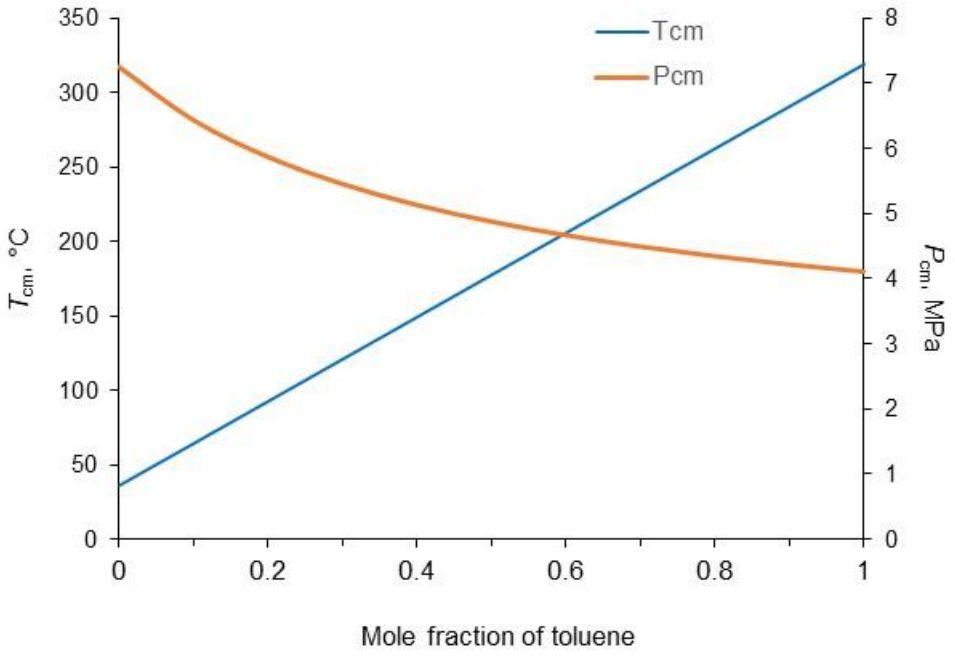

Figure S2. Pseudo-critical values of temperature and pressure of a mixture of toluene and nitrous oxide depending on the mole fraction of toluene.

Using the molar ratio of the supplied reagents, toluene/N_2O = 1:1, the pseudo-critical parameters of the initial mixture are 178 °C and 4.9 MPa.

XRD. X-ray diffraction patterns were recorded on Bruker D8 Advance and Tongda TD-3700 diffractometers using Cu Kα radiation at 40 kV and 40 mA at ambient temperature over the 2-theta angle range of 5–60° ($\lambda_{K\alpha1}$=0.15406 nm and $\lambda_{K\alpha2}$=0.15444 nm; Soller slit of 2.5°; step size of 0.02° and scan duration of ~4 h, no monochromator was used). The crystalline phases were matched by comparing the XRD patterns of the catalysts with those reported in the literature. The relative crystallinity was estimated by measuring the area under five most intense peaks in the patterns, relative to the parent ZSM-5 zeolite.

FTIR. Comparative characterisation of the Brønsted and Lewis acid sites (BAS and LAS) in zeolite samples was carried out using transmittance FTIR measurements in the 6000–900 cm^{-1} spectral range utilizing pyridine adsorption. FTIR analyses were performed at ~80 °C using self-

supported disks activated *in situ* at 450 °C for 5 h in vacuum (10^{-5} Torr, the temperature ramp was 1 K min^{-1}). FTIR spectra were collected using a Thermo iS10 spectrometer at a 4 cm^{-1} resolution (0.96 cm^{-1} data spacing). An excess of Py was admitted into the transmittance cell at 150 °C, then the saturated sample was evacuated for 20 min at 150 °C to remove physically adsorbed Py.

N_2 physisorption. The apparent surface area of the catalysts was calculated using the BET model for the P/P_0 relative nitrogen pressure <0.1; the micropore volume and the pore size distribution were computed using the non-linear density functional theory (NLDFT) model applied to the adsorption branch of the isotherms obtained from the nitrogen adsorption experiments carried out on an Anton Paar iQ Autosorb instrument. The total pore volume was determined at P/P_0 relative nitrogen pressure equal to 0.95.

ZSM-5 Characterisation Data

X-ray diffraction patterns of the parent ZSM-5 zeolite before and after high-temperature treatment shown in Figure S3 demonstrate that the degree of crystallinity and phase composition of the activated zeolite do not differ significantly from the original material, indeed, its crystallinity drops by no more than 10% upon calcination.

The nitrogen adsorption-desorption isotherms for the parent ZSM-5 sample are typical of a highly crystalline ZSM-5 zeolite, e.g. the values of the apparent BET area, 420 m^2 g^{-1}, and the micropore volume, 0.12 cm^3 g^{-1}.

The acidic properties of the parent ZSM-5 zeolite before and after high-temperature activation have been evaluated using FTIR spectroscopy with pyridine as a probe molecule (Figures S4 and S5). The spectra show two major OH bands, one typical of the silanol groups at 3744 cm^{-1}, and the other attributed to the bridging Si(OH)Al groups at 3610 cm^{-1}. In addition, the intensity of the OH-peaks associated with extra-framework Al species at 3785 and 3663 cm^{-1} has increased in the spectrum of the calcined zeolite, whereas the intensity of the band of bridging OH-groups has significantly decreased. Following Py adsorption, a negative peak at 3610 cm^{-1} is observed in the difference spectra, which is attributed to the acidic OH-groups interacting with Py. Using the intensity variations, the relative accessibility of bridging OH-groups is ~100% for both samples. In the Py region, the intensity changes of the peaks at 1546 and 1456 cm^{-1}, assigned to Brønsted and Lewis acid sites, indicate that the concentration of accessible BAS is significantly decreasing and the concentration of LAS is increasing following the high-temperature treatment.

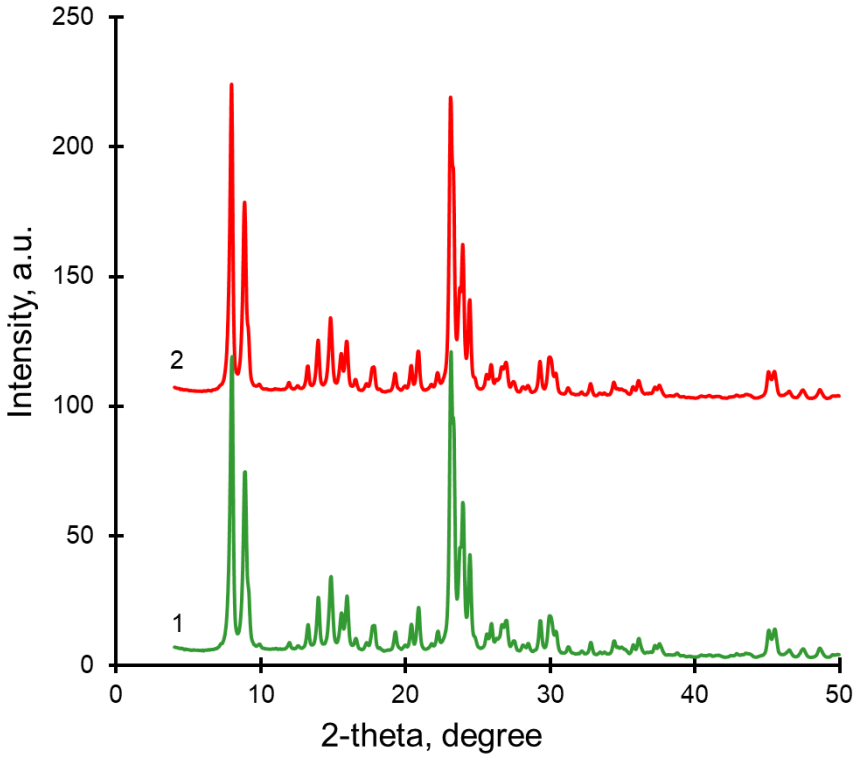

Figure S3. XRD patterns of the parent ZSM-5 zeolite (*1*; green) and the ZSM-5 sample following high-temperature activation (*2*; red). Patterns are offset for clarity.

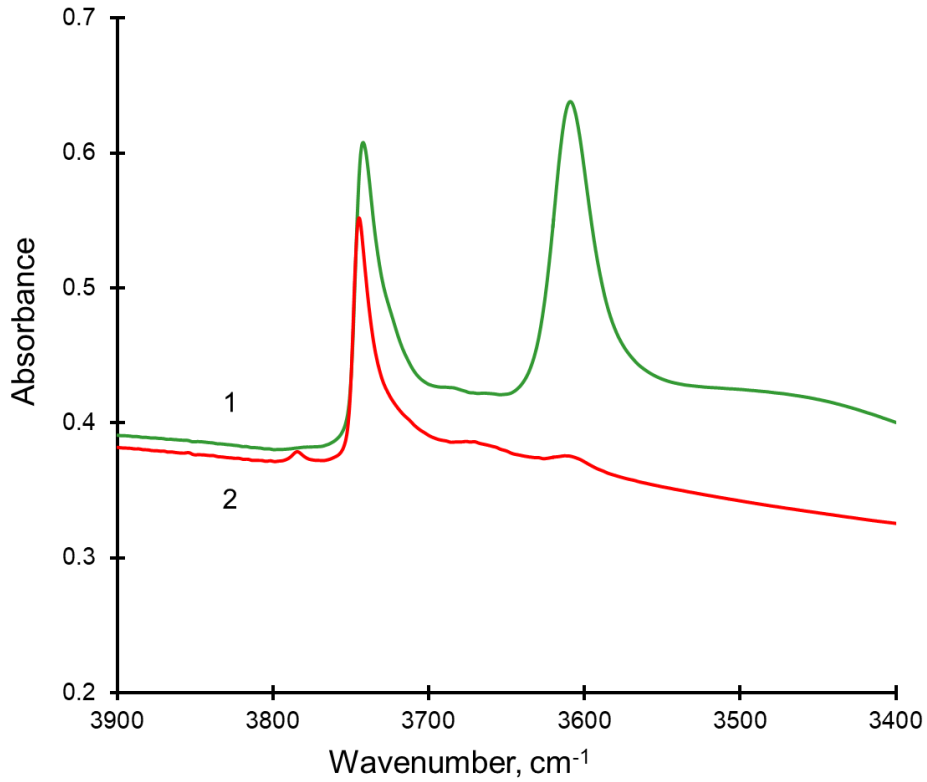

Figure S4. The OH-region of FTIR spectra of the parent ZSM-5 zeolite (*1*; green) and the ZSM-5 sample following high-temperature activation (*2*; red).

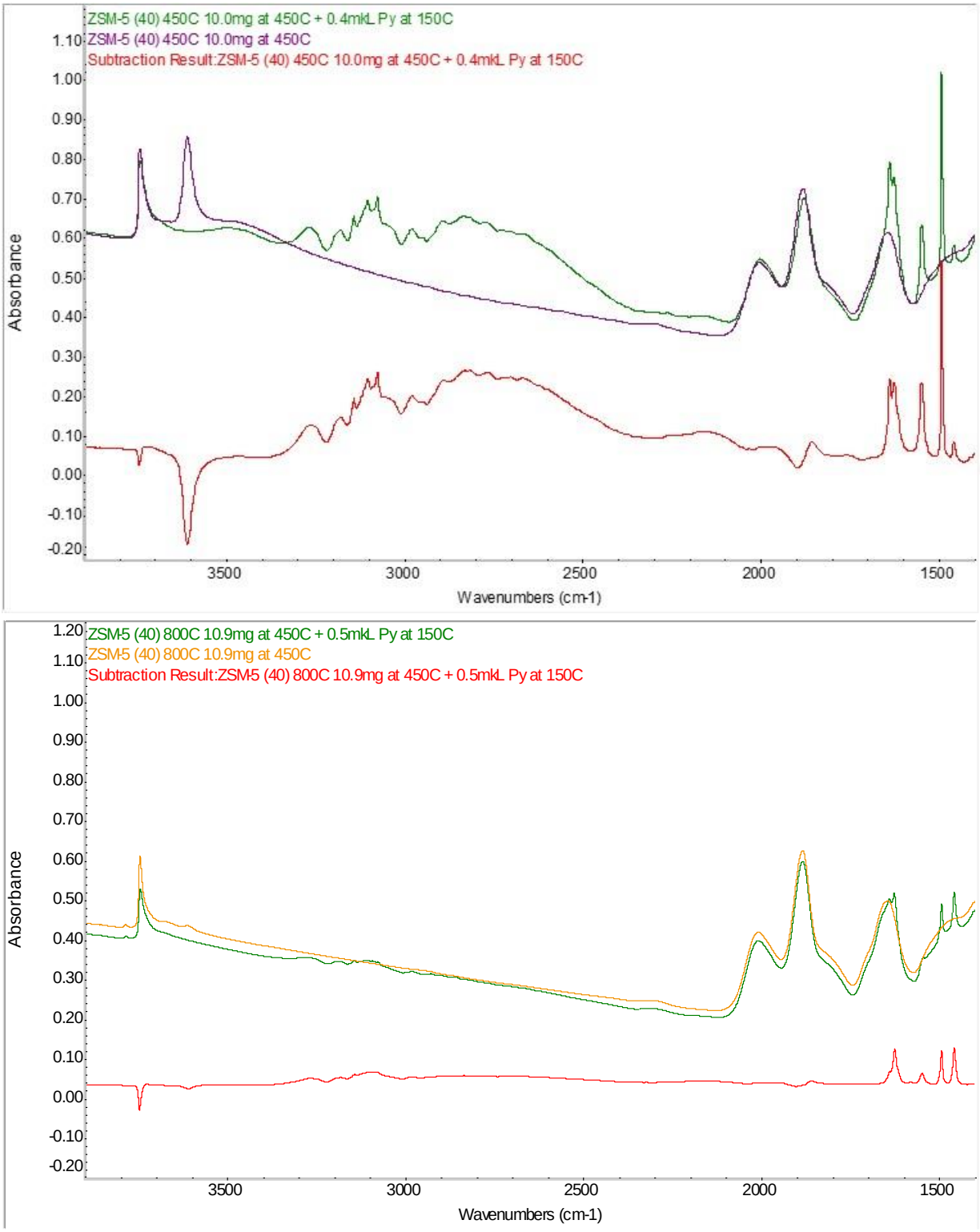

Figure S5. FTIR spectra of the parent ZSM-5 zeolite (top) and the ZSM-5 sample following high-temperature activation (bottom) before and after Py adsorption at 150°C, and the difference spectra (in red).

Catalytic Test Data

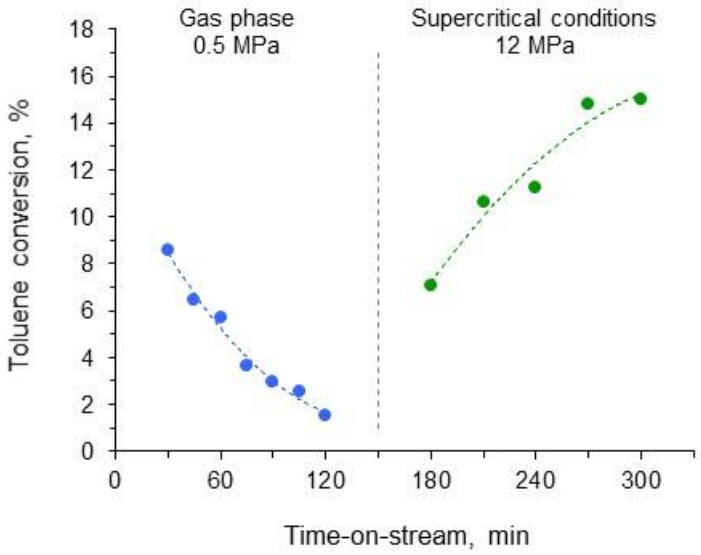

Figure S6. Toluene conversion in the reaction test involving a changeover from the gas-phase to supercritical conditions carried out at 395 °C.

Table S2. Catalytic test data of partial oxidation of toluene with N_2O on the ZSM-5 zeolite involving a changeover from the gas-phase to supercritical conditions carried out a 395 °C.

	P/Mpa	Time-on-stream, min	Toluene conversion, %	Selectivity, %				Cresols productivity, $g \cdot g_{cat}^{-1} \cdot h^{-1}$
				Cresols	Phenol	Disproportionation products	Condensation products	
Gas phase	0.5	30	8.6	33.5	4.2	41.8	20.5	0.30
		45	6.4	29.8	3.2	39.5	27.5	0.20
		60	5.7	32.1	2.3	34.0	31.6	0.19
		75	3.6	34.4	2.8	24.7	38.1	0.13
		90	3.0	32.1	1.4	25.6	40.9	0.10
		105	2.6	33.5	1.4	26.0	39.1	0.09
		120	1.5	32.1	1.4	25.1	41.4	0.05
Supercritical conditions	12	180	7.0	36.7	2.8	23.3	37.2	0.27
		210	10.6	32.6	2.7	32.6	32.1	0.36
		240	11.2	33.5	3.7	34.4	28.4	0.39
		270	14.8	26.5	4.2	42.3	27.0	0.41
		300	15.0	27.4	3.8	43.3	25.5	0.43