Disproportionation of Toluene over ZSM-5 under Near-Critical Conditions

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The nature of solute-solvent interactions in dilute mixtures in the vicinity of the solvent's critical point is of considerable theoretical interest. At infinite dilution (defined here as the limit of vanishing solute-solute interactions), the partial molar volume, energy, and enthalpy of any solute diverge as the solvent's critical point is approached. This behavior has been the object of numerous theoretical (Krichevskii, 1967; Wheeler, 1972; Leung and Griffiths, 1973; Rozen, 1976; Levelt Sengers et al., 1983; Chang et al., 1984; Kim et al., 1985; Levelt Sengers et al., 1986a, b, c; Sengers and Levelt Sengers, 1986; Chang and Levelt Sengers, 1986; Levelt Sengers, 1986; Gilbert and Eckert, 1986; Debenedetti, 1987; Debenedetti and Kumar, 1988) and experimental studies (Eckert et al., 1983, 1986; Smith-Magowan and Wood, 1981; Wood and Quint, 1982; Gates et al., 1982; Busey et al., 1984; Christensen et al., 1984; Kim and Johnston, 1987 a, b).

Eckert and coworkers (1983, 1986) measured the partial molar volumes of several nonvolatile organic solutes at infinite dilution in the vicinity of the critical points of carbon dioxide and ethylene. They observed very large, negative partial molar volumes (typically 100 times greater in magnitude than the solvent's molar volume at the experimental temperature and pressure) and interpreted this remarkable volume contraction in terms of the formation of large clusters of solvent molecules around each solute molecule. This mechanistic interpretation is consistent with the large volume changes (per solute molecule) which necessarily accompany the isothermal, isobaric addition of trace amounts of any solute to any highly compressible solvent (Wheeler, 1972; Debenedetti, 1987). Kim and Johnston (1987 a, b) have recently used solvatochromic measurements to study local compositions of pure supercritical solvents (1987a) and supercritical fluid-cosolvent systems (1987b) around infinitely dilute phenol blue. They found solvent enrichment around the solute in the former case and cosolvent enrichment within the solvent cluster in the latter.

A theoretical model for cluster formation in dilute supercritical mixtures has recently been proposed (Debenedetti, 1987; Debenedetti and Kumar, 1988). In this treatment, which is based on the application of fluctuation theory ideas (Kirkwood and Buff, 1951), the cluster size is defined as the excess number of solvent molecules surrounding each solute molecule, with respect to a uniform distribution at the prevailing density and temperature. This definition allows the calculation of cluster sizes from the measurement of solute partial molar volumes under infinite dilution conditions.

When applied to the experimental measurements of Eckert and coworkers (1986), this calculation indicates the existence of clusters of approximately 100 solvent molecules per solute molecule. Such numbers are, of course, no substitute for the experimental verification of the existence of clusters, nor do they provide a detailed enough picture of the mechanistic significance of the cluster concept. Basic questions such as the extent to which the motion of the solvent molecules belonging to a cluster at a given instant is correlated with the solute molecule's motion over a significant period of time remain unanswered. A lack of correlated motion, for example, would imply that the near-critical clusters are merely statistical in nature. Although the characteristics of cluster formation are not yet fully understood, the very magnitude of the observed volume changes (Eckert et al., 1983, 1986) and the corresponding calculated cluster sizes (Debenedetti, 1987; Debenedetti and Kumar, 1988) strongly suggest that unusual solute-solvent association effects arise in dilute mixtures in the vicinity of the solvent's critical point.

In this communication we describe the results of recent experiments designed as an indirect test of the soundness of a mechanistic interpretation of the near-critical cluster concept, and as an exploration of its potential application to reacting systems.

The disproportionation of toluene on ZSM-5 zeolite catalyst is a commercial route to *p*-xylene (Keading, et al., 1981; Keading, et al., 1984; Olson and Haag, 1984). The primary reaction products are benzene and a mixture of the three xylene isomers. The *p*-xylene diffuses much more easily (when compared to the other isomers) through the intracrystalline pores of the ZSM-5 zeolite catalyst, and is therefore favored (Wei, 1982; Olson and Haag, 1984). Secondary isomerization of *p*-xylene on the catalyst's surface (and possibly, upon reentering the pores) conspires to reduce the proportion of the valuable paraisomer in the product stream, making unmodified ZSM-5 a nonselective catalyst for toluene disproportionation (Keading et al., 1984). Catalyst modifications such as pore blocking and surface coating (Wei, 1982; Olson and Haag, 1984), which increase the intracrystalline diffusional resistance and inhibit the secondary isomerization of *p*-xylene on the external surface of the crystallite, respectively, have been employed in industrial practice (Keading et al., 1984) to enhance paraselectivity.

We have studied the disproportionation of toluene on an unmodified ZSM-5 catalyst in a differential reactor as a model reaction system to test whether the selectivity characteristics in the near-critical region are consistent with the assumed existence of clusters. The objective of our work was to examine the variation of selectivity (at small conversion levels) with pressure and temperature in the vicinity of toluene's critical point (4.1 MPa, 591.8 K). At low conversions, toluene acts both as primary reactant and solvent, with the reaction products being the solutes (in the bulk fluid phase outside of the zeolite crystals). If the reactor operating conditions are very close to the critical point of toluene, one can anticipate the formation of clusters of toluene around the solute molecules. Such clusters would disappear outside of the near-critical region (Debenedetti, 1987).

To the best of our knowledge, there is no reason to expect any anomalous behavior in the kinetics of adsorption of a (pure) solvent near its bulk critical point onto any surface. However, the situation would be very different in the case of trace solutes. If the cluster concept is mechanistically significant, the kinetics of solute adsorption onto a surface would be significantly depressed under near-critical conditions (when compared with conditions away from the solvent's bulk critical point), due to the severe steric constraints imposed upon the solute by the surrounding cluster of about 100 solvent molecules. Therefore, in our problem, the rates of the secondary isomerization reactions on the external surface of the catalyst may be expected to decrease as one approaches the critical point of toluene, provided clusters do indeed exist. Since intracrystalline diffusional resistance favors *p*-xylene, a depression of the secondary isomerization should translate into an enhancement in the paraselectivity. Thus, carrying out the reaction under near-critical conditions should enhance *p*-xylene selectivity. These speculations are based, of course, on a mechanistic interpretation of the clustering concept.

Experimental Procedure and Results

The unmodified ZSM-5 catalyst (Mobil) was pressed and broken into chunks of 1–4 mm in size before use. Following a degassing treatment at 811 K in flowing nitrogen, the catalyst was calcined in flowing air by gradually increasing (3–7°C/min) the temperature to 811 K and then cooled. The reactant toluene (ACS reagent grade, Aldrich) contained 0.1 wt. % benzene and less than 0.02 wt. % xylenes as received and was used without further purification.

The apparatus consisted of a fixed-bed, 1.25-cm-OD, stainless-steel reactor packed with 0.77 g of pretreated ZSM-5 catalyst. The temperature of the catalyst was measured using a stainless-steel sheathed thermocouple centered in the bed and was maintained to within 1°C of the desired temperature. Toluene was delivered to the reactor at a constant rate using a high-pressure syringe pump (ISCO LC-5000). The pressure was controlled using a back pressure regulator (Grove Model 155) downstream of the reactor and was measured with a digital pressure instrument (Heise Series 9) accurate to within 6 kPa. Pressure fluctuations were less than 6 kPa, and the pressure drop across the reactor was less than 30 kPa. The reactor effluent was collected in an ice water trap and analyzed using a gas chromatographic column packed with 5% SP-1200/5% Bentone 34 on Supelcoport.

Prior to performing near-critical experiments, toluene disproportionation was carried out at 673 K and 4.93 MPa (WHSV = 17 h^{-1}) for a period of seven hours to evaluate the activity of the catalyst. Toluene conversion was found to be 3% and the mole ratio of benzene/xylenes was 0.96 at these conditions. Toluene disproportionation was then carried out at 593 K (WHSV = 34 h^{-1}) and 598 K (WHSV = 85 h^{-1}) for various pressures around the critical point of toluene. For each pressure, the reactor effluent was sampled after 10–12 hours on stream at 593 K or after 4–5 hours on stream at 598 K.

The results obtained at 593 K are listed in Table 1 in the order in which the data were taken. Such a presentation allows one to determine whether catalyst deactivation was important. The results of toluene disproportionation experiments at 598 K are listed in a similar manner in Table 2. Para-xylene selectivity is shown in Figure 1 for the various reactor pressures examined at both 593 K (WHSV = 34 h^{-1}) and 598 K (WHSV = 85 h^{-1}).

Discussion

As seen in Figure 1, at 593 K which corresponds to a reduced temperature of 1.002 (with respect to toluene's critical point), an increase in *p*-xylene selectivity occurs in the immediate vicinity of toluene's critical pressure (4.1 MPa). A selectivity decrease, furthermore, occurs if the pressure is changed in either direction away from the critical region. This result is consistent with the existence of near-critical clusters which impose steric constraints upon the adsorption of the xylenes (solutes), inhibiting the secondary isomerization reactions on the external surface or in the interior of the zeolite crystallites.

As the temperature is increased to 598 K (reduced tempera-

Table 1. Toluene Disproportionation at 593 K, WHSV = 34 h^{-1}

Sample No.	Pressure, MPa	Para-xylene Selectivity, %	Toluene Conversion, %
1	4.95	33.6	0.517
2	3.36	28.9	0.498
3	4.43	35.5	0.517
4	3.80	33.4	0.467
5	4.31	35.7	0.523
6	3.97	33.7	0.491
7	4.14	35.9	0.493
8	4.18	36.2	0.489
9	4.21	36.3	0.501
10	4.11	35.9	0.492
11	4.25	36.2	0.495
12	4.16	36.3	0.483
13	5.28	34.9	0.452
14	5.64	33.0	0.429

Table 2. Toluene Disproportionation at 598 K, WHSV = 85 h^{-1}

Sample No.	Pressure, MPa	Para-xylene Selectivity, %	Toluene Conversion, %
1	4.25	38.4	0.393
2	5.29	37.2	0.390
3	4.42	38.7	0.391
4	4.33	38.5	0.368
5	4.15	38.1	0.348
6	3.31	37.7	0.339
7	4.37	38.0	0.338

ture 1.01), the selectivity exhibits a much less pronounced isothermal pressure dependence, Figure 1. This, again, is consistent with the near-critical cluster formation mechanism, since the theoretically predicted cluster size drops sharply away from the solvent's critical point (Debenedetti, 1987; Debenedetti and Kumar, 1988).

The paraselectivity was greater in the experiments performed at 598 K than those performed at 593 K, Figure 1. We believe that this difference is primarily due to the differences in toluene feed rates used in the two sets of experiments. At 593 K, a toluene WHSV of 34 h^{-1} was used resulting in toluene conversion around 0.5% while increasing the WHSV to 85 h^{-1} at 598 K decreased the conversion to 0.3%. A strong inverse dependence of paraselectivity on conversion in this reaction system is well-documented (Keading et al., 1981; Keading et al., 1984). (An increase in the paraselectivity was indeed observed in our experiments when the WHSV was increased at 593 K.) It is also possible that the higher selectivities observed at 598 K (when compared to the results obtained at 593 K) are in part a manifestation of increased diffusion limitations as the temperature is raised. It must be emphasized that the central idea underlying the implementation of this process under industrial conditions is to introduce diffusion limitations as a means of attaining high para-selectivity (Wei, 1982; Olson and Haag, 1984). When the temperature is increased, the Thiele parameter increases, which results in an enhancement of the selectivity towards the faster-moving xylene isomer, namely *p*-xylene (Wei, 1982; Sundaresan and Hall, 1986). In fact, to take advantage of this effect, the industrial reactors are typically run at temperatures much higher than those used in our study (Keading et al., 1981; Keading et al., 1984).

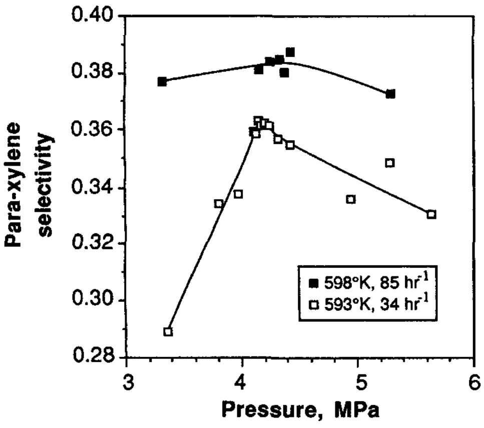

Figure 1. Selectivity towards paraxylene as a function of pressure at 593 and 598 K.

The experimental results reported in this study are not inconsistent with a mechanistic interpretation of near-critical clustering. The catalytic toluene disproportionation reaction was chosen as a model system in order to test the soundness of this picture. Our goal was not to improve on an already existing process, as there are much more spectacular and ingenious catalyst modification techniques to achieve a reduction of undesirable secondary *p*-xylene isomerization under industrial conditions (Keading et al., 1981; Keading et al., 1984; Olson and Haag, 1984). We believe, however, that our experiments should, at the very least, encourage further investigations of potential engineering applications of near-critical systems, of which selectivity enhancement in heterogeneously catalyzed reaction networks is but one example.

Acknowledgments

This work was supported by The National Science Foundation (grant #CBT-8612864). We are grateful to Mobil Chemical Company for providing the ZSM-5 sample, and to Dr. N. L. Avery and Dr. M. Smith (Mobil, Princeton) for their invaluable advice.

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Manuscript received Jan. 5, 1988, and revision received Mar. 29, 1988.