Heterogeneous catalysis in supercritical water

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Abstract

Fluids at temperatures and pressures near their thermodynamic critical points are attracting attention as media for heterogeneous catalytic reactions. Several factors have motivated this interest in catalytic reactions in supercritical fluids (SCFs), but the paradigm of pollution prevention is one of the most important. The increased awareness of environmental sustainability and the trend toward pollution prevention has led to a consideration of environmentally benign solvents such as supercritical water for chemical processes. This article provides an overview of the types of heterogeneous catalytic reactions that have been accomplished in supercritical water. Additionally, we provide new experimental results for the heterogeneous catalytic oxidation of phenol in supercritical water over bulk TiO_2 and compare the performance of different transition metal oxide catalysts for this reaction. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Water is attractive as a potential medium for industrial chemical reactions because it is environmentally benign. Of course, at ambient conditions water is not a good solvent for most organic chemicals. Near or above its thermodynamic critical point ($T_c = 647.3$ K, $P_c = 217.6$ atm), however, water offers enhanced solubilities for many organic compounds. Thus, operating chemical reaction processes in supercritical water (SCW) facilitates the use of environmentally benign solvents. Performing chemical reactions at supercritical conditions offers other potential advantages such as:

- providing concentrations of reactant gases (e.g., H_2, O_2) higher than those that can be obtained in conventional gas–liquid systems;

- eliminating inter-phase transport limitations that would exist in multi-phase reacting systems (e.g., hydrogenation, partial oxidation);
- providing easier product separation because solubility can be a strong function of pressure and temperature in the critical region;
- allowing in situ extraction of coke precursors and hence a longer time on stream for hydrocarbon processing catalysts;
- optimizing the strongly pressure-dependent properties of the supercritical reaction medium for a given reaction;
- providing higher diffusivities than liquids and better heat transfer than gases.

Of course there are potential disadvantages as well, such as materials compatibility issues and the elevated pressures required for supercritical water.

The field of reactions at supercritical conditions has grown tremendously. A 1986 review article [1] required only 12 pages and fewer than 60 literature citations to cover work done to that date. A review

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article in 1995 [2], however, required 56 pages and over 400 references to review work done largely in the nine years since the earlier review. More recently, eight different articles in a thematic issue of Chemical Reviews [3] deal largely or exclusively with chemical reactions at supercritical conditions. These articles consume nearly 200 pages of the issue. Given this explosive growth of information, the current trend is toward more focused reviews of some narrower portion of the broad field. Baiker [4], e.g., critically reviewed prior work in heterogeneous catalytic reactions in supercritical fluids. This recent review provides a thorough treatment for catalytic reactions in fluids other than water. Savage [5] reviewed reactions (including heterogeneous catalysis) in supercritical water, but he did not single out heterogeneous catalytic reactions for special treatment. Heterogeneous catalytic reactions were singled out in an earlier contribution [6] but no attempt was made to provide an exhaustive review.

Because heterogeneous catalytic reactions in SCW has not been the subject of a focused review, we provide an overview of the prior work in this field in the following section. This overview enumerates the types of heterogeneous catalytic chemistries that have been demonstrated in SCW. The type of reaction that has received the most attention to date is complete catalytic oxidation in SCW. The subsequent section of this article then adds to this field by presenting new experimental results for heterogeneously catalyzed oxidation of phenol over bulk TiO_2.

2. Overview of heterogeneous catalysis in SCW

To develop commercial organic chemical reaction processes in SCW one must be able to make and break carbon–hydrogen, carbon–carbon, and carbon–heteroatom bonds selectively. These reactions are among the different types of heterogeneously catalyzed reactions that have been demonstrated in water near or above its critical point. This section provides a brief overview of previous heterogeneous catalytic reaction studies that might be useful for the development of environmentally benign chemical technologies by using SCW as a reaction medium. We note, however, that there is additional previous work involving reactions that might not be significant for commercial-scale chemical synthesis in SCW. Some

of these studies [7–9] involved the addition of a solid catalyst (e.g., $ZnCl_2$, Fe_2O_3) to accelerate cracking reactions and heteroatom removal from compounds intended to mimic chemically important structures in different waste materials. Others examined the gasification of biomass and organic compounds over a carbon catalyst in SCW [10,11] and the feasibility of tire liquefaction in SCW [12]. We will not discuss these studies further in this overview.

2.1. Hydrogenation/dehydrogenation

Parsons and coworkers [13,14] showed that the addition of a PtO_2 catalyst greatly facilitated dehydrogenation reactions in SCW. Cyclohexanol was dehydrogenated via two parallel paths, dehydrogenation of the ring and oxidation of the alcohol group to cyclohexanone. Aromatization of the cyclohexyl ring also occurred as benzene and phenol were among the products. These experiments showed that the extent of dehydrogenation in SCW can be controlled by judicious selection of catalysts and pH.

Adschiri et al. [15] examined catalytic hydrodesulfurization of dibenzothiophene in SCW over a conventional $NiMo/Al_2O_3$ hydrotreating catalyst. Interestingly, they obtained higher conversions when using CO or formic acid instead of H_2 in the reaction mixture. The authors rationalized this result by invoking the occurrence of the water–gas shift reaction in the CO– and HCOOH–SCW media, which produced chemical species that hydrogenate dibenzothiophene more effectively than H_2 gas. The removal of sulfur and metals from petroleum fractions via hydrotreating in SCW has also been explored [16].

2.2. C–C bond formation

The use of near- and supercritical water as a medium for chemical synthesis requires ways to form and break carbon–carbon bonds. Conventional chemistries such as Friedel–Crafts alkylation [17,18], Diels–Alder reactions [19], aldol condensations [20], and alkyne cyclotrimerizations [21,22] have been demonstrated in high-temperature water, either with no added catalyst or with a homogeneous catalyst. Parsons and coworkers [23,24] in contrast, examined heterogeneous, palladium-catalyzed alkene–arene

coupling reactions in near-critical and supercritical water. These reactions can be classified as Heck arylation reactions. The reactions in high-temperature water behaved similarly to those in traditional organic solvents, but they were more sensitive to steric effects and the nature of the alkene.

Rearrangements and isomerization are another type of C–C bond forming reaction. Crittendon and Parsons [13] observed that cyclohexene rearranged reversibly to methylcyclopentene in SCW in the presence of a mineral acid or acidic metal salts. They attributed this ring contraction to acid catalysis and the rearrangement of a carbocation.

2.3. Partial oxidation

Converting methane to oxygenates or higher hydrocarbons has been an elusive goal in the chemical research community for several years. Chemistry that gives high yields of the target compound economically would allow use of vast methane reserves in remote locations. It is in this context that the heterogeneous catalytic partial oxidation of methane to methanol in SCW has been examined [25]. High selectivities to oxygenates were obtained, but only at very low methane conversions. The highest methanol yields available are only about 1%. Unless much higher methanol yields can be obtained, partial oxidation in SCW does not appear to be an economically viable route for converting methane to methanol.

2.4. Complete oxidation

Complete oxidation of waste organic carbon to CO_2 is the goal of supercritical water oxidation (SCWO). This technology provides an alternative to more established waste and wastewater treatment methods such as incineration and wet air oxidation. It can be viewed as a clean technology because it qualifies as a totally enclosed treatment facility and it can be used for in-process recycling and reuse of process water. The desire to reduce the severity of the processing conditions of SCWO and thereby improve the economics has motivated much recent research into heterogeneously catalyzed oxidation reactions in SCW. Ding et al. [26] provide a thorough review of work related to catalytic SCWO, published by early 1996.

Heterogeneous catalytic SCWO is the topic that has received the most attention in the more general field of heterogeneous catalysis in SCW. Abraham and coworkers were the pioneers in this field. Their comparison of gas-phase and SCW-phase catalytic oxidation of 1,4-dichlorobenzene over V_2O_5 [27,28] was the first published work on heterogeneous catalytic SCWO. Interestingly, the dichlorobenzene conversion from catalytic SCWO was lower than that from gas-phase catalytic oxidation, which led the investigators to conclude that water inhibited the reaction rate. The CO_2 yields and CO_2 selectivities from catalytic SCWO were much higher than those from gas-phase catalytic oxidation, however. The experiments also showed no difference in the kinetics between catalytic SCWO and conventional non-catalytic SCWO. Although these initial results were not uniformly encouraging, research continued with different, more suitable catalytic materials. The other early studies [29–32] in this area were feasibility studies or catalyst screening surveys wherein different transition metal oxide catalysts and different organic reactants were used to demonstrate that catalytic SCWO can provide substantially higher conversions and higher yields of CO_2 than uncatalyzed SCWO.

The more recent work in catalytic SCWO has tended to examine specific catalyst–compound combinations in more detail so that quantitative reaction rate laws and information about the catalyst stability and activity maintenance are available. Systems investigated include NH_3 [33] over a commercial MnO_2/CeO_2 catalyst, acetic acid [34] over a proprietary copper/zinc/cobalt oxide supported catalyst, pyridine [35–37] over MnO_2/CeO_2, Pt/Al_2O_3 and MnO_2/Al_2O_3, phenol over a proprietary copper/zinc/cobalt oxide supported catalyst [38], a commercial MnO_2/CuO supported catalyst [39], and bulk MnO_2 [40,41], and chlorophenol over CuO supported on zeolites [42,43]. Some of these studies included an assessment of mass transfer rates to and within the porous catalysts. In all cases, the catalyst accelerated the rate of disappearance of the target compound and the conversion of organic carbon to CO_2. The catalysts also typically reduced the yield of organic by-products. These results continue to motivate research into catalytic SCWO, which shows promise as a route to improved SCWO process economics [44].

In the following section, we present new experimental results for the catalytic oxidation of phenol in SCW over bulk TiO_2. We also compare the activity of TiO_2 with that of other transition metal oxides that have been used for catalytic SCWO of phenol.

3. Catalytic SCWO of phenol over TiO₂

We have oxidized phenol in supercritical water over three different catalysts, a commercial MnO_2/CuO catalyst supported on amorphous Al_2O_3 [39], bulk MnO_2 [40], and bulk TiO_2. We deemed it worthwhile to explore the behavior of bulk catalyst materials such as MnO_2 and TiO_2 before pursuing additional work with the more active supported catalysts because the reaction rate obtained with the commercial catalyst was always limited by the rate of pore diffusion [39]. Thus, we could do only a simplified kinetics study of catalytic oxidation with the supported catalyst. We hoped that using less active, less porous bulk materials would provide access to the intrinsic reaction kinetics.

Phenol was selected as the model compound for this research because it is ubiquitous in industrial wastewaters and it is a good "worst case" compound for SCWO kinetics studies [45]. All experiments were done in a tubular flow reactor that can be approximated as operating isothermally, isobarically, and in plug flow. A dilute aqueous solution of phenol and oxygen was fed to the reactor, which typically contained a packed bed of crushed (40/230 mesh) catalyst particles. The reactor effluent was cooled, depressurized, and then sampled and analyzed chromatographically to identify and quantify the reaction products. Detailed descriptions of the reactor system and experimental methods have been published previously [39,40].

Table 1 provides selected experimental results for catalytic oxidation of phenol over bulk TiO_2 in SCW at $381°C$ and 250 atm. W is the catalyst mass and F_{Ao} is the molar flow rate of phenol into the reactor. The concentrations of phenol and oxygen reported are those that exist at the reactor entrance at reaction conditions. The molar yields for CO and CO_2 are calculated as the product molar flow rate in the reactor effluent divided by the molar flow rate of carbon atoms into the reactor. Thus, a CO_2 yield of 100% would indicate complete conversion of the organic carbon in phenol into CO_2. We also report a carbon tally, which is the sum of the molar yields of CO, CO_2, and unreacted phenol. The carbon tally consistently being less than 100% indicates that carbon-containing products other than CO and CO_2 are produced during catalytic SCWO over TiO_2. The value of the carbon tally can be interpreted as the percentage of carbon atoms in the reactor feed stream that appear in the effluent as either CO, CO_2, or unreacted phenol.

Table 1
Results from phenol oxidation over TiO_2 in SCW at $381°C$ and 250 atm

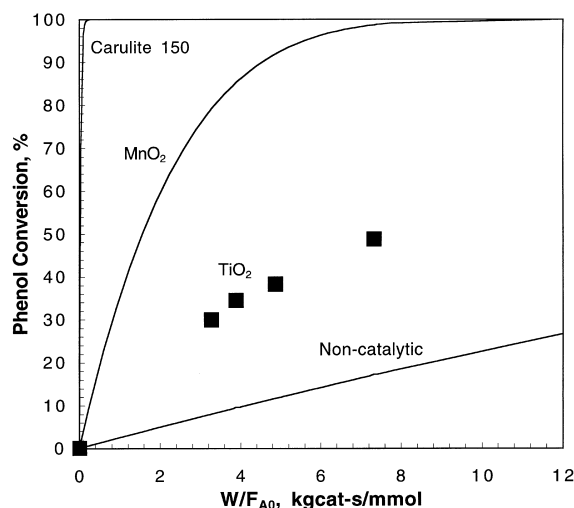| W/F_{Ao} (kgcat-s/mmol)	Phenol concentration (mmol/l)	Oxygen concentration (mmol/l)	Phenol conversion (%)	CO yield (%)	CO_2 yield (%)	Carbon tally (%)
19.7	0.7	24	70	2.7	25	58
14.8	0.7	26	71	2.1	21	53
5.2	2.8	25	47	1.3	17	71
2.3	2.7	26	30	0.6	7	78
7.2	2.0	17	44	1.0	14	71
5.0	2.0	17	39	0.5	8	70
3.9	1.9	17	30	0.5	8	79
3.2	2.0	17	24	0.3	7	83
7.3	1.9	27	49	1.7	14	67
4.9	2.0	26	38	1.2	11	74
3.9	1.9	27	34	0.7	8	74
3.2	2.0	27	30	0.6	8	79
7.0	2.0	50	49	1.8	21	73
5.1	2.0	51	45	1.3	18	74
3.9	2.0	51	36	0.8	12	77
3.1	2.0	51	34	0.5	11	78

Fig. 1. Phenol conversions from SCWO over different heterogeneous oxidation catalysts (reaction conditions: 381°C, 250 atm, $[Phenol]_o = 2.0 \, mmol/l$, $[O_2]_o = 27 \, mmol/l$).
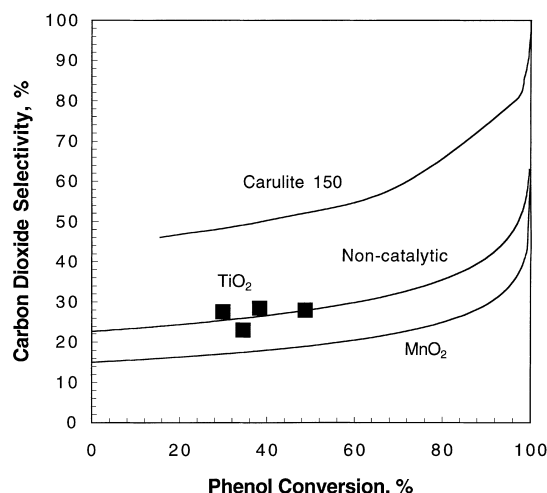

Fig. 3. CO_2 selectivities from SCWO of phenol over different heterogeneous oxidation catalysts (reaction conditions: 381°C, 250 atm, $[Phenol]_o = 2.0 \, mmol/l$, $[O_2]_o = 27 \, mmol/l$).

Figs. 1–3 compare the performance of the TiO_2 catalyst with two other heterogeneous catalysts we have examined and with non-catalytic SCWO. The data for phenol oxidation over TiO_2 appear as discrete points (squares), whereas the results for the commercial CARULITE catalyst (MnO_2/CuO on Al_2O_3) [39]
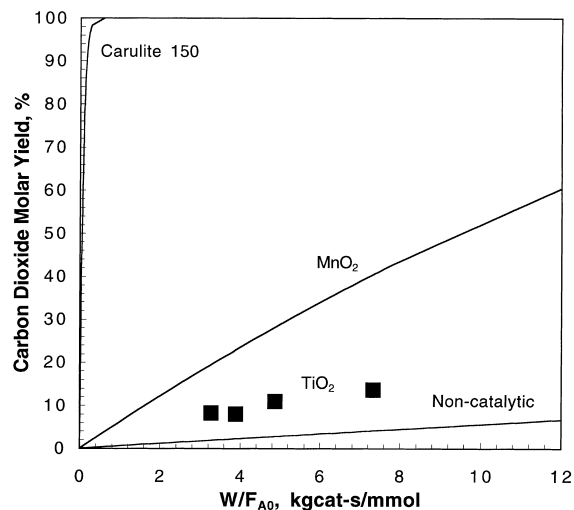

Fig. 2. CO_2 molar yields from SCWO of phenol over different heterogeneous oxidation catalysts (reaction conditions: 381°C, 250 atm, $[Phenol]_o = 2.0 \, mmol/l$, $[O_2]_o = 27 \, mmol/l$).

and bulk MnO_2 [40] and for non-catalytic SCWO appear as smooth curves. The results for non-catalytic SCWO were calculated by taking the reactor residence time to be the void volume of the catalyst bed divided by the volumetric flow rate through the reactor. These non-catalytic results provide the behavior expected if the catalyst were completely inactive. All of the curves in Figs. 1–3 were calculated from rate laws previously determined in our laboratory [39,40,46,47].

It is clear from Fig. 1, which displays the phenol conversion as a function of W/F_{Ao}, that the commercial CARULITE catalyst is the most active and that bulk TiO_2 is less active than bulk MnO_2 on a mass basis. All three catalysts, however, provide phenol conversions higher than those that would have been obtained by exclusively homogeneous oxidation reactions at the same conditions. Fig. 2 displays similar information for the CO_2 molar yields obtained from catalytic and non-catalytic SCWO. The rate of CO_2 formation is important because the objective of SCWO processing is not just to make the starting material disappear (perhaps by conversion to different organic compounds) but rather to convert organic carbon to CO_2. Again the supported CARULITE catalyst is most active. Bulk TiO_2 is less active than bulk MnO_2, but both transition metal oxides provide CO_2 formation rates that exceed that of conventional

non-catalytic SCWO. Fig. 3 shows how the CO_2 selectivity (CO_2 molar yield/phenol conversion) varies with the phenol conversion for the different catalysts and for non-catalytic SCWO. The CARULITE catalyst is the only one that provides CO_2 selectivities exceeding those available from non-catalytic SCWO. The bulk transition metal oxides, on the other hand, provided CO_2 selectivities that do not differ appreciably from the non-catalytic case.

The enhanced reaction rates evident in Figs. 1 and 2 but unchanged CO_2 selectivity in Fig. 3 for the bulk materials suggests that the reaction paths and mechanism for CO_2 formation over these materials are the same as that for non-catalytic SCWO. CO_2 formation from phenol in conventional, non-catalytic SCWO is thought to proceed via a sequence of free-radical reaction steps [48]. The first step is generation of phenoxy radicals from phenol. Thus, the role of the bulk transition metal oxide appears to be providing a faster rate of formation of phenoxy radicals, which then react in the fluid phase just as they would during non-catalytic SCWO.

Unlike the bulk transition metal oxides, the supported commercial catalyst provided CO_2 selectivities that were higher than those obtained from non-catalytic SCWO. Thus, it appears that the supported catalyst does more than simply increase the rate of generation of phenoxy radicals. It must also be involved in subsequent reaction steps that eventually lead to CO_2. The reason for this added attractive feature of the commercial catalyst is not presently clear. It might be related to some way in which the commercial catalyst differs from the bulk materials. These differences include the presence of multiple transition metal (Cu, Mn) oxides, the presence of the support, and perhaps the presence of other unspecified but proprietary compounds in the optimized commercial catalyst.

We deliberately selected experimental conditions that led to incomplete conversion of phenol because we are interested in determining the catalytic oxidation network and the reaction kinetics. Acquisition of additional data over a broad range of temperatures and phenol, oxygen, and water concentrations will allow us to develop a reaction rate law for catalytic oxidation over TiO_2. Our previous work [40] with MnO_2 and Krajnc and Levec's work [38] with their proprietary catalyst showed that the catalytic reaction

kinetics for phenol disappearance could be correlated by a Langmuir–Hinshelwood rate equation of the form

$$\text{rate} = -\frac{kK_1 K_2^{0.5}[\text{PhOH}][\text{O}_2]^{0.5}}{(1 + K_1[\text{PhOH}])(1 + K_2^{0.5}[\text{O}_2]^{0.5})}$$

This rate law is consistent with a reaction mechanism comprising adsorption of phenol on one type of catalytic site, dissociative adsorption of O_2 on a different type of site, and a rate-determining irreversible surface reaction between adsorbed phenol and adsorbed oxygen atoms. Preliminary analyses of the data obtained over the TiO_2 catalyst indicate that this rate law also provides a good correlation of the effects of the phenol and oxygen concentrations on the phenol disappearance rate.

4. Summary

Performing heterogeneous catalytic reactions at supercritical conditions offers potential opportunities for pollution prevention. Research and development activity in this field has been growing steadily and SCW shows promise as an environmentally benign reaction medium for heterogeneous catalytic reactions. Catalytic chemical transformations demonstrated to date in SCW include hydrogenation, C–C bond formation, partial oxidation, and total oxidation. This last application is the one that has received the most scrutiny because it forms the basis for catalytic SCWO, an emerging waste treatment technology. Research in our laboratory is providing reaction rate laws and reaction networks for heterogeneous catalytic oxidation of phenol in SCW. This information can be used for the design, analysis, and economic evaluation of catalytic SCWO processes.

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