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Supercritical Fluids in Heterogeneous Catalysis

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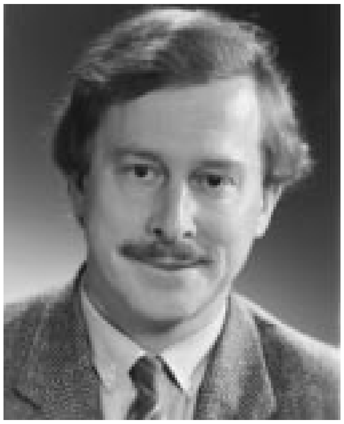

Alfons Baiker was born in Zurich in 1945. He studied Chemical Engineering at the Swiss Federal Institute of Technology (ETH) in Zurich, where he earned his Ph.D. in 1974. He subsequently spent some years at foreign universities as a postdoctoral fellow. During a research stay with Michel Boudart at Stanford University (1978–1980), he completed his habilitation thesis on ammonia synthesis kinetics. After returning to ETH he built up his research group at the Laboratory of Technical Chemistry, becoming Associate Professor in 1989 and full Professor in 1990. From 1993 to 1995, he was Head of the Laboratory of Technical Chemistry. His research lies in the areas of heterogeneous catalysis, chemical reaction engineering, and solid-state chemistry. His general goal is the development of environmentally benign chemical processes which make optimal use of raw materials and energy. Present research interests embrace catalyst design and novel catalytic materials, enantioselective catalysis, environmental and fine chemical catalysis, catalytic conversion of carbon dioxide, and the application of supercritical fluids in heterogeneous catalysis. Baiker was a guest professor at the University of California, Berkeley, and at the Max-Planck Institut für Kohleforschung, Mülheim a.d. Ruhr, Germany. He is Associate Editor of *Catalysis Today* and serves as a member of the Editorial Boards of several journals. He has published more than 400 journal articles/book chapters largely in the field of catalysis and holds numerous patents. Most recent honors include the Karl Ziegler award of the Max-Planck Society, Germany.

I. Introduction

Impetus for the utilization of supercritical fluids (SCFs) as media for chemical reactions originates from their unique solvent properties which have been convincingly applied and are now well-established in separation technology.[1,2] This technology takes advantage of the unusual properties of SCFs in the region near the critical point ($T_r \approx 1.0-1.1$ and $P_r \approx 1-2$),[3] where densities are a significant fraction of the liquid density. At these conditions, the fluid exists as a single phase, possessing favorable properties of both a liquid and a gas. The density is sufficient to afford substantial dissolution power, but the diffusivity of solutes in SCFs is higher than in liquids, and the viscosity is lower, enhancing mass transfer. Supercritical fluids also have unique properties in the sense that compounds which are insoluble in a fluid at ambient conditions can become soluble in the fluid at supercritical conditions,[4] or conversely, compounds which are soluble at ambient conditions can become less soluble at supercritical conditions.[5] It has been recognized for some time that the same properties that are advantages for separation (extraction, chro-

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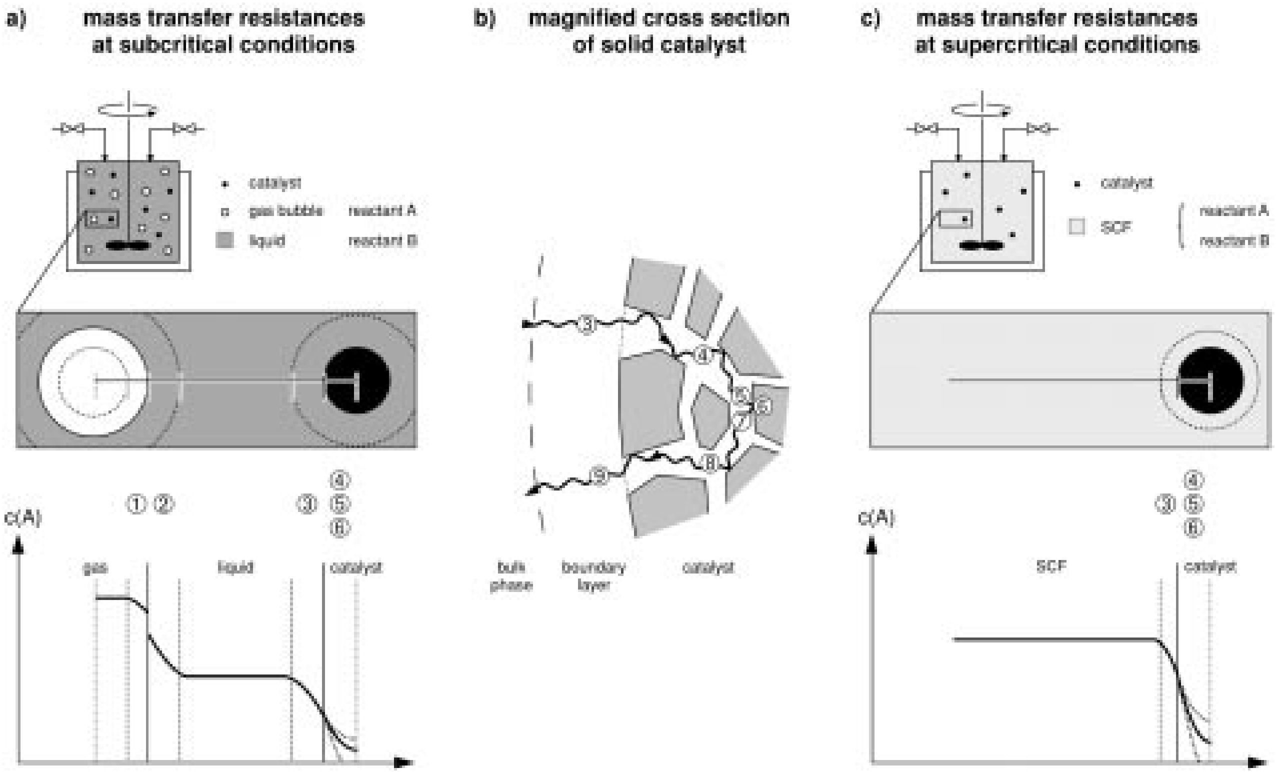

Figure 1. Sequence of physical and chemical steps occurring in heterogeneous catalytic gas/liquid reaction (e.g., hydrogenation of a liquid compound). Part a shows a representative section of the reactor content consisting of a gas bubble and a solid catalyst particle and corresponding mass-transfer boundary layers (resistances) at subcritical conditions. Part b provides a magnified cross section of the catalyst particle. A representative concentration profile of reactant A is depicted on the bottom. The following physical and chemical steps are relevant in the three-phase reaction: (1) diffusion of gaseous reactant A from bulk gas phase to the gas/liquid interface; (2) absorption of A at the gas/liquid interface and ensuing diffusion to the liquid bulk phase; (3) diffusion of reactants from bulk liquid phase through stagnant fluid film surrounding solid catalyst particle; (4) diffusion of reactants into porous network of the catalyst; (5) adsorption of reactant(s); (6) surface reaction; (7) desorption of products; (8) diffusion of products through porous network to outer surface of the catalyst; and (9) diffusion of products through boundary layer into bulk fluid. Part c shows a representative section of the reactor content, mass-transfer resistances, and a corresponding reactant concentration profile of the same reaction at supercritical conditions. Note that under supercritical conditions gas/liquid transfer resistance is eliminated (steps 1 and 2) and external fluid film diffusion resistance (step 3) is lowered due to lower viscosity of SCF.

matography, etc.) offer even more opportunities in terms of tuning reactions.[6,7] Conducting chemical reactions at supercritical conditions affords opportunities to tune the reaction environment (solvent properties), to eliminate transport limitations on reaction rates, and to integrate reaction and product separation. Reactions at supercritical conditions have been reviewed focusing on different aspects[6−17] over the past decade. The most comprehensive review, covering work on homogeneous and heterogeneous chemical reactions in and with supercritical fluids published up to 1993, has been given by Savage et al.[16] Here we focus on heterogeneous catalytic reactions, which possess several features which do not need special attention in homogeneous reaction systems. The work published up to early 1998 is covered. Special emphasis is given to the scope and limitations of the application of supercritical fluids in heterogeneous catalysis.

II. Physical and Chemical Processes in Heterogeneous Catalytic Reactions

By definition, in homogeneous catalysis reactants and catalyst form a single fluid phase, whereas in heterogeneous catalysis reactants and catalyst are present in different phases, rendering mass and heat transfer through interphases a necessary prerequisite for reaction.

When a heterogeneous catalytic reaction occurs, several physical and chemical processes must take place in proper sequence. This sequence of physical and chemical steps is schematically illustrated in Figure 1, parts a and b, for a solid-catalyzed gas/liquid reaction such as a hydrogenation of a liquid substrate. No matter how active a catalyst particle is, it can be effective only if the reactants (hydrogen, substrate) reach the external and internal catalytic surface. The catalytic process can be broken down into several steps: (1) transfer of gaseous reactant from bulk gas phase to gas/liquid interface (diffusion), and (2) from there to bulk liquid phase (absorption and diffusion); (3) transfer of both reactants (gas and liquid) from bulk liquid to external surface of the catalyst particle (diffusion through stagnant external film surrounding catalyst particle); (4) transfer of reactants into porous catalyst (internal diffusion); (5) adsorption of reactants following either step 3 or 4; (6) surface reaction; (7) desorption and transfer of product(s) by (8) internal and (9) external diffusion to bulk liquid or gas phase.

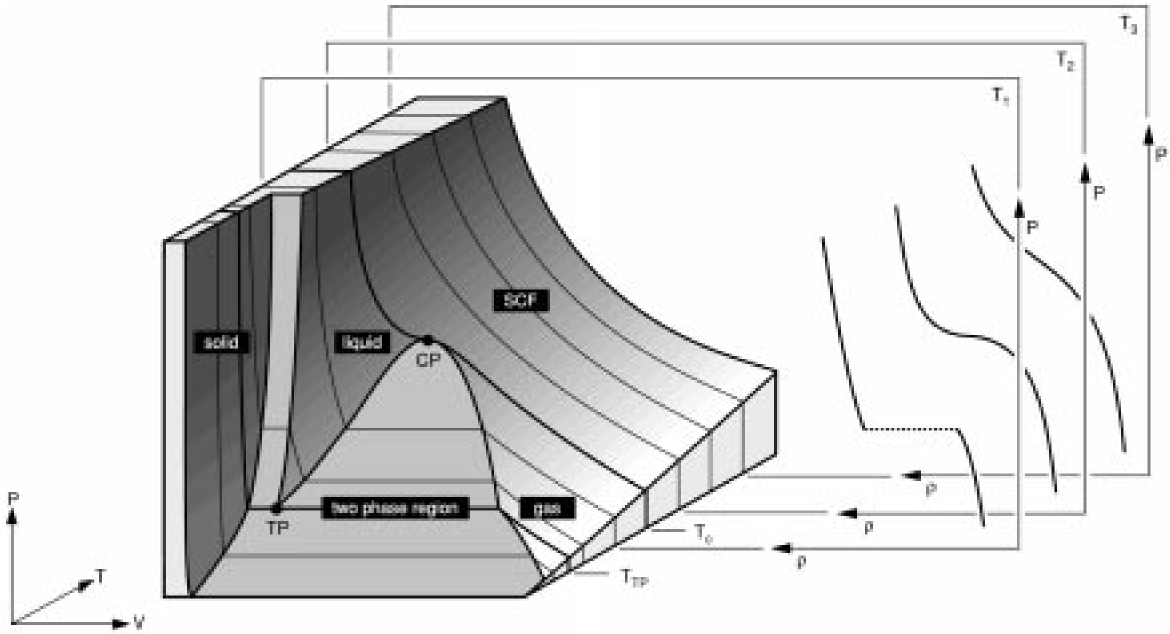

Figure 2. Phase diagram of a pure compound showing domains where solid, liquid, gas (vapor), and supercritical fluid exist. Isotherms T_2 ($T_2 > T_c$) and T_3 ($T_3 \gg T_c$) illustrate the pressure dependent density ρ of supercritical fluids which can nearly be adjusted from that of a vapor to that of a liquid. Note that the effect of pressure on density is greatest near the critical point, reflected by the greater slope of isotherm T_2 compared to that of T_3 which is farther from the critical temperature. Isotherm T_1 illustrates discontinuity in the density vs pressure function at subcritical conditions due to the phase change. TP stands for triple point; CP, critical point.

Figure 1c depicts the mass transfer resistances for the same reaction at supercritical conditions. Note that the gas/liquid resistance is eliminated under supercritical conditions. In principle, all the above steps can be affected either directly or indirectly by pressure, particularly when the reaction medium is changed from subcritical to supercritical. This provides an interesting potential for controlling rate and selectivity of heterogeneous catalytic reactions, which will be discussed in section IV and illustrated with examples in section VI.

III. Properties of Supercritical Fluids

A fluid is termed supercritical when its temperature exceeds the critical temperature (T_c). At this point the two fluid phases, liquid and vapor, become indistinguishable. Figure 2 illustrates the different domains in a phase diagram. Many of the physical properties of a supercritical fluid are intermediate between those of a liquid and a gas.[18−23] This holds true for properties of fluids which are decisive for mass and heat transfer (diffusivity, viscosity, thermal conductivity, heat capacity). At the critical point the isothermal compressibility of any pure fluid

$$\kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T \tag{1}$$

where ρ is density, is infinite and is very large under conditions usually met in practical applications of SCFs. Table 1 provides a rough comparison of the magnitude of some of these properties for liquids, gases, and supercritical fluids in the near critical region. Table 2 lists the critical data of SCFs most frequently used in chemical reactions. Critical temperature and pressure for other fluids are compiled in refs 20 and 24. As emerges from Table 1, diffusivity and viscosity of a supercritical fluid are more gaslike in the supercritical region, whereas density is comparable to liquid. Consequently a reaction which is diffusion-controlled in the liquid phase can be enhanced by conducting it at supercritical conditions, due to higher diffusivity and elimination of gas/fluid and fluid/fluid interphases. The unique property of an SCF is its pressure-dependent density, which can be continuously adjusted from that of a vapor to that of a liquid. This is illustrated by the isotherms T_2 and T_3 in Figure 2. Note that particularly in the region about the critical point large changes in fluid density and related properties such as materials solubility [20,25,26] are observed with small changes in pressure. These characteristics of SCFs provide the opportunity to engineer the reaction environment by manipulating temperature and pressure.

Table 1. Comparison of Magnitudes of Physical Properties of Liquids, Gases and Supercritical Fluids (SCFs) in the near Critical Region (Data Taken from Ref 1)

physical quantity	gas (ambient)	supercritical fluid (T_c, P_c)	liquid (ambient)
density ρ (kg m^{-3})	0.6−2	200−500	600−1600
dynamic viscosity η (mPa s)	0.01−0.3	0.01−0.03	0.2−3
kinematic viscosity ν^a (10^6 m^2 s^{-1})	5−500	0.02−0.1	0.1−5
diffusion coefficient D (10^6 m^2 s^{-1})	10−40	0.07	0.0002−0.002

[a] Kinematic viscosity was estimated from dynamic viscosity and density, $\nu = \eta/\rho$.

Table 2. Critical Data (Temperature, Pressure, and Density) of Supercritical Fluids Most Frequently Used in Chemical Reactions (Data Taken from Ref 24)

solvent	T_c, °C[a]	P_c, MPa[a]	ρ_c, kg m^{-3} [b]
sulfur hexafluoride (SF_6)	45.5	3.77	735
nitrous oxide (N_2O)	36.4	7.255	452
water (H_2O)	373.9	22.06	322
ammonia (NH_3)	132.3	11.35	235
carbon dioxide (CO_2)	30.9	7.375	468
methanol (CH_3OH)	239.4	8.092	272
ethane (C_2H_6)	32.2	4.884	203
ethene (C_2H_4)	9.1	5.041	214
ethanol (CH_3CH_2OH)	240.7	6.137	276
propane (C_3H_8)	96.6	4.250	217
propene (C_3H_6)	91.6	4.601	233
1-propanol ($CH_3CH_2CH_2OH$)	263.6	5.170	275
2-propanol ($CH_3CH_2(OH)CH_3$)	235.1	4.762	273
xenon (Xe)	16.5	5.84	1110

[a] The number of digits given indicates the estimated accuracy of this quantity. [b] Although values for the critical density are given to three decimal places, they cannot be assumed accurate to better than a few percent.

In many applications of SCFs dilute mixtures (solvent, reactant(s), product(s)) are important. All known applications of SCFs involve mixtures, where the solute is generally much less volatile and of higher molecular weight than the solvent. Such mixtures are termed attractive mixtures.[27] Dilute attractive mixtures are characterized by large and negative solute partial molar volumes and enthalpies near the solvent's critical point and over an appreciable range of supercritical pressures.

IV. Effect of Pressure on Heterogeneous Catalytic Reactions

A. Thermodynamics and Kinetics

Supercritical conditions frequently require relatively high pressure. Consequently, pressure effects on chemical equilibria and chemical reaction rates[28] have to be accounted for. Knowledge of the reaction volume ΔV_r, which is the difference between the partial molar volumes of the product(s) and those of the reactant(s), is crucial for predicting the effect of pressure on an equilibrium constant.

$$\left(\frac{\partial \ln K_x}{\partial P}\right)_{T,x} = -\frac{\Delta V_r}{RT} \tag{2}$$

$$\left(\frac{\partial \ln K_c}{\partial P}\right)_{T,c} = -\frac{\Delta V_r}{RT} + \kappa_T \sum \nu_i \tag{3}$$

Note that K_x is a mole fraction-based equilibrium constant, whereas K_c is the concentration-based equilibrium constant for which eq 2 has to be modified to include the isothermal compressibility (κ_T) of the reaction mixture and the stoichiometric coefficients ν_i (eq 3).

The effect of pressure on the chemical reaction rate is mostly described in the context of transition-state theory[29] used for interpreting the kinetics of elementary reactions. According to this theory, the magnitude and direction of the mole fraction-based rate constant k_x depends on the magnitude and sign of the activation volume $\Delta V^{\ddagger}$, which is defined as the difference between the partial molar volume of the activated complex and the sum of partial molar volumes of reactants.

$$\left(\frac{\partial \ln k_x}{\partial P}\right)_{T,x} = -\frac{\Delta V^{\ddagger}}{RT} \tag{4}$$

If the rate constant is related to a pressure-dependent measure of concentration:[30]

$$\left(\frac{\partial \ln k_c}{\partial P}\right)_{T,c} = -\frac{\Delta V^{\ddagger}}{RT} + \left(\frac{1-n}{P}\right)\left[1 - \left(\frac{\partial \ln \kappa_T}{\partial \ln P}\right)_{T,c}\right] \tag{5}$$

where n is the molecularity of the reaction.

Equations 4 and 5 have been derived assuming that the transition-state transmission coefficient is equal to unity, i.e., independent of pressure. From these equations it emerges that a negative $\Delta V^{\ddagger}$ results in a rate acceleration with increasing P, whereas with a positive $\Delta V^{\ddagger}$ the reaction rate is retarded. In high-pressure reactions in solution (liquid phase) the values of $\Delta V^{\ddagger}$ are typically in the range -30 to 30 cm^3 mol^{-1}, which represents approximately equal contribution from structure (volume changes in the activated complex as a result from bond formation or breakage or other mechanistic features) and solvation.[28] These values correspond to a rate acceleration or retardation of about a factor of 3.5 between atmospheric pressure and a pressure of about 100 MPa.[31] In an ideal situation, when there is no solvent contribution, knowledge of $\Delta V^{\ddagger}$, particularly for an elementary reaction, can be extremely valuable in terms of understanding the reaction mechanism. Near the solvent's critical point, values of $\Delta V^{\ddagger}$ are of the orders of liters per mole, owing to the large negative partial molar volumes of the reactants and transition states,[32] so that the solvation contribution is dominant. Consequently the $\Delta V^{\ddagger}$ values reported represent the pressure effect, but are generally not useful to extract some mechanistic information.

B. Local Enhancement of Density: Clustering

In most supercritical reaction mixtures, the solute(s) and the solvent molecules differ in size, shape, interaction strength, and polarity. Compared with a liquid medium, a SCF is much more compressible and has a larger free volume so that the attractive forces can move molecules into energetically favorable locations. A consequence of these features is the formation of a nonuniform spatial distribution of solvent molecules about a solute molecule. This phenomenon, which has been termed as local density enhancement,[33] clustering,[34] or molecular charisma[35] gives rise to interesting solvation effects not ordinarily found in liquid mixtures. Generally the characteristic energies for solute−solute and solute−solvent interactions are much stronger than those of solvent−solvent interactions and consequently the local environment around the solute can differ appreciably in density and composition from the bulk.[36] This phenomenon can affect the rates and selectivities of chemical reactions through both physical and chemical mechanisms.[37] Enhanced local density of solvent molecules about a solute may prevent solute−solute interaction, a scenario analogous to the "cage effect" [8,16,21,38−40] invoked to explain the behavior of some liquid-phase reactions. Alternatively, solute−solute clusters may form in which the local density of the solute molecules is higher than the bulk average solute density. These local-bulk anisotropy phenomena are unrelated to proximity to critical points, and make it possible to tailor the composition and density of local environments for specific reactions through the use of cosolvents. Tuning with cosolvents has its greatest effects when there is a specific interaction with a solute such as hydrogen bonding, charge-transfer complex formation, and dipole−dipole coupling.[33,41]

Local anisotropy phenomena also occur at supercritical fluid/solid interfaces as a consequence of different interaction strength (adsorption enthalpy) of solute (reactant), solvent and cosolvent with the solid surface. Fundamental knowledge of these interactions is important to understand the mechanism of solid-catalyzed reactions. Although there might be no reason to expect anomalous behavior in the kinetics of adsorption of a pure solvent near its bulk critical point onto any surface, the situation is very different in the case of trace solutes. If the cluster concept is mechanistically significant, the kinetics of solute (reactant) adsorption onto a surface would be notably depressed under near critical conditions, due to the severe constraints imposed on the solute by the surrounding cluster of solvent molecules. Unfortunately, there appears to be no fundamental work dealing with this aspect crucial for understanding catalytic surface reactions in solute−solvent (reactant-solvent) systems. Another possibility is that reactant−reactant (solute−solute) clustering can occur which also affects the adsorption process.

C. Phase Behavior and Solubility

To take advantage of the unique characteristics of an SCF reaction medium, it is necessary to be cognizant of the phase behavior[1,3,15,25,26,33] which is exhibited by the reaction mixture at high pressure. An interesting feature of using supercritical conditions for catalytic reactions is that all reactants can exist in a single homogeneous fluid phase, which eliminates mass-transfer resistances through interphases as encountered in multiphase systems. This feature together with the pressure-tunable solvent properties and the opportunity for easier separation of products can only be capitalized under supercritical conditions. Hence it is important to have knowledge of the boundaries of this single-phase, supercritical region. Identification of the supercritical fluid region is straightforward for a pure fluid, as represented by the phase diagram shown in Figure 2, but catalytic reactions will generally involve multicomponent systems for which the location of the phase border curves in pressure−temperature−composition ($P-T-x$) space may not be known. A further problem arises from the fact that the critical point of a reaction mixture is a function of its composition, which changes with the extent of reaction. Thus the critical point of the fluid in a reactor may change with time (batch reactor, autoclave) or with location (continuous fixed bed reactor). Consequently, an understanding of the phase behavior is a necessary prerequisite to make beneficial use of the supercritical state and for interpreting its effect on the rate and selectivity of a catalytic reaction. Experimentally determined critical data are however by far not available for all mixtures of interest, or the available data are confined to binary or ternary mixtures in a narrow concentration range. To fill this gap, there is continual research activity on the phase behavior and critical properties of binary mixtures. However, at this point there is no general equation satisfactorily describing binary phase diagrams.

Most reactions involve dilute mixtures composed of small-molecule volatile supercritical solvent and one or more solutes of low volatility differing from the solvent in mass, size, interaction strength, polarity, and shape. Solute solubility depends exponentially on density[42] and is therefore orders of magnitude larger in supercritical fluids than in ideal gases. As a consequence of the high compressibility of fluids near the critical point, their density and dissolving power can be tuned sensitively through small changes in pressure. Estimation of the solubility of the reactant(s) in supercritical solvents or in mixtures containing a component at supercritical conditions is key to successful use of supercritical reaction media. For these predictions, the physical properties of the solvent and the solute and an equation of state are necessary.[18,19,39] Unfortunately simpler forms of equations such as the ideal gas, truncated virial equation of state, and the basic form of the cubic equation of state, the van der Waals equation, are not reliable in describing fluids at high pressures. Modified cubic equation of states such as the Redlich−Kwong or the Peng−Robinson equations of state which incorporate temperature-dependent attractive terms are more successful. These equations of state are used to describe not only single fluids but also multicomponent fluid mixtures. For the latter the success of the equation depends on the use of proper mixing rules and assignment of interaction parameters.

Employing a cosolvent which undergoes a strong specific interaction (e.g., hydrogen bonding) with a solute provides an elegant and powerful tool to tune solute solubilities. Figure 3 illustrates the effect of basic cosolvents on the solubility of the protic solvent naphthol in supercritical ethane.[37,41] Unfortunately only very limited knowledge is presently available to make proper use of this potential tool. However, progress in understanding the molecular interactions involved will undoubtedly lead from empirical trial and error methods to rational design of solute−solvent−cosolvent systems.

D. Mass and Heat Transfer

In heterogeneous catalysis information on transport properties such as diffusivity, viscosity, and thermal conductivity is crucial for understanding a reaction system. A well-known advantage of supercritical fluids compared to ordinary liquids is that

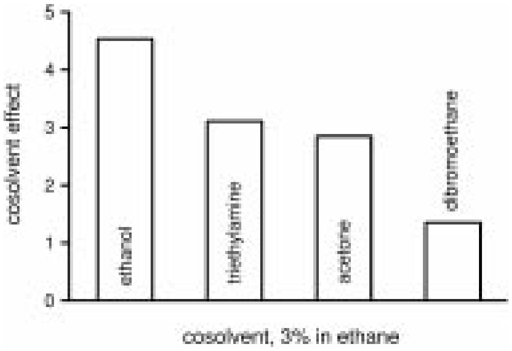

Figure 3. Effect of various basic cosolvents, capable of accepting protons, on the solubility of naphthol in supercritical ethane at 10 MPa and 50 °C. The cosolvent effect is defined as relative increase in solubility that comes about when the SCF is modified with cosolvent. (Reproduced with permission from ref 37.)

diffusion coefficients in supercritical fluids are higher than in liquid. This together with the elimination of interphases, which may exist in multicomponent systems under ordinary conditions, results in significantly enhanced mass transfer under supercritical conditions. The available data on diffusivity[20,22,43] is very limited, but recent research is expanding the database for binary diffusion coefficients and exploring the influence on solute diffusivities. The limitations of existing methods for correlating diffusivities such as the hydrodynamic Wilke–Chang correlation, Batchinski–Hildebrand free volume theories, or the dense gas Enskog relationship based on the hard sphere theory and its modifications have been discussed by Shenai et al.[44] Their data for the diffusivity of selected organic compounds in carbon dioxide, and in carbon dioxide/methanol and carbon dioxide/acetone mixed solvents indicate that both the increased local density of solvent around the solute in the pure solvent case and the preferential attraction of the cosolvent (methanol or acetone) around the solute in the mixed solvent systems significantly influence the diffusion of the solute.

The dynamic viscosity η of SCFs shows a weak deviation from normal behavior in the immediate vicinity of the critical point.[45] The viscosity of a supercritical fluid is comparable to that of the gas at the same temperature, but the density is at least 2 orders of magnitude higher (see Table 1). This explains why the kinematic viscosity $\nu = \eta/\rho$ is very low in the critical region, which is advantageous for mass transfer, since natural convection effects are inversely proportional to the square of the kinematic viscosity.[46]

V. Experimental Laboratory Techniques

A. Reactors

Typically reactions at supercritical conditions require pressures up to 40 MPa. The potential danger of such conditions should never be ignored and full safety precautions should be made for all experiments. For heterogeneous catalytic reactions two principal reactor types are suitable, batch reactors (autoclaves) or continuous flow reactors. Figure 4 shows schematically the most frequently used reactor types for the study of heterogeneous catalytic reactions at supercritical conditions.

1. Batch Reactors

Various batch reactors (autoclaves) suitable for conducting heterogeneous catalytic reactions at pressures and temperatures generally required for near critical or supercritical conditions are described in the

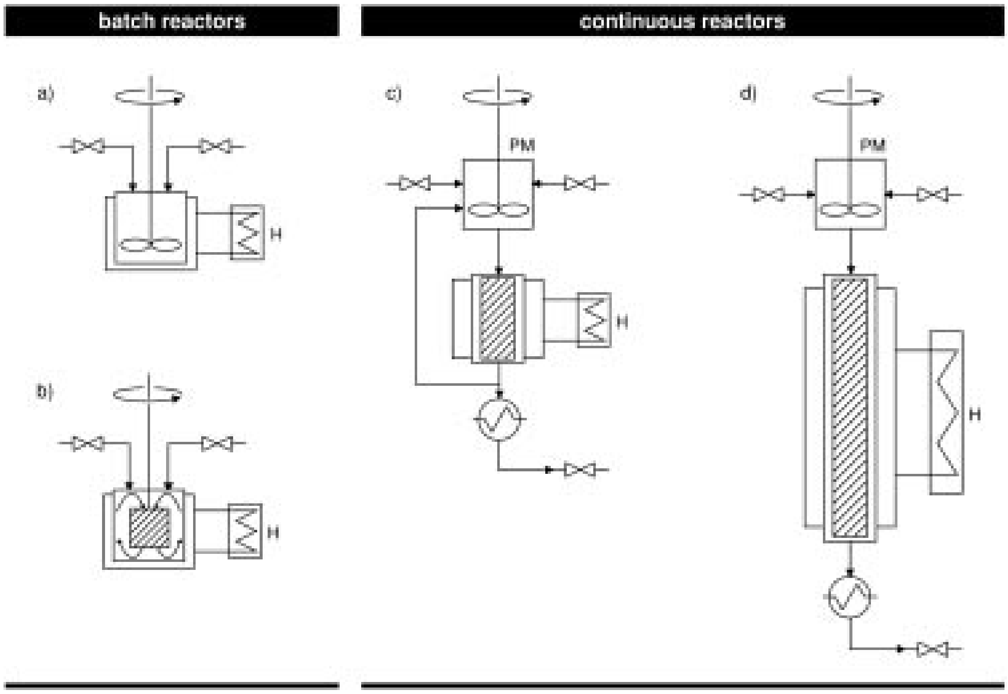

Figure 4. Laboratory reactors suitable for the study of heterogeneous catalytic reactions at supercritical conditions: (a) stirred autoclave, (b) stirred autoclave with internal recycle, (c) differential (gradientless) recycle reactor, and (d) continuous flow reactor. PM stands for premixing chamber; H, heat exchanger.

literature.[7,47−50] Although most of the work described in the literature has been performed in batch reactors which do not allow the reaction to be monitored visually, the installation of a window is highly recommended.[51−53] The window allows one to confirm that the reaction is single phase—a necessity for reactions near the critical point. Under these conditions changes in the composition of the reaction mixture due to conversion can easily induce phase changes. Another problem inherent to batch reactors is the external mass transfer from the fluid phase to the external catalyst surface. This mass transfer is greatly influenced by the mixing, i.e., the relative velocity of the catalyst particles to that of the surrounding fluid. Thus optimal conditions for efficient external mass transfer require not only high diffusivity and low viscosity of the fluid, but also large difference between fluid velocity and velocity of catalyst particle movement. Problems in kinetic measurements imposed by external mass transfer can be minimized by applying a batch reactor with internal recycle,[54] where the reacting fluid flows through a fixed catalyst bed.

2. Continuous Reactors

The low viscosity and efficient mass- and heat-transfer properties of supercritical fluids lend them particularly to the use of flow systems. Most suitable for kinetic measurements is the differential (gradientless) recycle reactor.[7,55,56] At sufficiently high internal recycle ratio (recycle flow/feed flow > 20) the composition of the reaction mixture can generally be considered to be uniform and reaction rates can be evaluated as with a continuous stirred tank reactor (CSTR). Although the differential recycle reactor allows the problems arising from external mass transfer and changing composition of reaction mixture to be surmounted, it has its limitation for the investigation of complex reaction systems due to the inherently low conversion in such reactors.

Many of the studies listed in Table 3 have been conducted in continuous tubular fixed-bed reactors.[50] In the tubular reactor the composition of the reaction mixture changes along the length of the reactor, with the implication that the phase behavior may also change, when working near the critical point. Visual monitoring of the reacting phase is generally not possible, thus leading to some uncertainty concerning the phase behavior. However, the extremely good mass- and heat-transfer properties and the simple construction of tubular fixed-bed reactors render them ideal for heterogeneous reactions, particularly for technical applications, both on grounds of safety (low reactor volume) and costs.

B. Phase Behavior

Knowledge of the phase behavior is a necessary requirement for designing heterogeneous catalytic reactions at near critical or supercritical conditions. Due to the limited predictability of theoretical calculations[39] of phase behaviors (cf. section IV.C) experimental measurements are indispensable. The different methods used to measure high-pressure phase equilibria have been the subject of several reviews.[36,57,58] The methods can be classified as "analytical methods" which involve the direct determination of the compositions of coexisting phases, and "synthetic methods" which entail the preparation of mixtures of known composition and the observation of their phase behavior in an equilibrium cell. The observation of the appearance or disappearance of a phase can be detected visually (visual synthetic method) or by other means, e.g., by analyzing the slope of the pressure vs volume curve of the mixture. Various phase-equilibrium apparatus based on different methods have been described in the literature. A very versatile high-pressure apparatus, which can be used for phase-equilibrium measurements with the analytical isothermal method as well as with the nonvisual and the visual synthetic method has been described recently by Dohrn and Haverkamp.[57] They compared the different techniques and tested them for the measurement of the phase behavior of systems containing CO_2, styrene, and a monomer. The apparatus was found to be suitable for measurements in the entire concentration range, including the determination of critical curves in multicomponent systems.

C. Spectroscopy

Spectroscopic studies that probe molecular scale interactions have played a major role in unraveling information on solvation and effects of local molecular phenomena (short ranged solute−solvent, solute−cosolvent, and solute−solute interactions) which can affect reaction rates. Together with theoretical and computational investigations they led to the ideas of local densities and local compositions around solutes (reactants) in supercritical solutions that are different than in the bulk. This development has been reviewed recently by Brennecke.[8] Several spectroscopic techniques such as ultraviolet absorbance, fluorescence emission, infrared, electron spin resonance, and nuclear magnetic resonance spectroscopy are amenable to high-pressure investigations. A survey of suitable techniques has been given by Hubbard and van Eldik in their review on effects of pressure on inorganic reactions.[59]

Vibrational spectroscopy (FTIR, FT-Raman) has been used successfully to monitor chemical processes in supercritical solutions. In situ monitoring is not only key to kinetic measurements but also to real time optimization of the tunable properties of supercritical fluids. Experimental techniques have been covered in several reviews[13,59−61] and will not be discussed here.

With regard to the in situ monitoring of heterogeneous catalytic surface reactions by vibrational spectroscopy, considerable problems arise at high pressures since the high gas concentrations together with the long beam path lengths give rise to intense gas-phase absorption bands making their subtraction from the in situ spectra unreliable. To circumvent this problem Moser and co-workers [62] have used an in situ cylindrical internal reflection infrared technique (CIR−FTIR), which permits the real-time analysis of supercritical fluids and heterogeneous catalytic processes at temperatures up to 500 °C and 6.8 MPa. The potential of CIR−IR was demonstrated in an in-situ study of heptane catalytic cracking at 475 °C and at subcritical and supercritical conditions which will be discussed in section VII.C.

Concluding, we can state that several spectroscopic techniques are amenable for investigating fluids at pressures generally required for supercritical conditions (<40 MPa). However, in situ monitoring of surface reaction under such conditions is still in its infancy. This is probably the most difficult and most crucial hurdle to take toward progress in the fundamental understanding of supercritical fluid−solid (catalyst) interactions and surface reactions.

VI. Opportunities for Supercritical Fluid Application

Proper use of supercritical fluids in heterogeneous catalysis can afford: enhancement of the reaction rate (A), control of selectivity (B), enhanced mass and heat transfer (C), increased catalyst lifetime and regeneration (D), or facilitate easier separation (E), and process intensification (F). Moreover, supercritical fluids offer several unique opportunities in catalyst preparation (G).

A. Effect of Pressure on Rate

A significant part of the effect of pressure on the reaction rate in the supercritical region is assignable to the thermodynamic pressure effect described in section IV.A (eqs 4 and 5), albeit other reasons such as enhanced mass transfer, or higher reactant solubility can also contribute to the increase of the global reaction rate. Note that for a reactant dissolved in a supercritical solvent, the pressure effect on the reaction rate constant reflects the relative strengths of the intermolecular interactions (both the repulsive size effects and the attractive interactions) between reactants and the transition state with the SCF solvent. This situation is very different from that in liquid solvents, where partial molar volumes are comparably small, so that the pressure effect on rate constants can be used to gain information on the size change occurring when going from the reactants to the transition state.

B. Control of Selectivity

For a network of parallel or competing reactions, the thermodynamic pressure effect on each of the individual rate constants may be different due to different activation volumes $\Delta V^{\ddagger}$. Thus increased pressure may favor one of the reactions over the others. This offers some potential to enhance the selectivity to the desired product by operating at the appropriate pressure and temperature, where the desired reaction is favored compared to the unwanted side reactions. However, this method of controlling selectivity is rather demanding, because the activation volumes of the various reactions need to be known. A handier tool for controlling selectivity originates from the fact that under supercritical conditions the reaction mixture can be single phase, which allows an independent control of the reaction parameters, such as temperature, pressure, and concentrations. Under subcritical multiphase conditions this control is impaired by the different behaviors exhibited by the phases. Further possibilities for selectivity control are linked with tuning of solute−solvent interactions (change of local density, clustering) and the use of cosolvents which through specific interactions (usually hydrogen bonds) with a transition state or a product can alter rates[63] and product distributions.[64]

C. Enhanced Mass and Heat Transfer

In the supercritical region diffusivities are greater and viscosities lower than they are in liquids (cf. section IV.D). As a consequence mass transfer controlled liquid reactions may be accelerated by working under supercritical conditions. Supercritical fluids possess significantly higher thermal conductivity than corresponding gases and consequently heat transfer is enhanced in these media. This effect can be utilized for better heat removal in highly exothermic gas-phase reactions, where careful temperature control is essential for selectivity and product stability.

D. Catalyst Lifetime and Regeneration

Supercritical fluids exhibit considerably higher solubilities than corresponding gases for heavy organics which may act as catalyst blocking agents and thereby deactivate catalysts and promote coking. This deactivation may be suppressed by changing working conditions from gas phase to dense supercritical medium.[65,66] Furthermore enhanced diffusivity can accelerate the transfer of poisons from the internal and external catalyst surface. Regeneration of catalysts deactivated by coking can be accomplished by extracting the carbonaceous deposits from the catalyst surface.

E. Facilitated Separation

The pressure tunability of the solubility of solutes near the critical point may allow the easy precipitation of the product, if it is less soluble than the reactants. This is used to advantage in the polymerization of ethylene, where polymers will fall out of the supercritical solution when they reach a certain molecular weight, corresponding to the solubility limit. In an equilibrium-limited reaction, this continuous removal of the product would enhance conversion. Conversely, a slight release in pressure after the reactor will precipitate unused reactant(s), allowing their reintroduction into the feed (reactant recycling). The same strategy is also applicable for separating product(s) from solvent(s).

F. Process Intensification

Higher reaction rates and facile product separation allow the construction of continuous reactors, considerably smaller than required for conventionally operated continuous reactors of equal performance.[50] This opportunity provides interesting advantages concerning process safety and space requirement of chemical plants.[67,68]

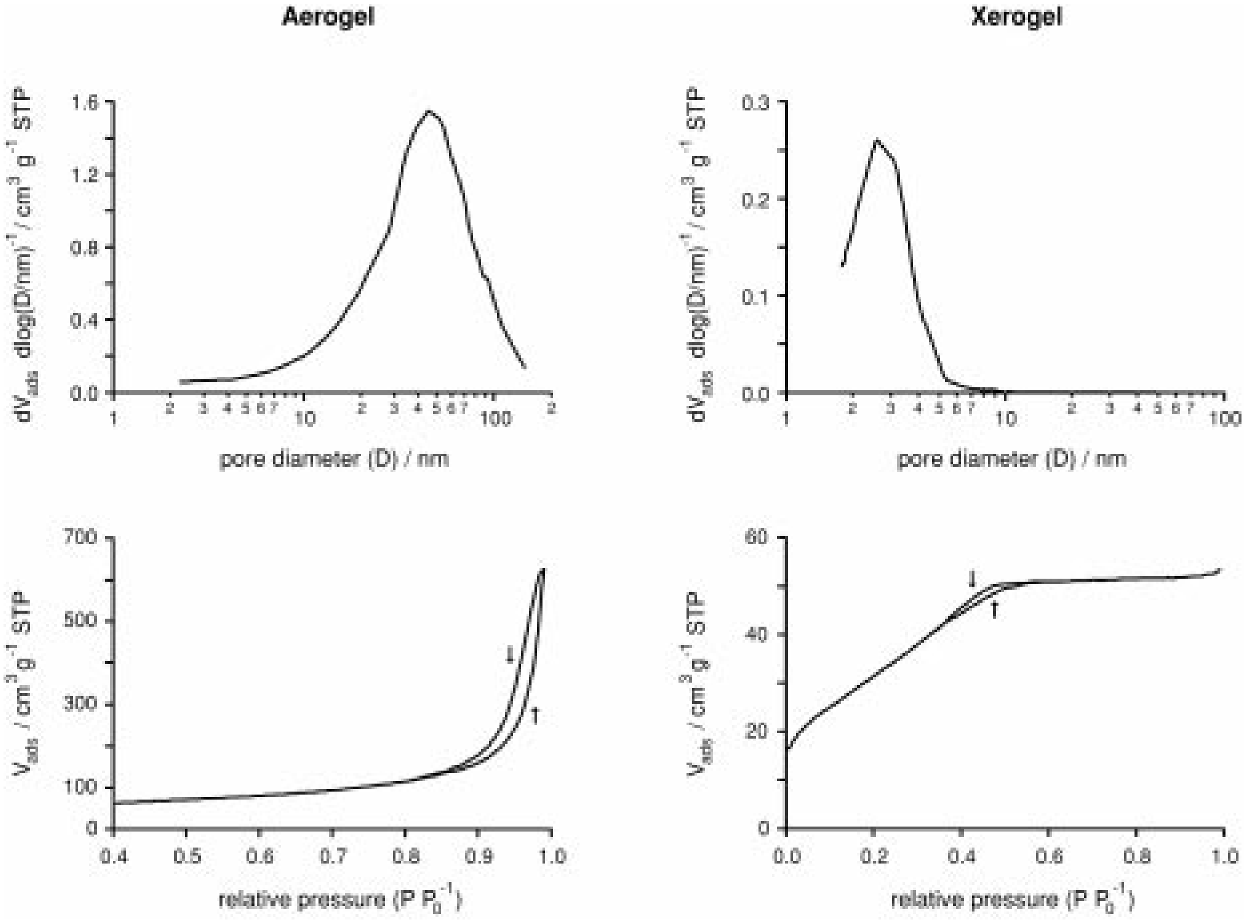

Figure 5. Effect of supercritical drying on the final textural properties of a sol–gel-derived catalyst (vanadia–niobia–titania with 20 wt % V_2O_5 and 6 wt % Nb_2O_5). The graphs show textural properties of this catalyst dried under supercritical conditions (high-temperature aerogel) and under normal conditions (xerogel). The curves are derived from nitrogen physisorption at 77 K after calcination of the catalysts in air at 200 °C. Top: differential pore size distributions; bottom: adsorption (↑)/desorption (↓) isotherms. (Adapted from ref 70).

G. Catalyst Preparation

Supercritical fluids provide unique opportunities in the preparation of catalytic materials and supports. Supercritical drying is crucial in the preparation of aerogels[69] via the solution sol–gel route. Drying of a sol–gel product by evaporation of the liquid (solvent) entrapped in the tenuous sol–gel network results in severe structural damages due to the acting capillary pressure when the liquid recedes into the sol–gel body. This capillary stress can be circumvented either by transferring the entrapped solvent into the supercritical state or by replacing the solvent typically with supercritical CO_2, thus eliminating any liquid–vapor interface inside the sol–gel product during solvent extraction. Figure 5 illustrates the effect of supercritical drying on the final structure of a gel.[70] The sol–gel method combined with ensuing supercritical drying provides unique opportunities for the preparation of mixed oxides and metal/metal oxide catalysts. For further information the reader is referred to recent reviews.[69,71,72]

Another interesting feature of supercritical fluid application in the synthesis of catalytic materials arises from the highly adjustable properties of supercritical fluids with small changes in temperature or pressure. This feature intimates the possibility of controlling the particle size and morphology of catalytic materials. Other particle-forming techniques involving the application of supercritical fluids entail the rapid expansion of supercritical solutions (RESS)[2,73] and the supercritical antisolvent (SAS)[74–76] technique. RESS is based on the rapid depressurization of a supercritical fluid phase in which the solute(s) of interest are dissolved, whereas in SAS the solute(s) are dissolved in a liquid organic phase and precipitation is achieved by bringing this solution into contact with a supercritical fluid having a low affinity for the solutes and a large mutual solubility with the organic phase. Although both techniques have not yet found significant application in the preparation of catalytic materials, they promise interesting opportunities for the control of particle size and morphology.

VII. Present Status of Research on Heterogeneous Catalytic Reactions in Supercritical Fluids

As emerges from section VI, the potential of supercritical fluids can be capitalized in various ways when designing heterogeneous catalytic reactions. Since many of the effects described in section VI may be operating in concert, proper assignment of an observation to a specific physical or chemical phenomenon is often only possible for simple well-characterized reactions. This renders heterogeneously catalyzed reactions less suitable for fundamental studies than homogeneous reactions. However, despite this inherent difficulty many interesting works applying supercritical fluids in heterogeneous catalysis have been published. Table 3 provides an overview of these studies, indicating the conditions and main features of the various investigations. For discussion we classify the various reactions according to Table 3. Supercritical water oxidation has been intentionally discussed briefly because it has been covered in a recent review.[12] Several classical industrial processes are conducted under supercritical conditions, such as ethylene polymerization,[77] ammonia synthesis,[78] and methanol synthesis.[79] They have been extensively reviewed and are therefore not listed in Table 3.

A. Alkylation

The effect of supercritical fluid operation on catalyst deactivation has been studied by Gao et al.[80,81] using the alkylation of benzene with ethylene on a Y-type zeolite as an example. Catalyst deactivation due to coke formation is an inherent problem of this reaction system. The authors compared the reactions under three different phases, in the liquid phase, at supercritical conditions of the reaction mixture, and under conditions where $scCO_2$ was used as a solvent. The experimental results showed that both supercritical operation modes resulted in significantly slower catalyst deactivation and improved selectivity to ethylbenzene due to suppressed formation of undesired xylenes. The slower catalyst deactivation was traced to the higher solubility and enhanced diffusivity of polynuclear aromatic compounds, which deposited on the catalyst surface and acted as precursors to coke formation, in supercritical reaction mixture and $scCO_2$. The higher selectivity of the reaction in supercritical media was attributed to faster removal of the product ethylbenzene from the catalyst surface due to higher diffusivity. Ethylbenzene can undergo isomerization to xylenes in a consecutive reaction step.

Li Fan et al.[82] investigated the effect of the supercritical fluid on alkylation reactions on Y-type zeolites. Two types of alkylation reactions were studied, isopentane ($T_c = 188$ °C, $P_c = 3.3$ MPa) with isobutene and isobutane ($T_c = 135$ °C, $P_c = 3.6$ MPa) with isobutene. The paraffins acted as both reactant and supercritical fluid. The supercritical-phase reaction exhibited higher catalyst activity, along with a remarkably longer lifetime, compared to the reaction in the liquid or gas phase. Figure 6 illustrates the phase effect on catalyst activity and stability. Very high initial activity, where the yield of alkylate (2,2,4-trimethylpentane) was as high as 70%, appeared at the liquid-phase reaction, but the activity declined to zero when the accumulated feed amount of olefin reached 15 mmol/cat g. Similarly, obvious deactivation was also observed for the gas-phase reaction. However, for the supercritical reaction catalyst deactivation was suppressed. Although the yield of alkylate decreased with time-on-stream, isobutene conversion remained almost 100%. For another liquid-phase reaction whose reaction conditions (125 °C, 5.0 MPa) were only slightly different from those of the supercritical phase reaction, it exhibited deactivation behavior similar to that of the gas-phase reaction. These phenomena were attributed to the deactivation of the active Lewis acidic sites of the catalyst through oligomerization forming high molecular weight olefins. Supercritical fluid was able to extract in situ and transport these high molecular weight olefins, thus extending catalyst lifetime. Several aspects of the work have been debated in a recent correspondence[83] and corresponding rebuttal.[84]

A comparative study of solid acid catalyzed 1-butene/isobutane alkylation in supercritical-phase, gas-phase, and liquid-phase has been reported by Clark and Subramaniam.[85] They showed that using molar excess of a low T_c diluent such as $scCO_2$, alkylation can be performed at supercritical conditions at temperatures lower than the critical temperature of isobutane (<135 °C), resulting in virtually steady alkylate (trimethylpentanes and dimethylhexanes) production for experimental durations of nearly 2 days. Although the alkylate yields (roughly 5−10% of C_{5+} products) and the 1-butene conversions (20%) were low when compared to conventional alkylate yields (>70%) and conversion (∼100%), the demonstration of steady alkylate production is a significant result. At the high temperatures (> 135 °C) required for supercritical operation without carbon dioxide, cracking and coking reactions were dominant. The authors concluded that the carbon dioxide based, fixed-bed, solid acid alkylation process shows promise as an environmentally safer alternative to conventional alkylation that employs liquid acid. However, a final assessment of the suitability of such a process certainly requires considering the extra costs associated with the high-pressure processing and carbon dioxide recycle.

Hitzler et al.[86] investigated continuous Friedel−Crafts alkylation of mesitylene ($C_6H_3(CH_3)_3$), and anisole ($C_6H_5OCH_3$), with propene or propan-2-ol in supercritical propene or $scCO_2$ using a polysiloxane-supported solid acid catalyst (DELOXAN, Degussa AG) in a small fixed-bed reactor (10 mL volume). For mesitylene alkylation with supercritical propene the selectivity to the monoalkylated product (1-isopropyl-2,4,6-trimethylbenzene) was significantly lower compared to alkylation with propan-2-ol in $scCO_2$, due to the formation of significant amounts of the dialkylated product and dimers of propene. Albeit the work clearly demonstrates the feasibility of continuous and sustainable Friedel−Crafts alkylation in supercritical fluid solution, no comparison was made with continuous alkylation in a conventional solvent using the same catalyst. Thus it is difficult to judge the technical potential of continuous alkylation from this work.

B. Amination

Fischer et al.[87] investigated the influence of pressure on conversion and product selectivity of the amination of amino-1-propanol with ammonia over a Co−Fe catalyst. The experiments, which were conducted in a continuous tubular reactor at 195 °C

Table 3. Survey of Heterogeneous Catalytic Reactions Carried out under Supercritical Conditions or in SCF Solvents (Work Published Prior to Early 1998 Is Considered)

reaction	catalyst	solvent	T, °C	P, MPa	r^a	S^b	a^c	ref(s)
A. Alkylation								
benzene and ethylene	Y-type zeolites		250−285	7.0−8.0	↑	↑	↑	80,81
isopentane and isobutene	H-USY, Y-type zeolite	isopentane	50−200	3.5−4.6	↑		↑	82−84
isobutane and isobutene	H-USY, Y-type zeolite	isobutane	50−140	3.5−5.0	↑		↑	82−84
1-butene and isobutane	zeolite H-USY, sulfated zirconia	CO_2	50−140	3.45−15.51			↑	85
mesitylene and propene	polysyloxane (DELOXAN) supported solid acid	propene	160−180	20.0				86
mesitylene and propan-2-ol	polysiloxane (DELOXAN) supported solid acid	CO_2	200−300	15.0−20.0				86
B. Amination								
amino-1-propanol	Co-Fe	NH_3	195	5.0−13.5		↑		87
C. Cracking								
heptane	promoted Octacat (H-Y zeolite)	heptane	325	3.4			↑	62
D. Disproportionation								
toluene to *p*-xylene and benzene	zeolite (ZSM-5)		320−325	3.36−5.6		↑	↑	88
1,4-diisopropylbenzene to cumene and 1,3,5-triisopropylbenzene	zeolite (type 13 NaHX)	benzene, *n*-pentane	260	20.0			↑	7,89,91
ethylbenzene to benzene and diethylbenzene	zeolites (USY, H-ZSM-5, H-mordenite), zeolite-HY	butane, pentane	300−400 >550	5.0			↑	56,91,92
E. Esterification								
oleic acid and methanol	K2411 sulfonic macroporous ion exchange resin	CO_2	40−68	0.95−1.3	↑			93,94
F. Fischer−Tropsch Synthesis								
CO and H_2 to liquid hydrocarbons	Ru 2% on Al_2O_3, Co on SiO_2, Fe	*n*-hexane	240	4.5	↓^{d}	e	↑	95,96,99,141
CO and H_2 to liquid hydrocarbons with addition of 1-olefins to produce wax	Co-La or Co on SiO_2 gel, Ru/Al_2O_3	*n*-pentane	210−240	4.5	↓^{d}	↑	↑	97−99
CO and H_2 to liquid hydrocarbons	100 Fe/5 Cu/4.2 K/25 SiO_2	propane	250	5.5		↑		100,101
CO and H_2 to liquid hydrocarbons	Fe	*n*-hexane	240	3.5−7.0				102
G. Hydrogenation								
fats and oils	5% Pd on C, 3% Pd on aminopolysiloxan	propane	50−100	7.0−12.0	↑	↑		103,104
fats and oils	Pd or Pt on DELOXAN support	CO_2	60−160	8.0−16.0	↑	↑		105,106
acetophenone	5% Pd APII DELOXAN	CO_2	90−300	12.0	↑	↑		107
cyclohexene	5% Pd APII DELOXAN, 5% Pt APII DELOXAN	CO_2, propane	40−320	6.0−12.0	↑			107
1,2-(methylenedioxy)-4-nitrobenzene	1% Pd DELOXAN	CO_2	90	14.0	↑			107
m-cresol, benzaldehyde, propionaldehyde, acetophenone, cyclohexanone, cyclohexanole, furan, nitrobenzene, *N*-benzylidenemethylamine, 2-butanone oxime, 1-octyne, 1-octene, cyclohexene, isophorone	various noble metal catalysts on DELOXAN aminopolysiloxane support	CO_2, propene						108
ethyl pyruvate to (R)-ethyl lactate	$Pt/\gamma\text{-}Al_2O_3$ and cinchonidine as modifier	ethane, propane	40−100	7.0−25.0	↑	↑		109,110
double bonds of unsaturated ketone	Pd/Al_2O_3	CO_2	150−220	12.0−17.5				54,55
dimethylamine to dimethylformamide	sol−gel $RuCl_2X_2$, X = $PMe_2(CH_2)_2Si(OEt)_3$	CO_2						111−116
H. Isomerization								
1-hexene to 2-hexene (*cis*/*trans*) and 3-hexene	$\gamma\text{-}Al_2O_3$/Al-metal shell catalyst		220−250	5.0−80.0	↑	↑↑^{f}	↑	7,65,89,90
1-hexene	$Pt/\gamma\text{-}Al_2O_3$	CO_2 and cosolvents *n*-pentane, *n*-hexane	250	18.0	↑	↑↑^{f}	↑	66,125−136
1-hexene to olefinic oligomers	$Pt/\gamma\text{-}Al_2O_3$		281	27.7				131
xylene isomerization to *p*-xylene	solid acid catalyst, various molecular sieves		320	3.2	↑		↑	137
I. Oxidation^g								
toluene to benzaldehyde	Co/Al_2O_3	CO_2	20−220	8.0		↑		138
propene to propylene glycol	$CaI_2/CuI/Cu_2O$ on MgO or γ-alumina		70−400	>7	↓	↑		139,140
isobutane to *tert*-butyl alcohol	SiO_2-TiO_2, Pd on carbon		153	4.4−5.4	↑		↑	141,142

[a] Change of reaction rate in the supercritical region with respect to subcritical conditions (↑ increase, ↓ decrease). [b] Change of selectivity in the supercritical region with respect to subcritical conditions (↑ increase, ↓ decrease). [c] Change of catalyst lifetime in the supercritical region with respect to subcritical conditions (↑ increase, ↓ decrease). [d] Higher olefin content. [e] Versus gas. [f] Changes cis/trans, double bond, and side reactions. [g] Oxidations in supercritical water (SCWO) have intentionally been omitted since they have been reviewed recently by Ding et al.[12]

and a molar feed ratio of reactants R−OH/NH_3 = 1:20 in the total pressure range 5.0−13.5 MPa, indicated a striking change of the selectivity to the desired product 1,3-diaminopropane from 4% to 40% in the

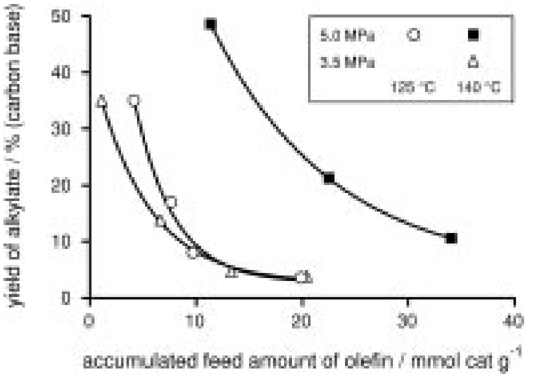

Figure 6. Effect of the fluid state on catalyst activity and stability during alkylation of isobutene with isobutane over commercial H-USY zeolite catalyst. Conditions: isobutene/isobutane 1:50, modified space time $W/F = 40$ g h mol^{-1}; (■) supercritical conditions (5.0 MPa, 140 °C); (○) liquid phase (5.0 MPa, 125 °C); (△) gas phase (3.5 MPa, 140 °C). (Reprinted from ref 82. Copyright 1997 American Chemical Society.)

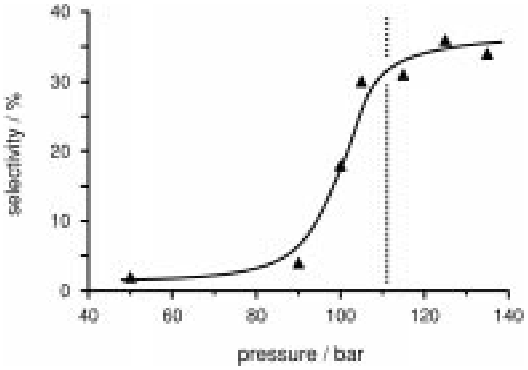

Figure 7. Influence of pressure on conversion and selectivity in catalytic amination of amino-1-propanol with ammonia over a Co−Fe (95/5) catalyst. Note the 10-fold increase of selectivity to 1,3-diaminopropane near the critical region of ammonia. Conditions: continuous tubular reactor, 195 °C, molar feed ratio of reactants R-OH/NH_3 1:40, total pressure range 5.0−13.5 MPa. Dashed line indicates critical pressure of NH_3. (Taken from ref 87.)

near critical region of ammonia ($T_c = 132$ °C, $P_c = 11.4$ MPa). Compared to selectivity, corresponding changes in conversion were small. The observed behavior is shown in Figure 7.

C. Cracking

Dardas et al.[62] used an in situ cylindrical reflectance infrared technique (CIR−IR) to study supercritical *n*-heptane cracking. In the supercritical regime heptane was found to undergo alteration of the IR absorption frequency of the C−H bonds. In situ CIR−IR indicated an increased heptane concentration within the pores of a commercial catalytic cracking Y-type zeolite during cracking at supercritical conditions. Results of CIR−IR analysis of catalytic cracking of heptane at 475 °C and at subcritical and supercritical conditions (Figure 8) showed that (i) a significant number of Brønsted acid sites and terminal silanols are consumed during catalytic cracking, (ii) new spectral bands appear between 3500 and 3100 cm^{-1}, corresponding to the interactions of the acid sites with the reactant and products (paraffin and olefins), and (iii) acid sites regained a significant percentage of their initial concentrations during supercritical cracking, indicating that the catalyst starts recovering its activity under these process conditions.

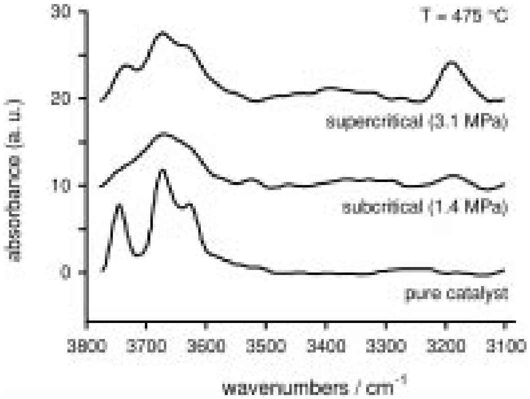

Figure 8. Cylindrical internal reflection infrared (CIR−FTIR) investigation of hydroxyl spectral region of a commercial catalytic cracking H-Y type zeolite (promoted Octacat) in the working state, i.e., during *n*-heptane cracking at 475 °C at subcritical (1.4 MPa) and supercritical (3.1 MPa) conditions. Conditions: heptane time-on-stream, 240 min for subcritical and 260 min for supercritical conditions; heptane residence time 0.50 s. (Reprinted with permission from ref 62. Copyright 1996 Academic Press, Inc.)

D. Disproportionation

Collins et al.[88] studied the disproportionation of toluene to benzene and a mixture of the three xylene isomers on an unmodified ZSM-5 catalyst in a differential reactor. The aim was to test whether the selectivity characteristics in the near critical region are consistent with the assumed existence of clusters formed between *p*-xylene (solute) and toluene (solvent). *p*-Xylene diffuses much more easily, compared to *o*-xylene and *m*-xylene, through the intracrystalline pores of ZSM-5 zeolite and is therefore the dominant product. However, selectivity to *p*-xylene can be lowered by secondary isomerization of *p*-xylene on the catalyst's external surface. The authors postulated that if the cluster concept is mechanistically significant, then the rates of secondary isomerization reactions on the external surface should decrease as one approaches the critical point of toluene, which acts as a solvent for the product xylenes. It was speculated that at these conditions, the kinetics of *p*-xylene (solute) adsorption would be significantly depressed due to severe steric constraint imposed by the surrounding cluster of toluene molecules. Thus performing the reaction under near critical conditions of toluene was expected to enhance *p*-xylene selectivity if the authors' hypothesis was correct. The kinetic results of *p*-xylene selectivity as a function of pressure, plotted in Figure 9, are consistent with the proposed mechanistic interpretation of near-critical clustering.

Tiltscher and co-workers[7,89,90] studied the disproportionation of 1,4-diisopropylbenzene under gaseous and supercritical conditions using a zeolite 13NaHX catalyst. The reaction was conducted in an internal differential recycle reactor in the presence of benzene

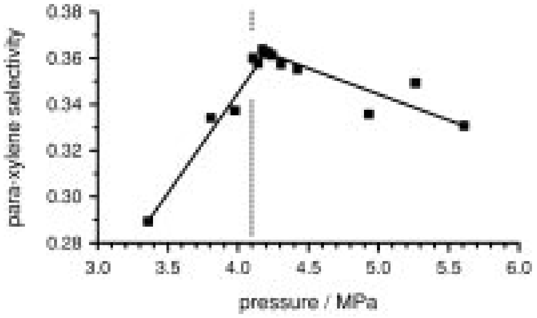

Figure 9. Effect of pressure on disproportionation of toluene over an unmodified ZSM-5 catalyst studied in a fixed-bed differential reactor. Selectivity to *p*-xylene is shown as a function of pressure at 320 °C and a WHSV of 34 h^{-1}. Dashed line indicates critical pressure of toluene. (Reprinted with permission from ref 88. Copyright 1988 American Institute of Chemical Engineers.)

and *n*-pentane as a diluent to lower the critical temperature of the reaction mixture. This reaction was selected as a model reaction, because starting from a compound of medium volatility (T_{bp} of 1,4-diisopropylbenzene at normal pressure 210.3 °C) two products with substantially different volatilities (cumene, $T_{bp} = 152.4$ °C; 1,3,5-triisopropylbenzene, $T_{bp} = 237.3$ °C) are formed. When reaction conditions with a gaseous phase were applied the emerging product solution contained rather large amounts of the lower boiling product, but relatively small amounts of the higher boiling one. Under these conditions catalyst activity declined rapidly, due to accumulation of the higher boiling product in the catalyst pores. This was confirmed by a pressure jump technique with pressure increase from the gaseous into the supercritical region which enhanced the desorption of the higher molecular compounds from the catalyst, leading to an immediately dark brown shading of the product solution. The authors concluded that raising the pressure in the supercritical region enhances desorption of the adsorbed products due to increased dissolution power of the SCF, and suggested that this effect can be used to prolong catalyst lifetime and to direct the product distribution of multiple reactions.

Niu and Hofmann[56,91,92] investigated the kinetics of the disproportionation of ethylbenzene over a HY-zeolite under supercritical conditions, using a concentration-controlled continuously operated recycle reactor. The authors concluded that the catalyst deactivates more slowly under supercritical operating conditions than under atmospheric pressure.

E. Esterification

Vieville et al.[93,94] investigated the esterifications of oleic acid by methanol catalyzed by sulfonic acid resins in supercritical CO_2. The esterification of carboxylic acids with alcohols is an example of a reversible reaction, which has been studied at supercritical conditions. The authors found similar parametric sensitivity of the reaction rate in supercritical carbon dioxide as in *n*-hexane. However the reaction was faster in supercritical carbon dioxide. They also suggested that due to the hydrophobic nature of the resins the reactants do not diffuse readily to the catalytic sites within the macropores of the sulfonic resin. Esterification only takes place on the surface via adsorption of oleic acid and reaction followed by desorption of methyloleate. The reaction appeared to be limited by external diffusion and desorption of reactants and products. The higher reaction rate in $scCO_2$ was attributed to increased solubilization of methyloleate and higher diffusivity.

F. Fischer–Tropsch Synthesis

Considerable effort has been expended in exploring the application of supercritical fluids in Fischer–Tropsch (FT) synthesis,[95–102] which provides a means to synthesize higher hydrocarbons in the liquid fuel range from synthesis gas (CO and H_2). The classical synthesis route involves an exothermic gas-phase reaction, and consequently efficient heat removal is essential. Another problem arises from condensation of higher hydrocarbons formed during reaction within the catalyst pores, which can cause catalyst deactivation. In a liquid-phase process these problems are mitigated due to improved heat transfer and better solubilities of higher hydrocarbons. However the lower diffusivity in the liquid-phase leads to mass-transfer limitations and consequently to lower overall reaction rate. These considerations have driven research on FT synthesis to the application of supercritical conditions, which combines the desirable properties of gaslike diffusivity and liquidlike solubility.

In some early studies, Fujimoto and co-workers[99] demonstrated that the supercritical FT reaction shows unique characteristics such as high diffusivity of reactant gases, effective removal of reaction heat and in situ extraction of high molecular weight hydrocarbons (wax), Although the rate of the reaction and the diffusion of reactants were slightly lower than those in the gas-phase reaction, the removal of reaction heat and waxy products from the catalyst surface were much more effective than those in the gas-phase reaction. Moreover, the olefin content of the product hydrocarbon was much higher in the supercritical phase reaction, compared to liquid- and gas-phase reaction. Fujimoto and co-workers concluded that in the supercritical phase reaction, both, the desorption and the diffusion of the product were so well-balanced that the overall mass transfer of the products was most effective in the supercritical phase and thus the hydrogenation of primary olefins was effectively suppressed.

Bukur et al.[100,101] studied the effect of process conditions on olefin selectivity during conventional FT synthesis and FT synthesis in supercritical propane. The experiments were carried out in a fixed-bed reactor charged with a precipitated iron catalyst. They found that the total olefin and 2-olefin selectivities were essentially independent of reaction temperature but changed significantly when conditions were changed from conventional (subcritical) operation to supercritical operation. Under supercritical conditions the total olefin content was greater while the 2-olefin content decreased. The authors concluded that undesired secondary reactions (isomerization, hydrogenation, and readsorption) of high molecular weight α-olefins occur to a smaller extent during supercritical operation, due to higher diffusivities and desorption rates of α-olefins in the supercritical propane than in the liquid-filled catalyst pores (subcritical conditions).

Snavely and Subramaniam[102] developed an on-line GC method for analysis of C_1-C_{30} products from FT synthesis, conducted in a supercritical hexane medium over an Fe catalyst in a continuous fixed-bed reactor. They showed that pressure and temperature affect the elution order of oxygenates relative to hydrocarbon in the nonpolar capillary column. This phenomenon was exploited for obtaining improved resolution in the product analysis. FT synthesis under subcritical and supercritical conditions were not compared in the study and consequently no information is extractable concerning this aspect.

G. Hydrogenation

In several hydrogenation processes, hydrogen is mixed with a liquid substrate and a solid catalyst. The mass-transfer resistances involved in the reaction are illustrated in Figure 1. The mass transport resistance between gas (H_2) and liquid phase can be eliminated by working in the supercritical regime, where a homogeneous reaction solution is formed. Hydrogen has a surprisingly low solubility in most organic solvents, whereas it is completely miscible with supercritical fluids. At a given pressure of gas the effective concentration of H_2 in a supercritical solution can be nearly an order of magnitude higher than in a conventional solvent. As a consequence, the hydrogen concentration at the catalyst surface can be greatly increased, leading to extremely high reaction rates compared to the normal liquid phase operation. However, it should be kept in mind that the solvation power of supercritical fluids is generally lower than that of corresponding liquids, which can create a problem in the application of supercritical solvents. A potential tool to obviate the solubility problem is the tuning of the solvent properties by addition of cosolvents. This possibility has so far not been demonstrated for heterogeneous catalytic reactions, but is likely to offer great potential. Present studies on hydrogenation in supercritical media mainly capitalize on the enhanced mass transfer and solubility of hydrogen and their influence on reaction rate and selectivity.

Supercritical fluids (carbon dioxide, propane, ethane) have been applied advantageously as solvents in several hydrogenation reactions, including hydrogenation of fats and oils,[103−106] and a great range of other organic compounds,[55,107,108] as well as the enantioselective hydrogenation of an α-keto ester.[109,110] In addition supercritical carbon dioxide has been successfully used as a reactant in the synthesis of formic acid derivatives.[111−116]

Before a vegetable oil can give consistency to margarine and shortening, about half of its double bonds have to be saturated. The purpose of the hydrogenation of fats and oils (hardening) is to create the desired melting profile and texture of these substances. As a result of hydrogenation, the oils become less sensitive to oxidation and their stability increases. In nature almost all double bonds in fatty acids are cis bonds, whereas during hydrogenation partial isomerization to the trans configuration occurs. *trans*-Fatty acids, which are questioned from a medical point of view, are favored at low hydrogen concentration at the catalyst surface. The classical process used for hydrogenation of fats and oils, invented by W. Normann in 1901,[117] is conducted in a batch reactor, where the oil, hydrogen, and the catalyst as a slurry are mixed intensively. The low solubility of hydrogen in oils and the transport resistances in the gas/oil/catalyst interfaces limit the reaction rate and cause the high content of *trans*-fatty acids.

Härröd and Møller[103,104] succeeded in overcoming the solubility problem and the transport resistance for hydrogen. They used near-critical or supercritical propane, which is miscible with both, oil and hydrogen thus forming an essentially homogeneous phase, and fed it into a continuous fixed-bed reactor packed with a commercial palladium catalyst. Under these conditions they achieved extremely high reaction rates, according to the authors about 400 times higher, for the partial hydrogenation of fatty acid methyl esters compared to the traditional technique. The tremendous rate enhancement was attributed to the elimination of gas/liquid mass transfer as a consequence of the essentially homogeneous phase under supercritical conditions, which facilitated the increase in the hydrogen concentration at the catalyst surface. Another benefit of supercritical conditions was that the concentration of *trans*-fatty acids was considerably reduced compared to conventional processes using the same catalyst and the same degree of hydrogenation. However, the problem of catalyst deactivation remained unresolved.

Tacke et al.[105,106] report full and partial hydrogenation of fats and oils, free fatty acids and fatty acid esters, using supercritical CO_2 as solvent. The reactions were conducted in a continuous fixed-bed reactor, containing a commercial-supported palladium catalyst. The authors observed up to 6 times higher space time yields compared to hydrogenation in a trickle-bed reactor, packed with an activated carbon-supported palladium catalyst. Other advantageous features of the supercritical CO_2 application were the extended catalyst lifetime and improved selectivity.

Supercritical carbon dioxide has been considered as an ideal apolar solvent for chemical reactions due to its moderate critical parameters and its easy product separation compared to conventional solvents. It is an environmentally benign fluid which is cheap, nontoxic, and nonflammable. However, little is known hitherto about its application as a solvent in heterogeneous catalytic hydrogenation.

Bertucco et al.[55] studied the catalytic hydrogenation of an unsaturated ketone in supercritical CO_2 using a gradientless internal-recycle reactor (cf. section V.A) with a supported palladium catalyst. The authors developed a simple homogeneous model to interpret the experimental results. A Peng−Robinson equation of state with mixture parameters tuned on experimental binary data provided a satisfactory interpretation of all binary and ternary vapor−liquid equilibrium data and was extended to multicomponent calculations. The kinetic model was able to describe the experimental results on the basis of the calculated compositions in the liquid phase, which are the reaction locus. The authors stress that a precise evaluation of liquid composition under the reaction conditions was essential to obtain good results in the kinetic modeling. However, the physical significance of parameters extracted from a homogeneous model applied to a heterogeneous catalytic process is doubtful, and limits the scope of such models.

Hitzler and Poliakoff[107] conducted the hydrogenation of organic compounds (cyclohexene, acetophenone, and 1,2-(methylenedioxy)-4-nitrobenzene) in a small (5 mL volume) continuous flow reactor using $scCO_2$ or supercritical propane as solvents and different commercial supported palladium catalysts. Cyclohexene hydrogenation was extremely rapid in both supercritical solvents and could be initiated without any external heating of the reactor. At flow rates >1.5 mL min^{-1} of cyclohexene, the authors have measured temperatures exceeding 300 °C in the catalyst bed, higher even than the critical temperature of cyclohexene itself ($T_c = 287.3$ °C, $P_c = 4.43$ MPa), originating from the heat generated by the exothermic reaction. Only a very small flow of $scCO_2$ was required to sustain the reaction. Using the example of acetophenone hydrogenation, the authors illustrated the particular advantage of supercritical fluids for controlling reaction conditions and, hence, the possibility to manipulate selectivity. The presence of a single phase within the reactor facilitated that the various parameters (temperature, pressure, concentration of H_2, etc.) could be adjusted independently. It was shown that the conditions can be tuned to maximize the yield of a particular product in the series of successive hydrogenation products (1-phenylethanol, ethylbenzene, 1-cyclohexylethanol, ethylcyclohexane). Unfortunately this selectivity tuning was not compared to that achievable under the normal pressure condition. Efficient continuous reactor operation was also demonstrated for the hydrogenation of 1,2-(methylenedioxy)-4-nitrobenzene (T_{mp} = 146−148 °C), which was dissolved in an inert solvent (MeOH−THF, 2:1 v/v). The reaction was performed at 90 °C, 14 MPa in $scCO_2$.

Very recently, the same research group greatly extended the above study on continuous catalytic hydrogenation in supercritical fluids.[108] Using $scCO_2$ and supercritical propane as solvents, and various noble metal catalysts on DELOXAN aminopolysiloxane support, they demonstrated that continuous hydrogenation in supercritical solvents can be applied to a wide range of organic compounds, including alkenes, alkynes, aliphatic and aromatic ketones and aldehydes, epoxides, phenols, oximes, nitrobenzenes, Schiff bases, and nitriles. Propane was favored as the supercritical fluid for the hydrogenation of nitrogen-containing reactants, such as oximes, Schiff bases, nitriles, and nitrobenzenes, to the corresponding amines, to avoid the formation of insoluble carbamic acid salts. Carbamic acids are formed by the reaction of amine groups with CO_2. The authors concluded that $scCO_2$ can be used for all reactions other than those producing amines. Of course, propane has the advantage of lower critical pressure than CO_2, but this is offset by its flammability. A definite advantage of the continuous hydrogenation described by the authors is that only small reactor volumes (5−10 mL) are required. The authors claim that even with a 5-mL reactor throughputs can be reached which are larger than those needed by most synthetic organic laboratories. However, for judging the economical value of this approach a comparison with corresponding continuous hydrogenations in conventional solvents and the extra costs imposed by the supercritical fluid application need to be considered.

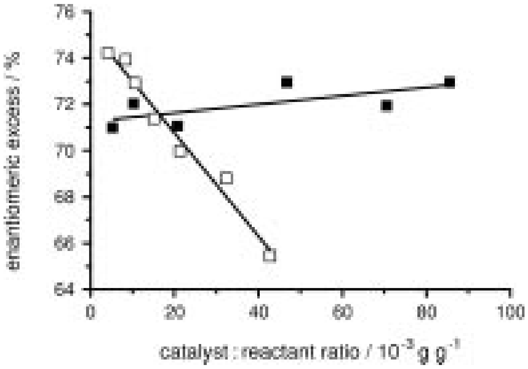

Figure 10. Enantioselective hydrogenation of ethyl pyruvate on Pt/alumina catalyst chirally modified with cinchonidine. Comparative study of the reaction carried out in ethanol (□) and in supercritical ethane (■), respectively. The enantiomeric excess ee = $(|R| - |S|)/(|R| + |S|) \times 100\%$ of the product (*R*)-ethyl lactate is shown as a function of the catalyst/reactant (ethyl pyruvate) weight ratio. General conditions: 500-mL autoclave, 20 mL of ethyl pyruvate, 0.45 g of catalyst, 0.088 g of cinchonidine, initial hydrogen partial pressure 7 MPa. Supercritical conditions: ethane, 6 MPa, 40 °C (P_c = 4.8 MPa, T_c = 32 °C). Subcritical conditions: ethanol, 6 MPa, 22 °C (P_c = 6.1 MPa, T_c = 241 °C). (Adapted from ref 109.)

Supercritical solvents were for the first time applied in heterogeneous asymmetric catalysis by Minder et al.,[109] who conducted the enantioselective hydrogenation of ethyl pyruvate over Pt/alumina modified with cinchonidine in supercritical ethane. The reaction time in a batch reactor (autoclave) could be reduced by a factor of 3.5 compared to experiments, where liquid toluene was used as a solvent under otherwise similar conditions. Enantiomeric excesses (ee) achieved with both solvents were comparable and showed the same temperature dependence. A striking feature of the reaction conducted in supercritical ethane is that the enantiomeric excess increases slightly with increasing catalyst/reactant ratio, whereas in suitable liquid solvents such as toluene or ethanol, a considerable decrease is observed due to mass-transfer limitation at higher catalyst/reactant ratios (Figure 10). This example demonstrates that supercritical conditions are also suitable for heterogeneous enantioselective catalysis. Tuning of supercritical solvent properties to influence the structure of diastereomeric transition complexes, thereby controlling enantiodifferentiation could be an interesting challenge in future research. Minder et al.[109,110] also pointed out that for hydrogenations catalyzed by platinum metals at low temperature, the use of $scCO_2$ can lead to catalyst deactivation caused by CO originating from the reduction of $scCO_2$ via reverse water gas shift reaction. This deactivation mechanism was evidenced by FTIR spectroscopy for the enantioselective hydrogenation of ethyl pyruvate over a Pt/alumina catalyst in $scCO_2$ at room temperature.

Noyori and co-workers [53,118−123] have shown that the use of $scCO_2$ as both reaction medium and reactant offers an efficient way for the homogeneous catalytic synthesis of *N*,*N*-dimethylformamide (DMF) and methyl formate (MF). The authors made use of a supercritical phase of CO_2 and H_2 in which the catalyst is dissolved. Thus $scCO_2$ serves as both a reactant and as solvent. In the presence of a $[RuCl_2(PMe_3)_4]$ catalyst and triethylamine, turnover numbers (TON) in MF synthesis up to 3500 were obtained in 64 h at 80 °C with corresponding turnover frequency values of 55 h^{-1}. In DMF synthesis, a maximum TON of 370 000 with a corresponding TOF of 10 000 h^{-1} was reported, which exceeded the previously reported values by a factor of 17. The high reaction rate was attributed to favorable mass-transfer effects, high solubility of H_2, and weak solvation of the catalyst compared to liquid solvents in the biphasic system. The application of complexes soluble in $scCO_2$ was reported to be crucial for achieving high activities in this reaction system. In a more recent study, Kröcher et al.[111] showed that the efficiency of the above system could even be further increased by applying a bidentate type Ru complex as catalyst.

Heterogeneous variants of the above solvent-free homogeneous processes for the synthesis of DMF and MF have been designed by Kröcher et al.[111−116] For this purpose heterogeneous silica-based hybrid-type Ru catalysts were developed. Silyl-ether complex analogues of different group VIII metal complexes were incorporated into a silica matrix, applying the sol−gel method. These heterogeneous hybrid gel catalysts can easily be separated from the reaction mixture by pressure release and filtration, and are stable under reaction conditions. The Ru catalysts proved to be most active, affording TONs up to 110 800 with corresponding TOFs up to 1860 h^{-1} in DMF synthesis. This TOF exceeds those previously achieved with heterogeneous catalysts by a factor of 600, with the additional benefit of much higher selectivity (ca. 100%). In MF synthesis similar exciting results were achieved. Turnover frequencies up to 116 h^{-1} were measured, exceeding the TOFs for the best hitherto known homogeneous catalyst by a factor of 2.

H. Isomerization

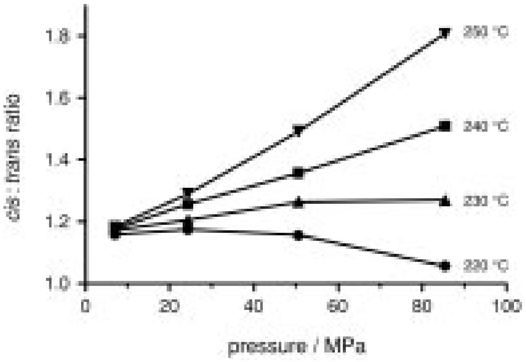

Figure 11. Effect of pressure and fluid state on initial reaction rates of cis-/*trans*-hexene-2 formation during isomerization of hexene-1 ($P_c = 3.1$ MPa, $T_c = 231$ °C) over a shell-type γ-alumina/Al metal catalyst. The upper two curves refer to supercritical temperatures, the lowest to conditions with a liquid reaction phase. Note that the cis/trans ratio increases markedly in the supercritical region, whereas a reversal effect seems to occur in the subcritical region, i.e., in the liquid phase. (Reprinted with permission from ref 7. Copyright 1987 Elsevier Science.)

One of the first reaction investigated under supercritical conditions was the double-bond and cis/trans isomerization of α-olefins.[7,89] Particularly the isomerization of 1-hexene turned out to be a suitable model system for investigating the effect of pressure on a heterogeneous catalytic surface reaction, due to similar critical data of the reactant ($T_c = 231$ °C, $P_c = 3.11$ MPa) and main products. This allows the experimenter to keep the reaction system in the desired fluid state, independent of conversion. Other interesting features of this reaction are the product formation via a system of complex parallel and consecutive reactions and the fact that trans isomers are thermodynamically more stable than cis isomers. However, cis isomers are kinetically favored at higher pressure due to steric effects. Figure 11 illustrates the influence of pressure and fluid state on initial reaction rates for *cis*-/*trans*-hexene-2 formation on a shell-type γ-alumina/Al metal catalyst, as reported in the original work by Tiltscher and Hofmann.[7] In accordance with the literature, the authors found that the initial cis/trans ratio cannot be influenced by variation of the temperature at low pressures and in a gas-phase reaction. However in the supercritical region the cis/trans ratio increases with pressure. This behavior is attributed to the kinetic favoring of *cis*-hexane-2 formation due to its enhanced desorption in the supercritical phase. Under liquid-phase conditions products remain longer on the surface, which favors the thermodynamically more stable trans isomer.

Subramaniam and co-workers have focused their attention on the isomerization of 1-hexene catalyzed by Pt/alumina for many years.[6,66,124−136] They explored the thermodynamical constraints of the system by analyzing the phase and reaction equilibria.[125] The authors' equilibrium analysis was confirmed by the conversion achieved in batch experiments. Continuous fixed-bed reactor experiments were used to investigate catalyst deactivation in hexene/CO_2 mixtures. The activity of the catalyst decreased at a subcritical pressure, whereas at a nearly identical temperature but supercritical pressure no catalyst deactivation was observed. The deactivation under subcritical conditions was attributed to the deposition of higher molecular weight oligomers which upon decomposition in the catalyst pores lead to coking.[126] The stable activity of the catalyst under supercritical conditions was explained by the solvent power of the SCF which presumably prevented deposition of higher molecular weight oligomers in the catalyst pores. This is a clear demonstration that catalyst deactivation caused by the deposition of higher molecular weight compounds can be suppressed by applying supercritical conditions, by virtue of the increased solvent power of SCFs. In subsequent work,[66,127,129,130] the main target of Subramaniam and co-workers was the role of supercritical fluid for coke extraction and the maintenance of catalyst activity. The studies led to the conclusion that near-critical reaction mixtures provide an optimum combination of solvent and transport properties that is better than either subcritical (gaslike) or dense supercritical (liquidlike) mixtures for maximizing the isomerization rates and minimizing catalyst deactivation rates. Liquidlike reaction media favor coke extraction and/or heat removal, whereas gaslike media enhance diffusion, rendering near critical reaction media most favorable for diffusion controlled reactions. More recent work of Subramaniam's group[131−136] concerns the kinetic description of the formation of coke compounds from olefinic oligomers and their reversible adsorption/desorption at the catalyst surface, as well as the optimization of the reaction conditions. The group's effort led to a detailed mathematical model, which consistent with the experimental observations predicts that (i) near critical reaction mixtures provide an optimum combination of transport and solvent properties for extracting coke precursors from the catalyst, thereby maximizing isomerization rates and minimizing catalyst deactivation rates and (ii) the mitigation of feed peroxides and the addition of inert cosolvents significantly reduce oligomers formation in the fluid phase, thereby curtailing coke formation (i.e., catalyst deactivation) rates.

Amelse and Kutz[137] describe a process to catalytically isomerize a stream comprising one or more xylenes and ethylbenzene under supercritical conditions. Various solid acid catalysts, such as amorphous silica−alumina and aluminum-, boron-, gallium-, or iron-containing crystalline silicate molecular sieves are applied. In contrast to the classical vapor or gas-phase xylene isomerization, the process involves reaction under supercritical conditions and subsequent isobaric cooling of the reactor effluent at a pressure greater than P_c to a temperature below T_c such that it passes from the supercritical phase to the liquid phase without a phase change. The latter allows a substantial reduction in the magnitude of the internal temperature pinch in the reactor effluent heat-exchanger for the supercritical condition process.

I. Oxidation

Supercritical fluids also offer several interesting properties for application in heterogeneous catalytic oxidation reactions. This holds true particularly for partial oxidation reactions, which depend critically upon the correct amount of oxygen at the catalytic site. In the supercritical state it is possible for both the component to be oxidized (e.g., hydrocarbon) and oxygen to exist as a single phase with viscosity and diffusivities intermediate to those properties for liquids and gases. Reaction pathways may be affected by supercritical solvents because some elementary reactions involve free radicals and can occur in a fluid phase. Rapid quenching of highly exothermic partial oxidation by pressure release from supercritical conditions should minimize losses in the yield of partial oxidation products due to thermodynamically favored total oxidation (combustion).

Dooley and Knopf[138] studied the partial oxidation of toluene to benzaldehyde with air in supercritical CO_2 in the presence of redox or acid catalysts. Catalyst screening tests embracing several oxides and mixed-metal oxides revealed that supported CoO, partially oxidized to Co(III), was the most active and selective catalyst. The reactions were conducted in a continuous fixed-bed reactor using a mixture of 1.5 wt % toluene and 6.5 wt % air in supercritical CO_2 at 8.0 MPa and 20−220 °C. Under these conditions, the toluene could be oxidized at low rates and conversions to benzaldehyde, benzyl alcohol, the cresol isomers, and a lesser amount of condensation products and carbon oxides. Benzoic acid in trace levels accelerated the reaction and was cooxidized to CO_2 and water. This observation together with the product distribution obtained and apparent activation energies for partial oxidation as low as 21 kJ mol^{-1} indicated the participation of free radicals such as benzoperoxy radical in the reactions. Compared to the low-pressure, vapor-phase processes, which proceed by mechanisms of the Mars−van Krevelen type, the high-pressure process in supercritical CO_2 affords much better selectivity to partial oxidation products. The characteristics of the latter process resemble those of the catalytically assisted, free-radical, homogeneous oxidation in the liquid phase.

Gaffney and Sofranko[139,140] investigated the selective oxidation of propene to propylene glycol in supercritical media using a heterogeneous catalyst comprised of copper iodide, copper oxide, and a reducible metal. Mechanistic studies indicated that initially propene, water, and iodine react to form propylene iodohydrin. This intermediate then reacts with carbon dioxide to form propylene carbonate, which quickly hydrolyzes to propylene glycol. There was no measurable loss of iodide from the catalyst after 50 h at reaction conditions. Higher propylene glycol selectivity was achieved in $scCO_2$ (90%) than in subcritical aqueous solvent (50%).

Fuijmoto and co-worker[141,142] reported the oxidation of isobutane to *tert*-2-butyl alcohol (TBA), using air as an oxidant, albeit with low yields ($\ll$5%). The reaction was conducted in a continuous fixed-bed reactor in the presence and absence of catalyst, changing the state of isobutane from liquid and gas phase to supercritical phase. The authors examined five types of catalysts, among which SiO_2-TiO_2 and Pd/carbon were most efficient. In either the uncatalyzed reaction or the catalyzed reactions the change from gas-phase isobutane to supercritical isobutane resulted in enhanced conversion of isobutane and oxygen. Generally also selectivity to the target products, TBA and isobutene, increased slightly upon change from gas or liquid phase to supercritical phase, as depicted in Figure 12. All catalyzed reactions showed significantly higher activities than noncatalytic reactions, which proved the promotional role of the catalysts in the reactions. Concerning the

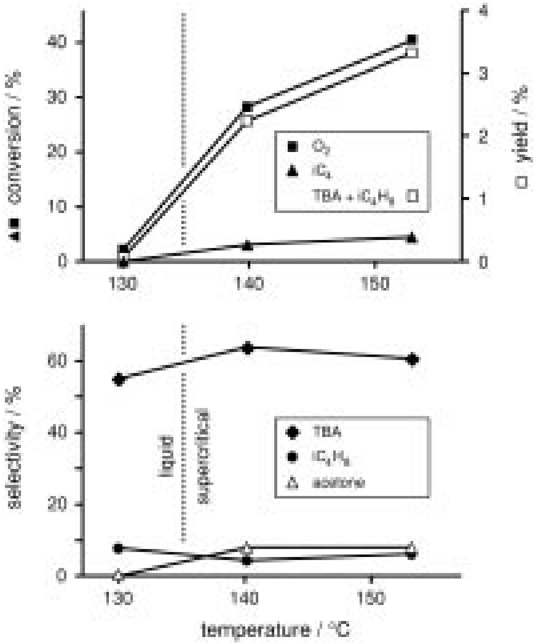

Figure 12. Effect of change of the fluid state of the reactant mixture in the oxidation of isobutane ($P_c = 3.65$ MPa, $T_c = 135$ °C) to *tert*-butyl alcohol TBA by air over a TiO_2-SiO_2 catalyst. Catalytic performance in supercritical phase and liquid phase is compared. Dotted vertical line indicates critical temperature. Conditions: 5.4 MPa, $W/F = 10$ g h mol^{-1}, catalyst weight 0.5 g, isobutane/air = 3 (mol/mol). (Reprinted with permission from ref 141. Copyright 1997 The Royal Society of Chemistry.)

reaction mechanism, in supercritical fluid, the authors suggested that dioxygen attacks the most active hydrogen of isobutane to form *tert*-butyl hydroperoxide (TBHP), which is used in epoxidation of olefins on TiO_2-SiO_2-type catalysts. The authors inferred that TBHP can form in supercritical isobutane coexisting with dioxygen. This autooxidation step can proceed without catalyst.[143] The TBHP formed can decompose homolytically, resulting in tertiary butoxy radical and hydroxy radical. TBA is suggested to be formed by combination of tertiary butoxy radical with a third hydrogen from another isobutane. In a consecutive reaction step the desired product TBA can dehydrate on acidic sites, resulting in increased isobutene formation. The main byproduct, acetone is assumed to originate from decomposition of tertiary butoxy radical, which also generates C_1 compounds such as methanol, carbon dioxide, or methane. It should be stressed that the above mechanism may be feasible, but is not proven so far.

Oxidation with air or oxygen in supercritical water provides several opportunities including increased solubility of oxygen and organics, and gaslike diffusion rates along with high liquidlike collision rates so that the oxidation takes place in a homogeneous mixture with no mass-transfer limitations at the phase boundaries.

Most of the work on chemistry in supercritical water has focused on supercritical water oxidation (SCWO), which is an effective means for complete oxidation of many organic wastes. The SCWO technique has been developed to treat organics in industrial wastewater streams and is an extension of wet-air oxidation (WAO) which operates at subcritical temperature and pressure. Advantages to conducting the oxidation reaction above the critical point include faster reaction rates, single fluid phase, and complete miscibility of nonpolar organics with supercritical water. Although most work on SCWO does not make use of a heterogeneous catalyst, some studies report on the effect of heterogeneous catalysts. The main motivation for using a catalyst is to reduce energy and processing costs. Complete conversion of organics at lower reaction temperature and relatively short residence times is the target. Studies on catalytic oxidation in supercritical water up to 1995 have been covered by Ding et al.[12] in a review which provides a useful database for catalyst selection and gives an account for the effectiveness of catalyst application in this field.

Compared to deep oxidation in supercritical water (SCWO), little attention has been devoted so far to partial oxidations in this medium. Dixon and Abraham[144] investigated the oxidation of methane in supercritical water and compared it to the gas-phase catalytic oxidation. The reaction was carried out in a batch reactor using a Cr_2O_3 catalyst. Supercritical water was found to inhibit the reaction, resulting in a rate of reaction in scH_2O being approximately one-half of that observed for gas-phase oxidation. Complete oxidation to carbon dioxide and water was always the favored reaction, but in the presence of water methanol was formed as an intermediate in low to moderate yield. In the presence of supercritical water the yield to methanol could be increased by approximately 1 order of magnitude in comparison to the gas-phase reaction.

VIII. Concluding Remarks

The unique properties of fluids just above the critical point can be applied beneficially in various ways in heterogeneous catalysis. The work accumulated in this field has been reviewed in this paper. Supercritical fluids, either used as solvents or reactants, provide several opportunities to enhance and control heterogeneous catalytic reactions. Important possibilities include (i) control of phase behavior, elimination of gas/liquid and liquid/liquid mass transfer resistances, (ii) enhanced diffusion rate in reactions controlled by external (fluid/particle) diffusion, (iii) enhanced heat transfer, (iv) easier product separation, (v) improved catalyst lifetime by dissolution of deactivating deposits, (vi) tunability of solvent properties by pressure and cosolvents, (vii) thermodynamic pressure effect on rate constants, and (viii) control of selectivity by solvent-reactant (solute) interaction.

A problem in interpreting the results of the presently available work on heterogeneous catalysis in supercritical fluids is that in many reactions more than one of the effects mentioned above may be operative, rendering a clear assignment of effects on rate and selectivity often difficult.This uncertainty in the quantification of effects is partly due to the complex interplay between mass transfer and chemical surface reaction. Consequently homogeneous reactions have been favored for fundamental studies.

On the other hand the importance of mass- and heat transfer in heterogeneous catalytic reactions renders this class of reactions particularly attractive for the application of supercritical fluids.

An extremely attractive facet is the use of supercritical solvents and their tunable density, more direct information about a reacting system can be gained than by studying the reaction in a variety of chemically different solvents. This tunability can be used to control phase behavior, separation, and rate and selectivity of catalytic surface reactions.

Supercritical CO_2 has gained most attention as solvent for application in heterogeneous catalysis so far. The fact that reactions in $scCO_2$[52] produce very similar results to reactions in nonpolar organic solvents (e.g., *n*-hexane) is of practical potential because in many cases replacing of those solvents by the environmentally benign $scCO_2$ will not entail a complete reassessment of chemistry. The fact that $scCO_2$ is only suitable as a solvent for nonpolar substances imposes a considerable limitation in practice. A possible way to overcome this limitation was recently demonstrated by Johnston et al.[145] They showed that aqueous microemulsion droplets in a carbon dioxide continuous phase with a nontoxic ammonium carboxylate perfluoro polyether surfactant exhibit properties which approach those of bulk water. Such microemulsions may extend the use of dense carbon dioxide as a solvent for hydrophilic substances and ions. Another environmentally benign solvent which has great potential to replace conventional solvents is supercritical water. When water is heated to the critical point, it expands by a factor of 3, destroying about two-thirds of the hydrogen bonds, and the relative permittivity ("dielectric constant") drops from 80 to 5.[146] Pressure and temperature can be used to tune the properties of sub- and supercritical water to mimic that of most organic solvents.[147] Supercritical water acts like a nonaqueous solvent, and it readily dissolves many organics and even gases such as oxygen. This renders water particularly attractive for replacing certain organic solvents for catalytic reactions at temperatures above 200−350 °C, where most organics become readily soluble. However, this relatively high-temperature range often precludes scH_2O application due to limited thermal stability of organic reactants and products. Other limitations are imposed by the corrosive properties of scH_2O.

A further step toward making $scCO_2$ a versatile practical solvent is the application of micelles whose cores can be designed to interact specifically with reactants to allow their incorporation into $scCO_2$. The discovery of surfactants with carbon dioxide soluble tails which allow to form microemulsions und emulsions with hydrophilic or hydrophobic cores[148] is a further step toward this aim.

Another promising concept is supercritical fluid phase transfer catalysis,[149] as demonstrated recently by Eckert's group.[150] The combination of supercritical fluids and phase-transfer catalysis may open new doors for environmentally benign chemical processes in heterogeneous systems.

To make proper use of the opportunities provided by supercritical fluids considerable further efforts are necessary, particularly, some fundamental aspects have to be addressed, which are either not or only little understood yet. Such aspects include the effect of local density variation of solvent and solute on the structure of the transition complex of surface reactions. Local molecular phenomenon can influence reaction rates, so that an understanding of the bulk physical properties of solvent and solute (reactant) may not be sufficient to predict pressure effects on surface reaction rates. Density changes of solute or reactant in the compressible region near the critical point may change their adsorption and desorption behavior, which in turn affects the surface reaction. Cosolvents used to enhance the solubility of reactants may also interact with the catalyst surface or even change surface properties of the catalyst. These are just a few among many aspects which need clarification to control rates and selectivities of surface reactions. In situ spectroscopic investigations will play a crucial role in answering some of these fundamental questions. So far spectroscopy has been almost exclusively applied to investigate solute−solvent, solute−cosolvent, and solute−solute interactions in homogeneous systems. Progress in the fundamental understanding of heterogeneous catalytic reactions at solid surface/supercritical fluid interfaces will tightly be bound to advances made in in situ spectroscopy of surfaces under these conditions.

Although many fundamental aspects have not yet been clarified, the potential of supercritical fluids in heterogeneous catalysis is already substantial, as the various examples shown in this review demonstrate. However for technical application of supercritical fluids the benefits gained have to be carefully weighed against the higher costs of supercritical process technology. This balancing will limit economic and beneficial applications in some cases. However, the potential of supercritical fluid application will continue to expand, driven by research uncovering new opportunities and substantiating the known potential in controlling of surface reactions and the synthesis of new catalytic materials.

IX. Abbreviations

DMF	*N*,*N*-dimethylformamide
ee	enantiomeric excess, $ee = (\|R\| - \|S\|)/(\|R\| + \|S\|) \times 100\%$
FT	Fischer−Tropsch
P_r	reduced pressure, $P_r = P/P_c$
MF	methyl formate
$scCO_2$	supercritical carbon dioxide
SCF	supercritical fluid
scH_2O	supercritical water
TBA	*tert*-2-butyl alcohol
TBHP	*tert*-butyl hydroperoxide
TOF	turnover frequency
TON	turnover number
T_r	reduced temperature, $T_r = T/T_c$
WAO	wet air oxidation
W/F	modified space time (W, catalyst weight; F, molar flow rate entering the reactor)
WHSV	weight hourly space velocity
ρ	density

X. Acknowledgments

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