As seen, for most substances the lowering of the CO_2 solubility by atmospheric gas components is drastical. Based on this fact a modification of the HPE process is proposed. Admixing components like N_2 or Ar behind the extractor reduces the solvent capacity so that the extract can be separated without changing pressure or temperature (Fig. 7). Compared to common procedures this technique has the advantage of delivering pure extracts in an isobaric and isothermic mode. Up to now isobaric separation methods worked with adsorbing materials or washing-solutions in the separator, requiring further steps for extract recovery.

The procedure as proposed here needs instead a solvent recovery, since the gas mixture leaving the separator is - by choice - a poor solvent. For recycling purposes it has to be separated into a solvent stream and the additional component. Gas separation processes using membrane technology [10, 11] seem to offer ways to handle this problem in a more economic way (small pressure drops) compared to the non-isobaric extract separation method usually applied if mainly extract quality is of importance.

4. Conclusion

Development work on HPE, concentrating on the solvent properties of dense gases and gas mixtures, aims at a broadening of its range of applicability.

Whereas in the food industry the quality of either the upgraded residual (e.g. decaffinated coffee beans) or the extract (e.g. spices, hop) often justifies the application of the HPE process in the chemical or petrochemical industry both fractions, the residual and the extract, have to be produced in a valuable quality. Considering this requirement, it is obvious that the extract-separation procedure is as important as the extraction step. A suitable choice of the composition of the gaseous solvents should offer a variety of applications beyond the classical field of extraction of vegetable products.

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Utilization of Supercritical Fluid Solvent-Effects in Heterogeneous Catalysis

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Catalysis / Chemical Kinetics / Fluid State / High Pressure / Supercritical Solvent

Comparative studies on fixed-bed catalytic isomerization of 1-hexene and disproportionation of 1,4-diisopropylbenzene were performed under liquid, gaseous or supercritical conditions. The kinetic measurements show that by variation of pressure in the different fluid states catalytic surface reactions as well as mass transfer effects between catalyst and fluid phase and/or transport processes inside porous catalysts can be influenced in a very sensitive way. Conclusions are drawn in view of new possibilities for the direction of yield and selectivity of multiple reactions, for the prolongation of catalyst lifetime, and the study of deactivation mechanisms on heterogeneous catalysts.

1. Introduction

Recent years have witnessed a remarkably increasing interest in investigations of fluid media in the critical or supercritical region, mainly due to their potential importance in new separation techniques [1-3]. Apart from the evident advantages in separation processes, no distinct utilization of the specific effects of pressure and temperature on physico-chemical fluid properties – especially in the near critical region – seems to have been made in the past in the case of heterogeneous catalytic reactions.

For these reasons comparative studies were performed with the fluid reaction phase in the different states. The objective, in view of these investigations, was to analyze the possibilities encountered with pressure variations in order to influence:

- catalytic surface reactions,
- mass transfer effects between catalyst and fluid phase and/or
- transport processes inside porous catalysts.

Fig. 1 shows schematically pressure and temperature variations applied in the p, T-diagram of a pure substance. The arrows symbolize the directions of parameter variations. Conditions were always defined in such a way that the heterogeneous catalytic systems contained only two phases, the solid catalyst and either a liquid or a gaseous or a supercritical reaction phase.

From theoretical considerations the results of isothermal pressure or isobaric temperature variations including changes of the fluid state gaseous \leftrightarrow supercritical or liquid \leftrightarrow supercritical were expected to be especially interesting.



Fig. 1 Scheme of pressure and temperature variations in the different fluid states (S: solid; L: liquid; G: gas; Tr: triple point; p_c : critical pressure; T_c : critical temperature; SCF: supercritical fluid)

2. Experimental

Kinetic measurements of heterogeneous catalytic reactions within the different kinetic regions and in different fluid states are, to some extent, more difficult than investigations of separation processes. Besides consideration of influences of the phase behavior of the system, which may change with degree of conversion, the efficiency of such a program depends greatly on the reaction system, the catalyst chosen, and the experimental set-up.

2.1. High Pressure Apparatus

The realization of the different fluid states necessitates the variation of temperature and pressure over sufficiently wide ranges. Reaction rates as well as physical properties of the reaction medium such as density or viscosity also vary markedly, up to two orders of magnitude. Since common experimental reactors cannot be easily adopted too for reactions with liquids and/or highly compressed gases, a novel type of an internal differential recycle reactor with a maximum working pressure of 2 kbar at temperatures of 570 K was developed [4]. The main advantages of this laboratory-scale reactor are, in addition to a very small dead volume, a central arrangement of the fixed catalyst bed, a defined adjustable axial flow through the packed bed, and most important of all, continuous pulsation-free internal circulation of the fluid by means of a screw-conveyor.

Fig. 2 shows the principle. The reaction mixture enters the reactor continuously and passes through the catalyst bed for several times before leaving. Recycle ratios $R = \dot{n}_{\rm K}/\dot{n}_{\rm o} > 20$ allow to apply the balance equation of the continuous stirred tank catalytic reactor (CSTCR) for the evaluation of kinetic data [5]. For stationary operating conditions of the reactor Eq. (1) holds:

$$r_i = \frac{\dot{n}_o}{W} (x_i - x_i^o) = \frac{1}{\tau^*} (x_i - x_i^o)$$
(1)

- \dot{n}_{o} total molar flow into the reactor
- W catalyst weight
- x_i^{o} reactor inlet mole fraction of component *i*
- x_i reactor outlet mole fraction of component *i*
- τ^* modified mean residence time.

Thus one gains decisive advantages in comparison to other experimental techniques: at constant \dot{n}_0 , p and T the reaction rate r_i of a component can be immediately obtained from determining reactor inlet and outlet concentrations.



Principle of an internal recycle reactor

2.2. Catalytic Systems

Two heterogeneous catalytic conversions were used. Each of them contains characteristic features for the present research program. The first one was double-bond and cis-/trans-isomerization of 1-hexene on γ -Al₂O₃:

1-hexene
$$\Rightarrow$$
 cis-/trans-2-hexene \Rightarrow cis-/trans-3-hexene (2a)

$$C_6H_{12} + C_6H_{12} \longrightarrow C_{12}H_{24} \xrightarrow{+C_6H_{12}} C_{18}H_{36} \cdots .$$
 (2b)

The main advantages of this system are:

- physical properties, especially the critical data of the reactant ($T_c = 504$ K; $p_c = 31.1$ bar after [6]) and the main products according to (2a) do not differ significantly; thus conditions can be easily adjusted in order to keep the reaction system also at different degrees of conversion in the different fluid states,
- in a side reaction (2b) low volatile higher molecular compounds are formed by oligomerization of the olefin after already few reaction steps. If these byproducts are not desorbed or separated from the catalyst surface to the same extent as they are formed the result is a decay of catalytic activity by catalyst coking.

In this way this model system allowed to study the influence of pressure in the different fluid states on hetergeneous catalytic surface reactions as well as on mass transfer between the catalyst and the fluid phase with respect to higher molecular compounds.

The second conversion was disproportionation of 1,4-diisopropylbenzene in presence of benzene and n-pentane as a diluent to lower the critical temperature of the reaction mixture:



This reaction was especially selected because from a compound of medium volatility (b.p. of 1,4-diisopropylbenzene at normal pressure: 483.5 K) one product is formed with higher (b.p. of cumene: 425.6 K) and one with lower volatility (b.p. of 1,3,5-triisopropylbenzene: 510.5 K).

For the measurements on hexene-isomerization methods were established for the synthesis of a shell catalyst on the basis γ -Al₂O₃/Al-metal with very low catalytic activity, a low catalytic active surface of about 5 m²/g and a thickness of the catalytic layer of less than one micron [7]. In the case of disproportionation reaction a highly active zeolitecatalyst (type 13 NaHX) with a particle diameter of 2 mm and a very high catalytic active surface of about 500 m²/g was employed. The micropores of this catalyst were large enough to house also the higher molecular reaction product.

3. Results

In accordance with the Ref. [8] we found that formation of cis- and trans-2-hexene occurs via reversible parallel reactions. At low pressures and gaseous reaction phase the initial cis-/trans-ratio cannot be influenced significantly by the variation of the temperature.

The latter can be seen from Fig. 3, which shows the obtained cis-/ trans-ratios of 2-hexene formation, extrapolated to initial reaction conditions, for 4 temperatures as a function of pressure. The upper two curves refer to supercritical temperatures, the lower to conditions with a liquid reaction phase. In the supercritical region the cis-/trans-ratio increases very markedly, and is lowered in the liquid state. The reversal of the pressure effect seems to occur at the critical temperature of the system because the second curve from below refers to a temperature only about 1 K lower than T_c .



Fig. 3

Influence of pressure and fluid state on cis-/trans-2-hexene formation at initial reaction time



Deactivation (DA) by coking under gaseous phase and reactivation (RA) in the supercritical region

Fig. 4 demonstrates the results of pressure effects on mass transfer from the catalyst surface into the fluid phase.

It is well known from literature that gas phase isomerization reactions of olefins on acid-base catalysts like γ -Al₂O₃ cannot be performed without deactivation processes caused by the formation and decomposition of low volatile compounds on the catalytically active surface sites [9–12]. Mainly at the beginning of a kinetic run catalytic activity rapidly decreases.

The lowest curve shows such a typical course. At a pressure of 15 bar and a temperature of 523.2 K (gaseous phase) after adjustment of stationary conditions under continuous operation of the reactor (4 h = $\sim 4 \cdot \tau^*$) the expected degree of conversion according to the dashed line cannot be reached. In the emerging colorless product solution only the isomeric hexenes could be analyzed.

After a reaction time of about 13 h an increase of pressure at the same temperature to a value higher than the critical pressure, e.g. to 500 bar, effects an immediately dark brown shading of the product solution, which gradually clears up again. After readjustment of stationary conditions the degree of conversion agreed with the expected value. In spite of the essentially higher reactivity under these conditions, even after extremely long reaction times no catalytic decay occurs.

The dark brown product solution which was sampled immediately after pressurization contained considerable amounts of C_{12} - to C_{30} -hexene oligomeric compounds besides the hexene isomers. Under gaseous reaction phase these oligomeric compounds remain on the catalyst surface due to their markedly lower volatility in comparison to hexenes and finally cause complete coking of the catalyst. After the reactivation period under supercritical conditions a small amount of hexene dimers could be analyzed in the product solution.

The pressure required for the reactivation is by far not as high as shown in this example. Distinct influences can already be obtained at the more accessible supercritical pressures of 50 to 150 bar. After the discovery of the in situ and inline technique for the reactivation of the catalyst under supercritical conditions, the kinetic measurements could be performed under continuous operation with a single catalyst charge for a period of 4 months without any loss of catalytic activity. The method also holds in the case of catalyst fouling and to some extent also for catalyst poisoning [13].

The results from the kinetic measurements on disproportionation of 1,4-diisopropylbenzene with the highly porous catalyst of zeolite-type appeared to be more complex. 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 catalytic activity drops down rather rapidly. The conjecture was that the higher boiling product accumulated within the catalyst.



Experimental (•) and theoretical (--) concentrations of the lower (upper curves) and the higher boiling reaction product of 1,4-diiso-propylbenzene disproportionation after a pressure jump from 25 to 200 bar (critical data of the mixture: $p_c = 43$ bar; $T_c = 528$ K)

To prove this, the transient reaction control technique was used with variations of the fluid state gaseous/supercritical [14]. The result of such an experiment is given in Fig. 5.

At first, for a period of 24 h (= $\sim 10 \cdot \tau^*$) the conversion was conducted at a pressure of 25 bar and a temperature of 533.2 K with a gaseous reaction phase. After this time pressure was raised under isothermal conditions within a rather short period of about 1 minute up to 200 bar. Immediately after the pressure increase the product solution again darkened caused by better desorption of higher molecular compounds from the catalyst.

The diagrams show the measured concentrations of the main reaction products cumene and 1,3,5-triisopropylbenzene in comparison with the expected transition function of the CSTCR (dashed lines). The deviation of the higher boiling product is significant, which can be traced back to better desorption under supercritical conditions of the substance previously formed under a gaseous phase. Catalyst lifetime appeared to be markedly longer in the supercritical region but, contrary to the experiments with the shell catalyst, reactivity was lowered.

With the aid of pressure jump experiments one can see and analyze counteracting effects in the case of highly porous catalysts: the higher the applied pressures in the supercritical region, the better is desorption of higher molecular compounds from the catalyst and the longer is catalyst lifetime, but on the other hand the lower reactivity normally appears. For practical applications it is necessary to optimize between these counteracting effects.

4. Conclusions

Comparative studies with the fluid reaction phase in the different states seem to be a powerful tool for the study of heterogeneous catalytic conversions. Especially increase of pressure and/or temperature into the supercritical region enables to influence catalytic activity very markedly.

Whilst pressurization at a constant temperature in the gaseous region usually favours sorption processes in heterogeneous catalytic conversions and thus low volatile compounds are correspondingly desorbed or separated not sufficiently from the catalyst surface, raise of pressure in the supercritical region obviously brings about the opposite effect. The reaction engineering advantages, which can be gained in this way, can be applied for the prolongation of catalyst lifetime as well as for the direction of yield and selectivity of multiple reactions.

The pressure jump technique with pressure increase from the gaseous into the supercritical region enables to test highly porous catalysts under severe conditions for practical applications. For instance the periodical supercritical desorption of low volatile compounds, formed under a gaseous phase, allows to analyze initial steps of catalyst coking mechanisms [15]. In comparison with other methods in this way the catalysts are not destroyed.

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New Developments in the Field of High-Pressure Extraction of Natural Products with Dense Gases

(Invited Lecture)

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Gases / High Pressure

A short historical review is followed by a survey of more recent work, some of it still unpublished. Solubility determinations in the pressure range up to 3000 bar and at temperatures up to 80°C yielded new surprising results for the substance classes of the triglycerides, wax esters and sterols. The difficult problem of the high pressure extraction of flexible viscous masses, such as crude lecithin and similar pastes and slimes, could be elegantly solved by the continuous high pressure jet procedure. In the field of separation of substances of high vapour pressure, e.g. essential oils, new paths were opened up. We succeeded in separating selectively undesirable fatty oils, waxes and colouring matter. The procedure for the continuous deterpenation for the recovery of high quality concentrated flavours is also new. We could further show the possibility of removing lipophilic pesticides from plant material, e.g. DDT, γ -HCH from sennae leaves and -pods.

Introduction

The numerous patents by Zosel (Max-Planck-Institut für Kohleforschung, Mülheim) between the years 1964 and 1977 gave the impulse in Europa for a detailed investigation of dense gases as extracting agents. The first symposium devoted to the subject, arranged in 1978 in Essen [1], was a milestone. It made the method generally known and gave rise for further investigations. There, we introduced a rapid procedure for the microanalytical evaluation of the solubility of natural products in supercritical gases [2]. The corresponding apparatus is now