Catalytic dehydrogenation of a mixture of C_{10}–C_{14} n-paraffins to linear C_{10}–C_{14} monolefins in a supercritical phase

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The catalytic dehydrogenation of a mixture of C_{10}–C_{14} n-paraffins (n-alkanes) to linear C_{10}-C_{14} monolefins (alkenes) over a commercial Pt-Sn/γ-Al_2O_3 catalyst was observed to be two to three times higher in a supercritical phase of the reactant themselves than in the gas phase; this indicated that the thermodynamic equilibrium was strongly shifted under supercritical conditions.

The preparation of linear C_{10}-C_{14} monolefins (alkenes) from a mixture of C_{10}–C_{14} n-paraffins (alkanes) by catalytic dehydrogenation is an important process in the production of synthetic detergents and surface-active agents.[1] Because of equilibrium limitations and deep dehydrogenation of monolefins, the present industrial process at most reaches *ca.* 12% conversion with 92% selectivity. Neither conversion nor selectivity have been significantly enhanced although the catalysts used have been highly improved. A new technique is thus required to improve the process.

Supercritical fluids (SCFs), which are fluids above their critical temperatures and pressures, have been used for extraction and separation since their discovery 170 years ago by Baron Charles Cagniard de la Tour.[2] In recent years, much interest has been generated in supercritical reactions[3] and some comprehensive reviews appeared.[4,5] Generally, supercritical fluids not only enhance the reaction rate, but also shift chemical equilibria, and hence significantly improve the performance of heterogeneous catalysis as a result of the enhancement of the physicochemical properties of the fluid near the critical state.[6,7] The supercritical catalytic dehydrogenation of a mixture of C_{10}–C_{14} n-paraffins to a mixture of linear C_{10}-C_{14} monolefins was thus investigated for improvement in conversion and selectivity.[8]

The feedstock composition of the C_{10}–C_{14} n-paraffin mixture is given in Table 1. The dehydrogenation of C_{10}–C_{14} n-paraffins to linear C_{10}–C_{14} monolefins was carried out over commercial Pt-Sn/γ-Al_2O_3 catalyst (DEH-7 supplied by UOP) at supercritical conditions for the C_{10}–C_{14} n–paraffin mixture in a downflow fixed bed reactor with inner diameter of 1.4 cm. The products were determined by the UOP analysis methods in which the conversion is represented by bromine value, the

diolefin content by diolefin number, and the aromatics were determined by UV spectrometry.[9] Typical data are shown in Fig. 1 and Table 2.

Fig. 1 indicated that the pressure strongly influenced the performance of the reactions. When the reaction pressure was below the critical pressure (region A) of the reactant, the reaction conversion was low. At reaction pressures of >2.5 MPa (region C), the conversion of the reactants was slightly higher than the calculated equilibrium conversions, which might be due to the higher solubility of the products in the higher density supercritical phase relative to the gas phase. Only when both the pressure and temperature of the reaction system approached critical conditions for the C_{10}–C_{14} n-paraffin mixture, was conversion greatly increased and highly exceeded the equilibrium conversion. This fact indicated that the equilibrium is strongly shifted under supercritical conditions for the reactants, which might be due to either the high solubility of the products in supercritical fluids[10] or quick desorption of monolefins from the catalyst surface.[11,12] Table 2 shows that the diolefin content in the supercritical phase was relatively lower than that in the gas phase, and aromatics were scarcely observed in the supercritical phase (*cf.* 0.9–1.5% in the gas phase). These results can be attributed to the fast desorption of the main products (*i.e.* monolefins) from the surface of the catalyst, which prevents deep dehydrogenation of the main products to diolefins and aromatics,[11] so leading to a high selectivity of linear C_{10}–C_{14} monolefins ($>98\%$).

Unlike the present industrial processes in which a large amount of hydrogen is used (typically mol ratio H_2 : alkanes =

Table 1 Feedstock composition of the n-C_{10}–C_{14} paraffin mixture

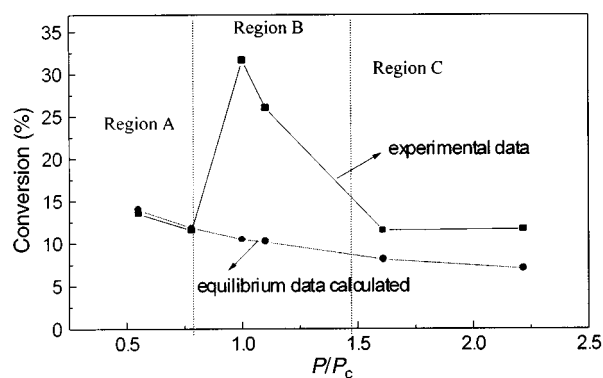| Component	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}
Composition (wt%)	8.76	32.42	36.12	22.45	0.23

Fig. 1 Comparison of the experimental data with the equilibrium conversion calculated at different P/P_c values in the absence of hydrogen at 713 K.

Table 2 The dehydrogenation of a mixture of C_{10}–C_{14} n-paraffins in supercritical (SC) and gas phases (GP)

	T/K	LHSV^a/h^{-1}	p/MPa	H_2:HC^b (mol ratio)	Monolefin (wt%)	Diolefin (wt%)	Aromatics (wt%)
GP	725–738	28–32	0.1–0.4	8:1	8.0–12.0	0.20–0.50	0.9–1.5
SC	673–743	32	1.7–2.1	0:1	13.5–30.7	0.21–0.33	0
SC	673–743	32	3.5–4.4	1:1	8.6–20.4	0.11–0.21	0

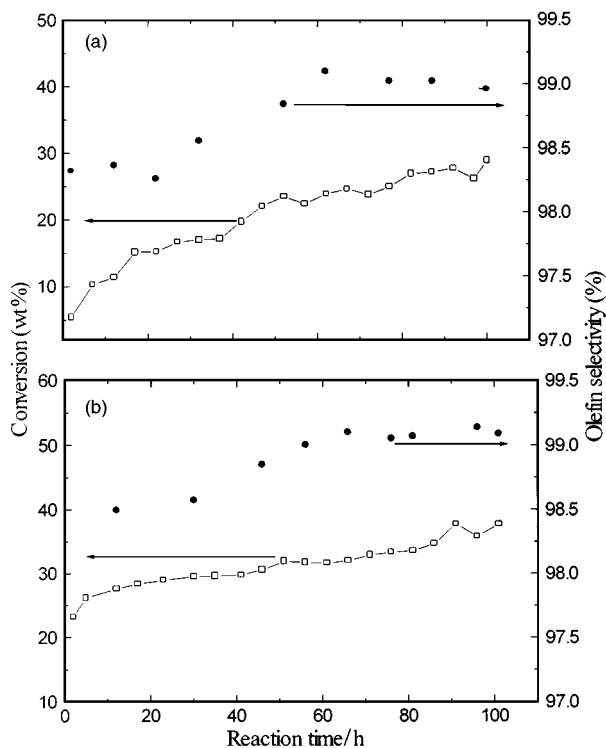^{a} Liquid hour space velocity. ^{b} HC = Alkanes.

Fig. 2 Variation of conversion and selectivity with reaction time in the supercritical phase of the reactant. (a) mol ratio H_2:alkanes = 1:1, 4.0 MPa, 723 K, LHSV = 32 h^{-1}; (b) mol ratio H_2:alkanes = 0:1, 2.0 MPa, 723 K, LHSV = 32 h^{-1}.

8:1) to avoid severe coke formation, supercritical dehydrogenation could be carried out without hydrogen (see Table 2 and Fig. 2). Fig. 2 indicates that both the activity and the selectivity scarcely decreased over 100 h in the absence of hydrogen in the supercritical phase of a mixture of C_{10}–C_{14} n-paraffins. Moreover, TG–DTA illustrated a reduction of coke formation over the catalysts used in the supercritical phase. This is as expected if the formation of carbonaceous species on the surface of the catalyst is suppressed by supercritical fluids.[13,14] Indeed, a partial pressure of hydrogen was detrimental on the performance of the supercritical phase, possibly owing to a change of supercritical conditions in the presence of hydrogen. The mechanism of the process is currently under investigation.

The above results indicate that reaction in a supercritical phase leads to a substantial improvement in both conversion and selectivity as well as the reduction of coke formation in the catalytic dehydrogenation of a mixture of C_{10}–C_{14} n-paraffins to linear C_{10}–C_{14} monolefins.

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