

Air oxidation of supercritical phase isobutane to *tert*-butyl alcohol

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***tert*-2-Butyl alcohol can be synthesized efficiently on SiO₂-TiO₂ or Pd-C catalyst if air is directly introduced to the supercritical-phase isobutane.**

As the initial material in methyl *tert*-butyl ether (MTBE) production and methyl methacrylate (MMA) synthesis where MTBE is high-octane-number gasoline additive and MMA is a resin material, *tert*-butyl alcohol (TBA) is of increasing importance.^{1,2} On the other hand, TBA can be used to produce isobutene *via* a dehydration reaction. Commercially, production of isobutene from isobutane *via* direct dehydrogenation needs high reaction temperatures (500–600 °C) and a catalyst which is deactivated quickly. Here we report a new synthesis of TBA where air is used directly as oxidant to convert isobutane to TBA. This synthesis can be conducted efficiently if isobutane is in the supercritical phase on selected catalysts.

Wide attention has recently been devoted to supercritical fluid applications in catalytic systems, both in homogeneous and heterogeneous systems, such as the Fischer-Tropsch reaction, alkylation and carbon dioxide conversion.^{3–6} However, organic oxidation in the supercritical phase has hardly been studied until now, especially when air is used directly as oxidant. It is also of theoretic interest to pursue the reaction behaviour of oxygen species such as peroxide in supercritical fluid. It is expected that high solubility, high diffusion capacity—especially the cluster structure formed around solute molecules—and the special ionization effects of the supercritical fluid might exert a strong influence on the reaction mechanism.

Listed in Table 1 are the reaction performance data for two catalysts and a non-catalytic case, in the supercritical, gas and liquid phases.† In either the non-catalytic reaction or the catalysed reaction, changing the state of isobutane from the gas phase (44 bar) to the supercritical phase (54 bar) gave remarkably enhanced conversion of isobutane and oxygen. Meanwhile, selectivities for the target products (TBA and isobutene) increased slightly when moving from the gas phase to the supercritical phase. Exceptionally, Pd-C catalyst exhibited obvious changes in both conversion and selectivity of the reaction if the phase changed. When the total pressure was increased from 44 bar to 54 bar, the total yield of TBA and isobutene was enhanced from 0.31 to 2.70%.

All the catalysed reactions showed higher activity than the non-catalytic reactions, which proved the promotional role of the catalysts in the reaction.

More interestingly, if the total pressure of the gas phase reaction was as low as 12 bar, the reaction did not proceed, even if SiO₂-TiO₂ was utilized. Similarly, for the liquid phase reaction on SiO₂-TiO₂, the reaction rate was very low, as shown in Table 1.

Generally, the main byproduct of the reaction was acetone. The combustion product, CO₂, was formed only in very small amounts. CO was not detected. Lighter hydrocarbons were formed in small amounts as well, and consisted of 98% methane. The total amount of all C₁ species was equal to that of acetone, which indicates the decomposition of C₄ to C₃ species (acetone) and C₁ fractions. The carbon balance of the total products was higher than 97%, indicating remarkably low carbon deposition on the catalyst surface.

As indicated in Table 1, this reaction depended greatly on temperature and pressure, which implied the effect of the reaction phase. Fig. 1(a) shows a comparison of the reaction performance on SiO₂-TiO₂ catalyst under 54 bar while the reaction temperature was varied around the critical point (408 K). It is clear that isobutane and oxygen conversions were enhanced remarkably when the state of the isobutane changed from the liquid phase to the supercritical phase. Consequently, TBA yield was enhanced in the supercritical phase. The reason for the high isobutene selectivity on Pd-C catalyst in the supercritical phase is not as yet clear. It is well known that the formed TBA can be dehydrated rapidly on acidic sites of a catalyst, but the carbon support here is generally neutral.

Concerning the selectivity of the products, as exhibited in Fig. 1(b), TBA selectivity as well as acetone selectivity was enhanced and isobutene selectivity was suppressed in the supercritical phase reaction on SiO₂-TiO₂ catalyst.

For the oxidation mechanism in supercritical fluid, it is suggested that dioxygen can attack the most active hydrogen of isobutane to form *tert*-butyl hydroperoxide (TBHP, Bu^tOOH). TBHP is known as an oxygen donor in the epoxidation of alkenes.⁷ It is inferred that TBHP can form in the supercritical phase from isobutane coexisting with dioxygen. This auto-oxidation step can proceed without catalyst,⁸ which happened in the inductive period during the initial stages of the reaction.

Table 1 Reaction performance of catalytic oxidation of isobutane by air in the supercritical phase or the gas phase^a

Catalyst	Total pressure/ bar	Isobutane conversion (%)	O ₂ conversion (%)	TBA selectivity (%)	Isobutene selectivity (%)	TBA and isobutene yield (%)
none	44	0.3	2.5	55.0	7.0	0.2
none	54	1.2	9.9	58.1	8.1	0.8
SiO ₂ -TiO ₂	44	2.9	24.0	59.0	5.2	1.9
SiO ₂ -TiO ₂	54	4.9	40.6	61.2	6.3	3.3
SiO ₂ -TiO ₂	12	0.0	0.0	0.0	0.0	0.0
SiO ₂ -TiO ₂ ^b	54 ^b	0.1	1.1	55.5	7.7	0.1
Pd-C	44	0.5	4.2	61.2	2.1	0.3
Pd-C	54	3.1	25.6	64.8	20.1	2.7

^a Isobutane: air = 3:1, W/F = 10 g h mol⁻¹, catalyst weight = 0.5 g, T = 426 K. ^b Liquid-phase reaction where the reaction temperature was 403 K.

TBHP can decompose homolytically, resulting in *tert*-butoxy radical and hydroxide radical. *tert*-Butoxy radical then combines with a third hydrogen from another isobutane to form TBA. TBA can be dehydrated on acidic sites, leading to the increase in isobutene selectivity. For the main byproduct, acetone, it could be derived from decomposition of *tert*-butoxy radical, accompanied by C1 compounds such as CO, CO₂ or CH₄.

Concerning the role of the catalyst, it is inferred that the catalyst might improve the efficiency of the oxidation of isobutane with TBHP, resulting in the enhanced conversion. Methanol is probably a byproduct, together with acetone, as in some published reports.^{7,8} However, in our supercritical phase reaction, not only methanol but also CO₂, CH₄ formation accompanied acetone formation. It is suggested that the formation route of CO₂ and CH₄ is different from that of

methanol. Detailed studies on the reaction mechanism will be reported in the near future.

Because the reactions reported above were conducted with a molar ratio of isobutane to O₂ = 15 : 1 (isobutane to air = 3 : 1), it is expected that the TBA yield might be enhanced further if the oxygen partial pressure was increased.⁹

Under the standard reaction conditions, the reaction required 3 h to reach a steady state from the reaction start. Catalyst deactivation was not observed during the supercritical phase reaction even after continuous reaction for 30 h.

Footnotes

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† A typical flow-type fixed-bed reactor was employed, and the isobutane was fed by a high-pressure pump. Isobutane has a critical temperature of 408.13 K and a critical pressure of 36.48 bar. For the catalytic reaction, representative examples reported here are for reactions on commercially available amorphous SiO₂-TiO₂ (Fuji Silysia Chemical Co.), and a home-made palladium catalyst (2.5 wt%) supported on active carbon (Shirasagi, Takeda Pharmacy Co.). All products was analysed by gas chromatography (Shimadu GC-14B or Hitachi 163). A capillary column (TC-1) coupled with a flame ionization detector was used for analysis of the oxygenates and heavy hydrocarbons. A molecular sieve column and an active carbon column, with a thermal conductivity detector, were utilized for inorganic gas analysis. Lighter hydrocarbons with determined by an active alumina column with a flame ionization detector. The standard reaction conditions are as follows: ratio of isobutane to air = 3 : 1; W/F (total) = 10 g h mol⁻¹; catalyst weight = 0.5 g; reaction temperature = 426 K. The total pressure for the gas phase reaction is 44 bar and that for the supercritical phase is 54 bar. Correspondingly, the partial pressure of isobutane is 33 bar and 41 bar, respectively. The feed ratio of isobutane to air was 3. When the total pressure was higher than 48 bar (36 bar of isobutane and 12 bar of air), the phase of the reaction became supercritical. The reaction at a total pressure of 54 bar was in the supercritical phase.

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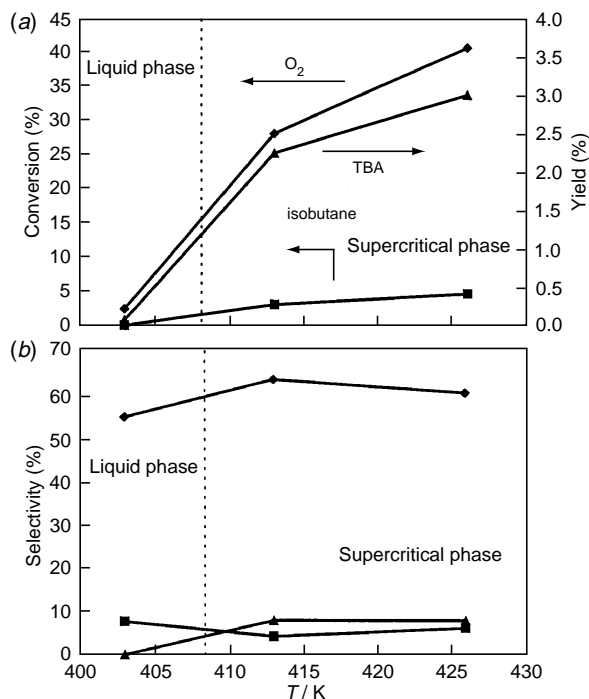


Fig. 1 Comparison of the reaction performance around the critical point: (◆), TBA, (■) isobutane, (▲) acetone. SiO₂-TiO₂ catalyst, 54 bar, W/F = 10 g h mol⁻¹, catalyst weight = 0.5 g, isobutane : air = 3 : 1.