Radical Type Catalytic Oxidation of Butane at Low Temperatures over *in-situ* Prepared Silica Species

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Silica species prepared by *in-situ* method using silicon alkoxide as precursor were found to be active for radical type oxidation of butane at low temperatures, i.e., below 650 K.

Silica itself is generally thought to be inactive for catalytic reactions. Although there are some reports about the catalysis of silica, such as partial oxidation of methane,[1-5] dehydrogenation of ethanol[6] and ammoximation of cyclohexanone,[7] the catalytic activity of silica is very low. For example, partial oxidation of methane over silica is achieved only at higher temperatures, above 1000K.[5] This is also due to the difficulty in the activation of light alkanes. For the partial oxidation of light alkanes, radical type oxidation at high temperatures or mild oxidation over transient metal oxide catalysts at moderate temperatures are generally applied. Among these, the oxidation of butane over $(VO)_2P_2O_7$ catalyst is known to be efficient process for the industrial production of maleic anhydride.[8]

In the present study, we found that the silica species prepared by *in-situ* method are significantly active for oxidative dehydrogenation and partial oxidation of butane at low temperatures, below 650 K. The activity of the *in-situ* prepared silica species was comparable to that of $(VO)_2P_2O_7$ catalyst, although the product distributions are different from each other. This communication represents the novel type of silica species as oxidation catalyst.

The oxidation of butane was carried out in a conventional flow apparatus at atmospheric pressure. A Pyrex-glass tube with 10 mm inner diameter was used as a reactor. The reaction conditions were as follows; butane/O_2/N_2 = 2%/18%/balance, flow rate = 64.2 ml min^{-1}, reaction temperature = 603-763K. Tetraethylorthosilicate (TEOS, Kishida Chemical, 99%) was fed by saturation in the feed gas at 273 K and the concentration in the feed gas was 0.046%. Silica powder (JRC-SIO-8, 303 m^{2}g^{-1}) was supplied from the Committee on Reference Catalyst of the Catalyst Society of Japan.

Figure 1 shows the conversion of butane with reaction temperature. In the flowing TEOS (open circles), the conversion of butane steeply increased between 603 and 623 K and the conversion of 40 to 60 % was obtained above 623 K. Then, the conversion gradually decreased with increasing temperature, and again it increased above 723 K. This activity was reproducible even when the catalytic run was conducted in the order of decreasing temperature (closed circles). In the case of the empty reactor without TEOS (open triangles), only small amount of butane was converted at 603-763 K. When silica powder was packed in the reactor, the conversion was slightly increased especially at high temperatures. However, it was quite low below 673 K. It should be noted that the color of the tube turned to white after the reaction with flowing TEOS, suggesting the deposition of silica species on the wall of the tube reactor.

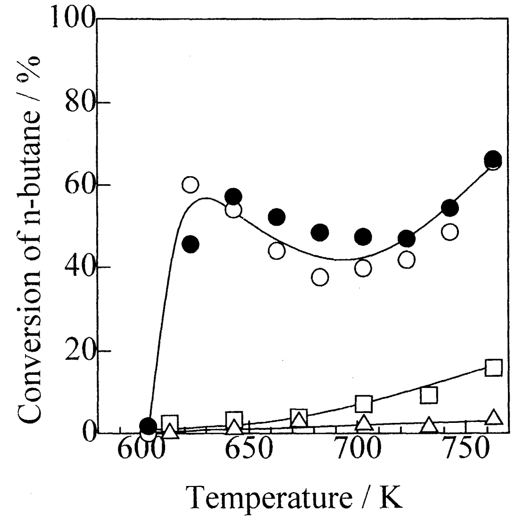

Figure 1. Conversion of butane in empty reactor with flowing TEOS (○,●), in empty reactor without flowing TEOS (△) and over silica powder (□).

Figure 2 shows the conversion of butane with time-on-stream. In the presence of TEOS, the conversion of butane steeply increased with time-on-stream and attained constant value after 75 min. Even after TEOS was removed from the feed stream, the conversion of butane remained essentially unchanged for longer than 1000 min. This result strongly indicates that the oxidation is not a homogeneous reaction in gas-phase but a heterogeneous reaction over the solid silica species derived from TEOS. Turnover number for butane conversion calculated from the amounts of loaded TEOS for 300 min and reacted butane for 1115 min was 84 and that of oxygen conversion was 225, respectively. These numerals clearly indicate that the reaction proceeds catalytically. Or, in other words, the *in-situ* prepared silica species provide catalytic sites which are stable even in the oxidation condition of butane, i.e., in the presence of hydrocarbon, oxygen, water and carbon oxides.

The temperature dependence of the conversion shown in Figure 1 suggests that the reaction in the presence of TEOS is quite unique and is entirely different from the conventional catalytic reactions. The decrease in the conversion above 623 K is unusual. Further, the steep increase in the conversion between 603 K and 623 K corresponds to the activation energy of 550-700 kJ mol^{-1} which is extremely higher than those in usual catalytic oxidation reactions. The unique temperature dependence should be due to some particular structure of silica species prepared by the *in-situ* method.

Table 1 shows the product distribution of the oxidation of butane in the presence of TEOS. Butene and acetaldehyde were

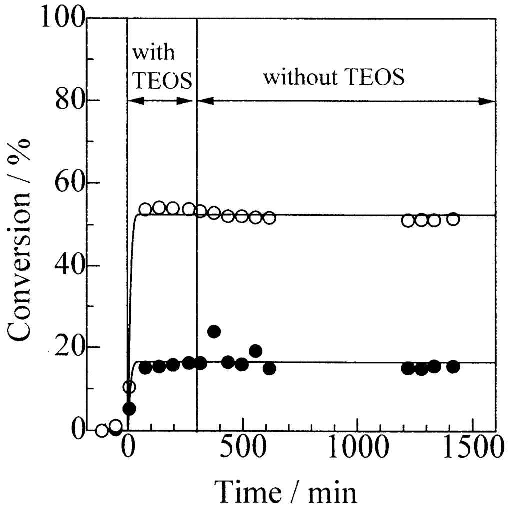

Figure 2. Conversion of butane (○) and oxygen (●) at 643 K with time-on-stream.

the main products in the organic molecules. The selectivity of butene increased from 15.3% to 26.6% with the increase in the reaction temperature. Propene, ethene, ethane and methane were also produced as hydrocarbon products. As for the oxygenated products, alcohol, aldehyde, ketone and furan were observed. Maleic anhydride was not formed at all, though this is the main product of butane oxidation over $(VO)_2P_2O_7$ catalysts.[8,9] The product distribution indicates that the oxidation of butane over the silica species is entirely different from that over $(VO)_2P_2O_7$ catalysts.

Euker and Leinroth reported the oxidation of butane in an empty reactor at 598 K.[10] The product distribution in their experiment was similar to our result, i.e., butene and acetaldehyde were the main products and other minor products, such as ethene, methylethylketone and furan, were observed. The formations of alkene, aldehyde, ketone and 2-methyl THF were also observed in the gas-phase oxidation of pentane.[11-13] The contribution of radical species is generally suggested in the gas-phase oxidation of alkanes,[10-13] and the formation of alkylperoxy species was confirmed by ESR spectra.[14] The similarity in the product distribution suggests that radical type-reaction may be involved in the present case. Or, in other words, silica species *in-situ* prepared seem to provide active sites catalyzing radical type reaction.

Table 1. Product distribution in butane oxidation in the presence of TEOS

Temperature / K	643	703	643[a)]
Conversion / %			
butane	53.6	39.3	57.3
oxygen	14.3	8.0	19.6
Selectivity / C-mol%			
methane	0.1	0.3	0.1
ethane	0.0	0.1	0.0
ethene	4.5	5.2	4.3
propene	1.4	3.3	1.2
butene	15.3	26.6	12.7
acetaldehyde	20.1	17.6	20.2
acetone	2.7	2.5	2.6
2-propanol	1.4	2.0	0.7
methylethylketone	1.7	2.7	1.3
crotonaldehyde	0.3	0.5	0.3
furan	1.9	1.8	2.7
2,5-dihydrofuran	1.2	1.5	0.8
others	3.9	3.6	6.7
$CO + CO_2$	45.5	32.3	46.4

[a)]in the run of decreasing temperature.

It is reported that the evacuation of silica powder at high temperatures enhances or generates catalytic activities. Yoshida et al. reported the photocatalytic oxidation of propene to methyloxirane over silica powder evacuated at higher than 1073 K.[15] Matsumura et al. reported a good relationship between the evacuation temperature, the number of silanol groups, and the activity for dehydration of ethanol over silica powder.[6] Furthermore, they also found the formation of radical oxygen sites of SiOO$^-$Si species over silica powder in CO oxidation conditions.[16] The active sites such as those generated by high temperature evacuation could be easily formed on the silica species *in-situ* prepared from TEOS.

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