

The Carbon-Supported Palladium–Vanadyl Sulfate–Sulfuric Acid Catalyst System for Heterogeneous Wacker Reactions

In the last few years the Wacker process for the ultimate production of acetic acid has been replaced by the more economical method of methanol carbonylation. However, research attempts to improve the Wacker-type solution catalyst by immobilizing catalyst components, or by searching for chlorine-free redox systems are still important in order to develop an industrial technology for the oxidation of higher olefins with good catalyst activity and stability. Some significant advances in both homogeneous and heterogeneous catalysis have been realized in applications of heteropoly acid (1) and V_2O_5 (2) as unique oxidants for palladium. These systems, however, appear to lack sufficient activity or stability for the oxidation of higher olefins other than ethylene and propylene.

The authors have recently reported that the $PdSO_4-H_3PW_6Mo_6O_{40}$ catalyst system functions with good efficiency in the homogeneous oxidation of 1-butene to give methyl ethyl ketone (MEK) selectively (3). This information, together with our recent suggestion that heteropoly acid may interact with palladium (4), has inspired us to design a solid Wacker catalyst of palladium–heteropoly compound system on activated carbon, since the carbon has been proved to be a suitable support to immobilize heteropoly acid firmly (5). Through a close examination on an active heterogeneous catalyst system of $PdSO_4$ –12-vanadophosphate, vanadyl sulfate, which had gradually formed *in situ* by the decomposition of 12-vanadophosphate on the carbon, was found to be a real effective oxidant for palladium. In this paper we report the catalytic performance of the carbon-supported

$Pd-VOSO_4-H_2SO_4$ system in the heterogeneous Wacker reactions of 1-butene and ethylene under the vapor-phase conditions. The intrinsic effect of heteropoly compounds as oxidants for palladium on carbon will be reported elsewhere.

EXPERIMENTAL METHODS

The carbon-supported $PdSO_4-VOSO_4-H_2SO_4$ catalyst was prepared by impregnating an active carbon (Kraray GC, 1656 m²/g) as granules of 20 ~ 40 mesh with $PdSO_4$ and $VOSO_4$ in a dilute aqueous sulfuric acid, evaporating at 50°C *in vacuo*, then drying at 60°C for 15 h. The carbon support had been treated with boiling 1 N HNO_3 for 3 h prior to use. A certain amount of H_2SO_4 , which is essential to enhance catalyst efficiency, was incorporated simultaneously into the catalyst. The carbon-supported $PdCl_2-VOSO_4$ catalyst was obtained by introducing $PdCl_2$ and $VOSO_4$ into the carbon separately; first the support was doped with the $PdCl_2$ dissolved in 0.5 N HCl, washed to remove HCl, then $VOSO_4$ was incorporated from an aqueous solution on evaporation *in vacuo*.

The oxidation reactions were performed in an ordinary flow system using a Pyrex glass reactor with a fixed bed of about 2 g of catalyst. 1-Butene and ethylene employed were of 99.0 and 99.5% purity, respectively. The time on stream denoted in each of the following experiments represents the time elapsed just after the reaction attained a stationary state (2 h after the start of the feed of olefin, dioxygen, and water). The reactor effluent was collected in a set of ice-cooled traps and analyzed by means of GLC using a PEG 1000 column (1 m).

RESULTS AND DISCUSSION

In the oxidation of 1-butene, MEK was obtained in a good yield with the carbon-supported $\text{PdSO}_4\text{-VOSO}_4\text{-H}_2\text{SO}_4$ catalyst having a specific formulation: Pd content 0.5 wt%, $\text{PdSO}_4\text{:VOSO}_4\text{:H}_2\text{SO}_4 = 1\text{:}10\text{:}5\text{-}15$ mole ratio. An example of the performance of this active catalyst is illustrated in Fig. 1. The turnover frequency of the catalyst attains about 30 MEK mol/Pd g-atom/h at 115°C (Fig. 1a). Higher $\text{VOSO}_4/\text{PdSO}_4$ ratios cause the increase of by-products such as acetaldehyde, acetic acid, and biacetyl. It was experimentally confirmed that these by-products were generated via the secondary oxidation of the product MEK by the catalytic action of VOSO_4 alone. Another by-product, 2-butanol, was formed through the hydration of 1-butene with the H_2SO_4 on carbon. The selectivity to carbon dioxide based on 1-butene was less than 0.5%. A spectrum of the by-products is shown in Fig. 1b.

The use of carbon support is necessary for the $\text{PdSO}_4\text{-VOSO}_4\text{-H}_2\text{SO}_4$ catalyst system, because other supports, such as $\alpha\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$, and SiO_2 , were all ineffective, giving only a stoichiometric amount of MEK with respect to the palladium supported. The VOSO_4 on such ineffective supports was oxidized to V_2O_5 under the

reaction conditions. In contrast, the VOSO_4 on carbon, even when H_2SO_4 was not present, remained intact during the reaction, and most of it could be recovered on extracting with hot water. Accordingly, VOSO_4 is probably the real active oxidant for palladium in the present carbon-supported catalyst. The carbon support appears to play an essential role of maintaining VOSO_4 at an active state during the reaction. Figure 1a also indicates that higher reaction temperatures not only accelerate undesirable side reactions but also cause the decrease in catalytic activity. Similar temperature effect on catalytic activity has previously been reported by Kunugi *et al.* (6) in the study on the oxidation of ethylene with a carbon-supported $\text{PdSO}_4\text{-H}_2\text{SO}_4$ system having no additive oxidants. As those authors asserted, the concentration of water on the catalyst surface probably decreases at high reaction temperatures (i.e., more than 120°C) owing to hydrophobicity of activated carbon, resulting in a slowdown of the Wacker reaction, while hydrophilic sulfuric acid presumably works for enriching water on the carbon surface. An alternative reaction path which involves the hydration of 1-butene with H_2SO_4 followed by the oxidative dehydrogenation of 2-butanol over Pd or Pd- VOSO_4 seems improbable, because the

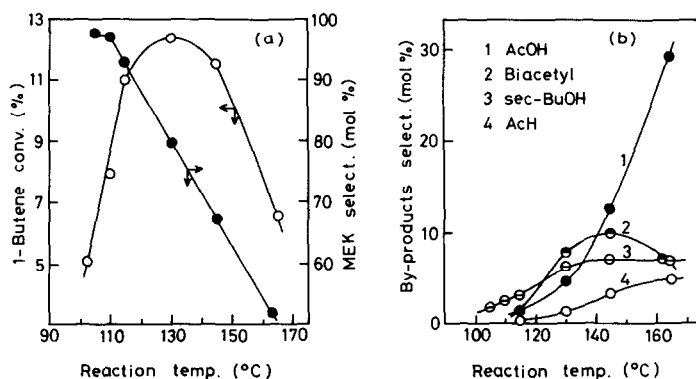


FIG. 1. 1-Butene oxidation over carbon-supported $\text{PdSO}_4\text{-VOSO}_4\text{-H}_2\text{SO}_4$ catalyst at 1 atm. Pd: 0.5 wt%; $\text{PdSO}_4/\text{VOSO}_4/\text{H}_2\text{SO}_4$ (mol ratio): 1/10/15; W/F: 14 g-cat · h/mol; feed: 1- C_4H_8 17%, O_2 12%, H_2O 71%; selectivities were based on the converted 1-butene; data denoted average values for 3 h of time on stream.

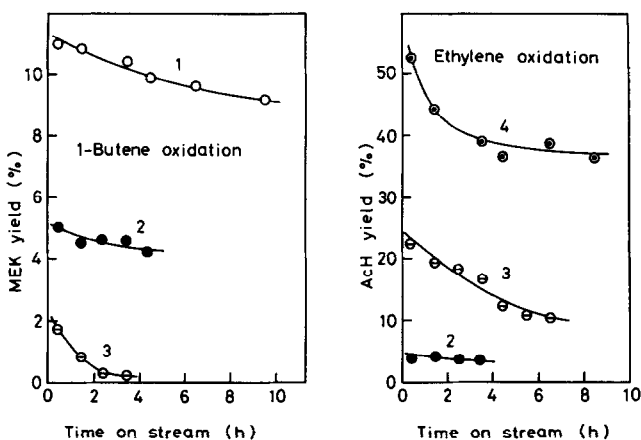


FIG. 2. Oxidation of 1-butene and ethylene over carbon-supported palladium catalysts at 115°C and 1 atm. Pd: 0.5 wt%; Pd salt/VOSO₄/H₂SO₄ (mol ratio): 1/10/15; W/F: 15 g-cat · h/mol; feed: olefin 17%, O₂ 12%, H₂O 71%; curve 1: PdSO₄-VOSO₄-H₂SO₄, curve 2: PdSO₄-H₂SO₄, curve 3: PdCl₂, curve 4: PdCl₂-VOSO₄; yields were based on the olefin fed.

amount of the by-product 2-butanol increased monotonously with the H₂SO₄ content of catalyst, and it was never influenced by the kind of support and the contents of PdSO₄ and VOSO₄, although the MEK yield attained the maximum at a H₂SO₄/PdSO₄ ratio of about 5 on the carbon support.

Figure 2 shows the comparative data of catalyst efficiency for the heterogeneous Wacker reactions with several carbon-supported catalyst systems. Incorporation of VOSO₄ into the parent catalyst systems of PdSO₄-H₂SO₄ and PdCl₂ remarkably promotes the oxidations of 1-butene and ethylene, respectively. It is noted that the PdSO₄ coupled with H₂SO₄ is far more active than PdCl₂ in the oxidation of 1-butene, but the situation is quite the reverse for ethylene. In the oxidation of ethylene, the selectivity to acetaldehyde based on the converted olefin was as high as 99 mol%: no acetic acid was formed, and only a trace amount of MEK was detected as a by-product probably via the dimerization of ethylene and successive oxidation. Propylene was likewise selectively oxidized to afford acetone (C₃H₆ conversion 9 ~ 10%) in the presence

of the PdSO₄-VOSO₄-H₂SO₄ catalyst under the same reaction conditions as denoted in Fig. 2. To characterize the present catalyst system, detailed work including the study on redox behavior is under way.

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