STEAM REFORMING OF METHANOL OVER GROUP VIII METALS SUPPORTED ON SiO₂, Al₂O₃ and ZrO₂

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Received August 4, 1993
Accepted November 16, 1993

The activity and the selectivity for the title reaction were greatly improved over Group VIII metals supported on ZrO₂. The support effect upon the reaction was marked for Pd-based catalysts.

INTRODUCTION

The steam reforming of methanol, CH₃OH + H₂O \(\rightarrow\) CO₂ + 3H₂, has been extensively studied over supported copper catalysts [1-3], which exhibit high activity and high selectivity for this reaction. On the other hand, few publications appeared on the present subject over transition metal catalysts [4-6]. The selectivities for steam reforming were much lower than those over supported copper catalysts [1-6]. Experiments were mostly limited for catalysts supported on Al₂O₃.

In the present work, the steam reforming of methanol was carried out over various Group VIII metals supported on SiO₂, Al₂O₃ and ZrO₂. We showed that the turnover frequency and the selectivity for steam reforming were greatly affected by the kind of the support.
EXPERIMENTAL

Twelve kinds of catalysts (Ni/SiO$_2$, Ni/Al$_2$O$_3$, Ni/ZrO$_2$, Rh/SiO$_2$, Ru/SiO$_2$, Ru/ZrO$_2$, Pd/SiO$_2$, Pd/Al$_2$O$_3$, Pd/ZrO$_2$, Pt/SiO$_2$, Pt/Al$_2$O$_3$, and Pt/ZrO$_2$; metal loading, 1 wt.%) were tested for the reaction. Supported Ni and Pd were prepared by impregnation of SiO$_2$ (Japan-Chromato Ind. Co.), Al$_2$O$_3$ (JRC-ALO-4 supplied by Catalysis Society of Japan) and ZrO$_2$ (prepared by decomposition of zirconium oxynitrate, Kanto Chem. Co. Inc.) with solutions of Ni and Pd nitrates. Ru/SiO$_2$ and Ru/ZrO$_2$ were prepared by impregnation of SiO$_2$ and ZrO$_2$, respectively, with solutions of RuCl$_3$. Pt/ZrO$_2$ and Pt/Al$_2$O$_3$ were prepared by impregnation of ZrO$_2$ and Al$_2$O$_3$ with solutions of tetrammine Pt(IV) chloride. Rh/SiO$_2$ and Pt/SiO$_2$ were prepared by ion exchange between protons of surface hydroxyls of silica and ammine cations of Pt and Rh prepared from H$_2$PtCl$_6$ and RhCl$_3$, respectively. The resulting catalysts were dried in air at 383 K overnight and were subsequently calcined in air at 773 K for 3 h.

Experiments were carried out in a flow system at 101.3 kPa. The mixture of methanol and water was fed in a reactor by a micropump and vaporized before entering the catalyst bed. Inlet partial pressure of either methanol or water was kept at 24.3 kPa. Nitrogen was used as a diluent.

The reactants and products were analyzed by gas chromatography. The selectivity, $S$, for steam reforming was determined on carbon basis, i.e. $S = \frac{P_{CO_2}}{(P_{CO_2} + P_{CO} + 2 P_{CH_3OCH_3})}$, where $P_{CO_2}$, etc., represent the "outlet partial pressure" of CO$_2$, etc. The numbers of surface metal atoms exposed on the supported Ni, Rh and Pt were determined by hydrogen chemisorption at room temperature, whereas those on supported Pd catalysts were determined by hydrogen chemisorption at 373 K [7]. The dispersities, $D$, of the metals were estimated from the amount of chemisorbed hydrogen and the total number of metals loaded.