Mechanistic Study of Methanol Decomposition to Carbon Monoxide and Hydrogen over Ni/SiO$_2$-MgO

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Mechanistic studies of methanol decomposition on Ni/SiO$_2$-MgO were performed by use of deuterium isotopic species. In the exchange reaction of methanol with a deuterium molecule, one hydrogen in methanol was much more readily exchangeable than the other hydrogen atoms, suggesting that dissociation of methanol to form a methoxy group and its reverse reaction are fast. Perdeuterio methanol (CD$_3$OD) decomposed more slowly than the other isotopic species, CH$_3$OH and CH$_3$OD. The difference in the activation energies of CD$_3$OD and the other two isotopic species was about 1 kcal mol$^{-1}$. Formaldehyde decomposed to CO and H$_2$ faster than methanol. These results suggest that methanol decomposition be initiated by dissociation of H of the OH group followed by successive removal of the H atoms, and that the rate determining step involves removal of H from the methoxy group.

1. Introduction

Methanol decomposition to form carbon monoxide and hydrogen is a useful reaction for fuel cell and on-board reforming for vehicle fuel applications. Transition metal catalysts are known to be active for such reactions.$^{11-19}$ In our previous paper, catalytic activities of transition metals supported on different types of supports for the decomposition of methanol to carbon monoxide and hydrogen were reported.$^{11)}$ Among the catalysts examined, Ni/SiO$_2$-MgO exhibited the optimal catalytic performance with respect to activity and selectivity. Some reasons for its high activity and selectivity were suggested to be due to the stability of the metallic Ni finely dispersed on the support.

Mechanistic studies of methanol decomposition on Ni and Cu wires at temperatures 527—673 K were reported by Yasumori et al.$^{19,20}$ They concluded that dissociation of the methoxy group to hydrogen and formaldehyde is the rate determining step on Ni wire; and on Cu wire, the reaction proceeds via formaldehyde to methyl formate and finally to carbon monoxide and hydrogen.

In the present work, the mechanisms of methanol decomposition in the temperature range of 463—523 K over the Ni/SiO$_2$-MgO catalyst were studied by use of deuterium isotopes. It is suggested that the abstraction of an H from the methyl group of the surface methoxy species is the rate determining step.

2. Experimental

Catalyst preparation The Ni/SiO$_2$-MgO catalyst was prepared by impregnation of SiO$_2$-MgO with a Ni(NO$_3$)$_2$ aqueous solution followed by evaporation to dryness and calcination at 773 K in air. Silica magnesia was prepared by addition of aqueous magnesium nitrate to aqueous sodium silicate. The precipitate was washed, dried, and calcined at 823 K for 2 h. The amount of Ni in the catalyst was adjusted to 5% by weight. The catalyst was reduced in a hydrogen stream at 723 K and outgassed at the same temperature before use.

Reaction procedures A closed recirculation reactor was employed for carrying out the reactions. A catalyst sample (20 mg) was placed in the reactor and pretreated as mentioned above. Methanol (40 Torr) was introduced into the reaction system and recirculated. The products were periodically withdrawn from the system for gas chromatographic analysis. In some experiments, D-labeled molecules (CH$_3$OD, CD$_3$OD) were used in stead of CH$_3$OH. Formaldehyde, one of the expected intermediates, was also used as a reactant. Exchange of methanol with D$_2$ was carried out to earmark the labile hydrogen of the methanol molecule involved. The isotopic distribution in the exchanged methanol was measured by mass spectrometry.
Temperature-programmed desorption (TPD) of methanol and formaldehyde  Methanol or formaldehyde was adsorbed on the catalyst at room temperature for 60 min followed by outgassing for 30 min at the same temperature. TPD was run at the rate of temperature increase of 11 K·min⁻¹. The desorbed molecules were analyzed by mass spectrometry. To calibrate the sensitivity of the mass spectrometer, argon was introduced into the system at a constant rate (10⁻³ Torr), and the peak intensities of the gasses evolved were expressed as relative intensities to Ar peaks (I/Im).

3. Results

Isotopic distributions of methanol resulted from methanol-D₂ exchange at 423 and 523 K are given in Table 1. At 423 K, methanol decomposition scarcely took place; only the exchange took place at 423 K. The exchange at both temperatures resulted in the predominant formation of methanol molecules containing one D atom (d₁). The H atom which is more susceptible to exchange differs in nature from the three other H atoms. It is suggested that the labile H atom be the H atom in the hydroxyl group, indicating that the dissociation of methanol to a methoxy group and a hydrogen atom and its reverse step are fast compared to the dissociation of the hydrogen atoms of the methyl group.

Formaldehyde decomposed over Ni/SiO₂-MgO mostly to H₂ and CO, but with formation of a small amount of methyl formate which was the main product over SiO₂-MgO. The methyl formate formed in the products over Ni/SiO₂-MgO was that probably formed on the catalyst support.

The decomposition rate of formaldehyde over Ni/SiO₂ is compared to that of methanol over the same catalyst in Fig. 1. Formaldehyde decomposed to H₂ and CO much faster than did methanol. If methanol undergoes decomposition to H₂ and CO through formaldehyde, the steps from formaldehyde to H₂ and CO should not be involved in the rate determining step of the reaction.

Arrhenius plots of the decomposition of CH₂OH, CH₃OD, and CD₃OD, are shown in Fig. 2. Perdeuteriomethanol, CD₃OD, decomposed...
more slowly than CH$_3$OH and CH$_3$OD. The relative rates at 523 K and the activation energies of decomposition are summarized in Table 2. Simple theoretical calculations indicate an isotope effect ($k_{H}/k_{D}$) of 3.3 and activation energy differences of 1.2 kcal·mol$^{-1}$ for C-H bond cleavage and 1.3 kcal·mol$^{-1}$ for O-H bond cleavage, respectively, if the bonds are completely broken in the transition states.$^{12}$ The observed isotope effects and activation energy differences are close to the theoretical values. Therefore, the C-H bond cleavage is suggested to be involved in the rate determining step.

The effects of CO and H$_2$ pressures on the decomposition rate are shown in Fig. 3. The decomposition rate increased on admission of 5 Torr of hydrogen, and became constant on further increase in hydrogen pressure. The presence of CO, on the contrary, decreased the rate of methanol decomposition. A rate law for the reaction retarded by one of the products can be expressed by:

$$\frac{dx}{dt} = \frac{k(1-x)}{1+ax}$$  \hspace{1cm} (1)

where $x$ represents the fractional conversion at reaction time $t$, $k$ is a first-order rate constant, and $a$ is a constant related to retardation. By integrating Eq. (1), the following Eq. is obtained.

$$\frac{1}{1-x} - \frac{1}{1-x_0} = a \frac{x}{t} + k$$  \hspace{1cm} (2)

For the reaction at 523 K, $(1/t)\ln 1/(1-x)$ is plotted against $x/t$ in Fig. 4. The linear relationship demonstrates that Eq. (1) is valid for the reaction.

The TPD profiles of the gases evolved when methanol and formaldehyde were preadsorbed on the catalyst are shown in Figs. 5 and 6. For the
sample on which methanol was adsorbed, most of the CO and H₂ evolved simultaneously at 473 K. It is to be noted that evolution of a small part of CO preceded the simultaneous evolution of CO and H₂. Evolution of formaldehyde was not appreciable. For the sample on which formaldehyde was adsorbed, methyl formate evolved at 373 K, and the major part of CO and H₂ evolved at about 448–458 K. In this case too, a small fraction of CO evolved before the simultaneous evolution of CO and H₂. As the formation of methyl formate occurred only on the support, it is considered that methyl formate has evolved from the catalyst support.

4. Discussion

All the results suggest that the rate determining step in the methanol decomposition over Ni/SiO₂-MgO is the release of an H from the methyl group as shown by Eq. (4) in the following reaction mechanism.

\[
\begin{align*}
\text{CH₃OH} & \rightarrow \text{CH₂O} + \text{H} \\
\text{CH₂O} & \rightarrow \text{CH₂O} + \text{H} \\
\text{CH₂O} & \rightarrow \text{CO} + \text{H}_2
\end{align*}
\]  

The observation that preferential exchange of one D atom occurring in the exchange of methanol with D₂ and that no isotope effect for CH₃OD indicate that the dissociation of H of the OH group in methanol and its reverse reaction are fast and, therefore, are not involved in the rate determining step.

The predominant incorporation of one D atom also suggests that the rate determining step be the reaction (4) in the above reaction mechanism. If reaction (4) and its reverse reaction were fast, methanol containing two D atoms would have been formed much more readily. In addition, the isotope effects and activation energy differences are consistent with the values expected if the rate determining step is the release of H from the methoxy group. The conclusion on the rate determining step in the present study is consistent with the conclusion obtained for the Ni wire catalyst by Yasumori et al.,

The simultaneous evolution of the major part of CO and H₂ in the TPD experiments for adsorbed methanol suggests that the release of two H atoms from the adsorbed formaldehyde (5) be fast. If the release of the second H atom from the adsorbed formaldehyde were slow, H₂ evolution would have preceded the CO evolution.

The evolution of a small part of CO that preceded simultaneous evolution of CO and H₂, which was observed in TPD for both methanol and formaldehyde, suggests that adsorption of hydrogen be stronger than that of CO. As the presence of hydrogen accelerated the decomposition rate, the adsorbed hydrogen did not block the active sites. It is plausible that the hydrogen initially formed is retained on the surface and the adsorbed hydrogen atom enhances reaction (3). A reaction scheme for methanol decomposition on the Ni/SiO₂-Mg may be illustrated as shown in Fig. 7.

Methanol is dissociatively adsorbed to form a methoxy group and an H atom. The methoxy group undergoes decomposition to form adsorbed formaldehyde (CH₂O) and H atoms. This reaction is the slow step. The adsorbed formaldehyde decomposes to form CO and H probably through the formyl group. The initially formed carbon monoxide is retained on the surface to block a part of the active sites. The H atom resulting both from the dissociation of the methoxy group and that from the decomposition of the adsorbed formaldehyde are also retained on the surface but they will not retard the reaction. They will be recombined and desorbed from the surface.

References

要旨

Ni/SiO₂-MgO 触媒上でのメタノールの一酸化炭素と水素への分解の反応機構の研究

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メタノールの CO と H₂ への分解反応を Ni/SiO₂-MgO 触媒上で行い, 重水素を用いる同位体法で反応機構を検討した。メタノールと重水素分子との交換反応では, メタノールの 1 つの水素原子は他の水素原子よりも交換しやすかった (Table 1)。このことより, メタノールのメトキシ基と H 原子への解離とその逆反応は速いことがわかった。ホルムアルデヒドは, メタノールと同様に CO と H₂ に分解するが, その分解速度はメタノールの分解速度よりかなり大きかった (Fig. 1)。ホルムアルデヒドを反応させると, 二酸化メチルが生成するが, この反応は SiO₂-MgO のみを触媒として用いたときにも進行した。

メタノールの同位体である CH₃OH, CH₃CD, CD₃OD の中では, CD₃OD の分解が他の 2 つの同位体の分解よりも遅く, 活性化エネルギーは約 1 kcal mol⁻¹ 大きかった (Fig. 2, Table 2)。

メタノール分解の反応速度は, H₂ 分圧に依存しないが, CO 分圧が大きくなると低下した (Fig. 3)。速度式は, CO の吸着限界量の入った (1-x)/(1+ax), x: メタノールの分離率, a: 定数で表される (Fig. 4)。

昇温脱離を, メタノールあるいはホルムアルデヒドを吸着させた触媒について行ったところ, CO と H₂ はほぼ同じ温度で脱離した (Figs. 5, 6)。

以上の結果は, メタノールから CO と H₂ に分解する反応では, 最初に OH 基の解離が起こりメトキシ基を生成し, 以後逐次的に H が 1 つずつとれていく機構によって反応が進行していることを示し, メトキシ基のメチル基から H が解離する段階が律速であることを示唆している (Fig. 7)。

Keywords
Decomposition, Isotopic study, Methanol, Reaction mechanism, Supported catalyst