# Methane dry reforming reaction on Ru(0 0 1) surfaces

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A B S T R A C T

Methane dry reforming on a Ru(0 0 1) single-crystal surface was investigated using a high-pressure reactor directly combined with an ultra-high-vacuum system for temperatures between 700 and 800 K and under initial CH$_4$ and CO$_2$ pressures in a range of 50–240 Pa. In the CH$_4$–CO$_2$ reaction, dry reforming (DRM) proceeds accompanied by a quasi-equilibrated reverse water gas shift reaction. The rate of the DRM reaction exhibits first-order dependence on CH$_4$ pressure and is almost independent of CO$_2$ pressure, giving an apparent activation energy of 110 kJ/mol. These kinetic parameters are in good agreement with those reported on Ru-supported oxide catalysts. From the exchange reaction between $^{13}CO_2$ and CO, a very low activation energy of 7.2 kJ/mol and a TOF around 18 are obtained for CO$_2$ dissociation on the bare Ru(0 0 1) surface. In the CH$_4$–$^{13}CO_2$ reaction, the exchange reaction between $^{13}CO_2$ and CO is also quasi-equilibrated. These results are consistent with ultraviolet photoelectron spectroscopy and low-energy electron diffraction measurements for postreaction Ru surfaces, which show that carbon species derived from the decomposition of CH$_4$ are substantially removed as CO by oxygen atoms supplied from the dissociation of CO$_2$. Taking the respective reaction orders of CH$_4$ and CO$_2$ into consideration, it is concluded that the rate-limiting step for the DRM reaction is the breaking of the C—H bond in CH$_4$.

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## 1. Introduction

Global warming is now a serious environmental problem. CH$_4$ and CO$_2$ are considered to be dominant gases in greenhouse emissions. For this reason, the reduction of their concentration is becoming an urgent issue and it is further desirable to convert them into useful materials. One of the promising attempts so far is the reforming of CH$_4$ molecules [1–3]. There are two main reforming processes for producing CO and H$_2$, called synthetic gas, from CH$_4$: steam reforming (SRM): CH$_4$ + H$_2$O → CO + 3H$_2$, and dry reforming (DRM): CH$_4$ + CO$_2$ → 2CO + 2H$_2$. Here, the product of CO and H$_2$ with equal molar ratio in the DRM reaction is more suitable for subsequent Fischer–Tropsch synthesis. Since these reactions are highly endothermic processes, the reforming process will inevitably proceed at higher temperatures. It might feasibly induce side reactions such as CH$_4$ decomposition and CO disproportionation. As a result, these reactions cause carbon deposition and result in the deactivation of catalysts [4,5]. Accordingly, it is necessary to reduce the reaction temperature by using active catalysts promoting the scission of C—H bonds in CH$_4$ molecules. On the other hand, the production of CO and H$_2$ from CH$_4$ and CO$_2$ is typically influenced by the simultaneous occurrence of the reverse water gas shift (RWGS) reaction, resulting in H$_2$/CO molar ratios less than unity [6,7].

Among numerous materials as potential catalysts for the reforming of CH$_4$ with CO$_2$, noble-metal-supported catalysts have been found to exhibit promising performance in terms of conversion and selectivity to synthesis gas, and Ru, Rh, and Ni catalysts are categorized as active metals [8–10]. Ni-based catalysts have a high activity and a lower cost, but they tend to cause coking, leading to deactivation in the long term [4,5]. On the other hand, noble metal catalysts are known to have the least carbon deposition.

To develop a highly active catalyst, it is essential to identify its reaction mechanism and rate-determining step (RDS). Several reaction mechanisms for DRM are proposed corresponding to various intermediates on the catalyst surfaces reflecting different reaction conditions and support oxides [11–13]. In these reaction mechanisms, the RDS may involve CH$_4$ dissociation [14–19], CH$_x$O decomposition [20,21], and reactions between carbon species and oxygen-containing species on the catalyst surface [22]. In these reaction mechanisms, the most important step is the activation of CH$_4$ and CO$_2$ molecules.

Surface science research related to the activation of methane has been performed theoretically and experimentally on Ni [23–25], Ru [26–28], Rh [29,30], and Pt [31] single-crystal surfaces. The relevant step for CH$_4$ activation related to stable CH$_x$ intermediates and the effect of defect sites such as steps and kinks have

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been investigated. Although surface steps and higher-index surfaces are generally more reactive than flat, low-index surfaces, it has been shown that the presence of steps did not give significant promotion to $CH_4$ dissociation on Ni[1 1 1] and Ru[0 0 1] surfaces in bulb experiments [27].

On the other hand, it is assumed that $CO_2$ activation on transition metal surfaces is structure-sensitive [32]. It has been reported that $CO_2$ adsorbs onto metal surfaces as a physisorbed linear state and a chemisorbed partially charged bent state. The latter has been demonstrated to be an intrinsic precursor for $CO_2$ dissociation into CO and oxygen atoms on Ni[1 0 0] and [1 1 0] surfaces [33,34]. On most metal surfaces, however, $CO_2$ dissociation is not well understood, due to its very low probability, and therefore many studies have been carried out in coadsorption systems with alkali metals stabilizing $CO_2$ adsorption. Similarly, $CO_2$ is more efficiently activated on oxide supports than on metal surfaces, because $CO_2$ adsorbs readily onto basic sites in the oxide support and generally has a higher binding energy than on metal surfaces [35–37].

According to Wei and Iglesia [38], C—H bond activation rates increased with increasing Ru dispersion on oxide-supported Ru catalysts. They suggested the higher reactivity of coordinatively unsaturated surface atoms, but so far little is known about the surface structure sensitivity of the reforming reaction. It can reasonably be assumed that the (0 0 1) surface of hcp Ru metal is the most exposed facet plane of Ru particles on oxide supports. The object of the present study is to evaluate the intrinsic reactivity of the Ru(0 0 1) surface for the DRM reaction as a typical representative model structure exposed on Ru-based catalysts. Surface characterization of the Ru sample was performed in an ultrahigh-vacuum (UHV) chamber before and after the DRM reaction. Kinetic experiments were carried out in a reactor directly connected to the UHV system and the origin of CO product was studied by the use of $^{13}CO_2$. Also, turnover rates of $CO_2$ dissociation were measured by the exchange between CO and $^{13}CO_2$ on the clean Ru surface, which was compared with $CH_4$ dissociation rates on Ru(0 0 1) in the literature [27].

## 2. Experimental

The experiments were performed in an ultra-high-vacuum (UHV) chamber equipped with facilities for X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), low-energy electron diffraction (LEED), and temperature-programmed desorption (TPD) [39]. A Ru(0 0 1) sample purchased from Surface Preparation Laboratory (SPL) was heated above 1300 K by passing current through Ta lead wires. The temperature was measured by a chromel–alumel thermocouple spot-welded to the side of the crystal. The Ru(0 0 1) crystal was cleaned by repeated $Ar^+$ sputtering and annealing at 1300 K until no impurities were observed by PES. For kinetic measurements, the sample was vertically transferred to a high-pressure reaction cell with a volume of about 0.2 L so that the sample could be sealed from the main UHV chamber instantly. Reactant mixtures of $CH_4$ (99.9% purity) and $CO_2$ (99.8% purity) or $^{13}CO_2$ (CEA, chemical purity > 99%) were introduced into the reaction cell via bellows valves from a gas inlet system with a capacitance manometer. Under reaction conditions, it operated as a batch-type reactor in the pressure range 50–240 Pa. Gas components close to the Ru sample were conducted by a stainless steel capillary into a variable leak valve, which permitted a certain amount of continuous gas leak between the UHV chamber and the reaction cell. The methane dry reforming reaction was monitored by the quadrupole mass spectrometer (QMS) intensities of the respective reactant and product. To minimize degassing from the mass filament, each QMS measurement was carried out as quickly as possible. QMS intensities were corrected by subtract-

ing the contribution of residual gas in the UHV chamber, which was obtained by interruption of the gas leak using pneumatic on–off operation of a metal valve inserted in the gas leak line. Reaction rates were calculated based on the QMS intensities normalized by Ar intensity, taking QMS sensitivity toward $H_2$, CO, $CH_4$, and $CO_2$ against Ar as a pressure calibration into consideration.

## 3. Results and discussion

### 3.1. Methane dry reforming reaction

#### 3.1.1. $CH_4$–$CO_2$ reaction

Fig. 1 shows the effect of initial $CH_4$ partial pressure on the methane dry reforming reaction at 740 K, while initial $CO_2$ partial pressure was kept at 160 Pa. The concentrations of reactants ($CH_4$ and $CO_2$) and products (CO and $H_2$) during the course of the reaction were monitored by QMS every 10 min after $CH_4$, $CO_2$, and Ar were introduced into the reactor. The ordinate represents relative QMS intensities of reactants and products divided by that of Ar, which was included at an internal standard pressure of 40 Pa. In the initial 20 min, it was observed that CO (filled diamonds) formed together with decrease of $CO_2$ (filled squares), and then the concentrations of CO and $H_2$ (filled circles) increased at a rather low steady rate, in good accordance with the decrease of both reactant partial pressures during the course of the reaction. The initial rather low intensity of hydrogen is considered to be caused by further oxidation to $H_2O$ via the reverse water gas shift (RWGS) reaction, because it is frequently reported that the DRM reaction is influenced by simultaneous occurrence of the RWGS reaction, resulting in $H_2$/CO ratios less than unity [6,7]. However, $H_2O$ could not be quantitatively measured by QMS due to its stickiness to the wall of the UHV chamber. As is shown in Fig. 1, the increase of the initial $CH_4$ partial pressure from 80 to 240 Pa decreased the difference between initial CO and $H_2$ formation, because the contribution of the RWGS is lowered, corresponding to the reduction in the $CO_2$/$CH_4$ molar ratios. As a result, the dry reforming of methane (DRM) reaction tends to proceed stoichiometrically from the beginning to a large extent. On the other hand, the change of initial $CO_2$ pressure from 80 to 160 Pa for 160 Pa initial $CH_4$ pressure affected the reaction in the reverse direction, as from Fig. 1c to Fig. 1b, but further increase of $CO_2$ pressure had little effect on the formation rate of CO and $H_2$.

Fig. 2 displays He I UP spectra taken from Ru(0 0 1) after DRM reaction at 740 K and a $CO_2$/$CH_4$ equimolar ratio over the course of the reaction. Initially, the state just below the Fermi level decreased with a considerable increase of work function as a result of the presence of negatively charged species on the surface. At an elapsed time of 20 min, emission at 6.4 eV due to oxygen atoms clearly appeared. Further progress of the reaction caused no additional spectral change. However, in the case of reactor gas evacuation temperatures below 390 K, UPS demonstrated emissions at 6.4, 7.7 and 10.8 eV due to adsorption of oxygen and CO during cooling, indicating that a partly clean Ru surface remained during the reaction [40]. In accordance with the result in UPS, a $(2 \times 2)$ ordered structure was observed in LEED by the presence of oxygen species on Ru(0 0 1) [41].

#### 3.1.2. Simulation based on DRM reaction

The rate is described by the DRM reaction ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$) accompanied by the quasi-equilibrated RWGS reaction ($H_2 + CO_2 \rightarrow H_2O + CO$). Taking the dependence on reactant partial pressures into consideration, each gas component in the figure is expressed by broken lines based on a reaction process obeying first-order kinetics for $CH_4$. The rate constant is assumed to