Methane dry reforming reaction on Ni(110), (111) and Ru(001) surfaces

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Abstract: Methane dry reforming on Ni(110) and (111) surfaces was investigated for temperatures between 770 and 870 K and under initial CH_4 and CO_2 pressures in a range of 50 to 240 Pa. The intrinsic reactivity for methane dry reforming reaction increased in the following order; Ru(001) > Ni(110) > Ni(111) and apparent activation energies of 83 and 88 kJ/mol were obtained for Ni(110) and (111) surfaces, slightly smaller than the activation energy of 110 kJ/mol on Ru(001) surfaces.

Keywords: Methane reforming, Carbon dioxide, Ni(110), (111) surfaces.

1. Introduction

Global warming mainly caused by CH_4 and CO_2 is now getting a serious environmental problem. Hence, the reduction of their concentration and further conversion into useful materials are urgently required. One of promising attempts is reforming process of CH_4 molecule represented by dry reforming reaction (DRM) ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$) producing CO and H_2 with equal molar ratio. For the reaction of CH_4 with CO_2, Ru and Ni supported catalysts have been found to exhibit best performance in terms of conversion and selectivity to synthesis gas [1]. Several reaction mechanisms for DRM are proposed corresponding to various intermediates on the catalyst surfaces reflecting different reaction conditions and support oxides [2]. The object of the present study is to evaluate the intrinsic reactivity of Ni(110), (111) surfaces for DRM reaction as a typical representative model structure exposed on Ni based catalysts and compare with that on Ru(001) surface [3]. Surface characterization of Ni samples was performed in an UHV chamber before and after DRM reaction. Kinetic experiments were carried out in a reactor directly connected to the UHV system and the origin of CO product is 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 Ni surfaces to compare with CH_4 dissociation rates on Ni(111) in the previous study [4].

2. Experimental

The experiments have been performed in an UHV chamber equipped with facilities for XPS and UPS, LEED and TPD [5]. After cleaning in UHV system, the Ni samples are instantly transferred to a reactor cell. The batch-type reactor enables us to investigate methane dry reforming reaction in a pressure range of 50 – 240 Pa close to practical conditions. The reaction is followed by a QMS using a variable leak valve.

3. Results and discussion

Figure 1 displays CH_4-CO_2 reaction on Ni(110) surface at 830 K under initial CH_4 and CO_2 pressures of 80 Pa and an internal standard Ar pressure of 40 Pa. In the beginning, the reaction occurs quite slowly accompanied with CO formation and CO_2 consumption. Absence of H_2 production seems to be caused by occurrence of reverse water gas shift reaction (RWGS). After 10 min elapsed, methane dry reforming reaction (DRM) proceeds according to the equation ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$). Since the initial low reactivity is not significantly observed on Ni(111) surface with close packed structure, Ni(110) surface tends to be initially covered by oxygen atoms derived from CO_2 dissociation, which are removed gradually

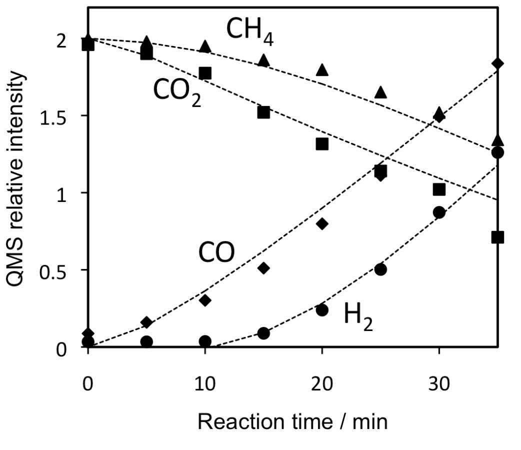

Figure 1. CH_4-CO_2 reaction on Ni(110) at 830 K.

along with the progress of the reaction. In the present study, DRM rates are dependent on first order with respect to CH_4 pressure and almost independent of CO_2 pressure, respectively. Broken lines in the figure are based on a reaction process obeying first order kinetics for CH_4 and the rate constant is assumed to increase monotonously with reaction time corresponding to the removal of adsorbed oxygen from the Ni surface. The rate is simulated by DRM reaction accompanied with quasi-equilibrated RWGS reaction. Furthermore, in order to measure CO_2 dissociation rate separately, the following exchange reaction ($CO + {}^{13}CO_2 \rightarrow {}^{13}CO + CO_2$) was studied at lower temperatures from 630 K to 690 K than DRM reaction experiments as a function of CO pressure under a constant pressure of 80 Pa ${}^{13}CO_2$. The exchange reaction is described by a model based on bimolecular exchange reaction, showing first order in each concentration of ${}^{13}CO_2$ and CO. Thus, CO_2 dissociation rate on the Ni clean surface is obtained by extrapolating CO pressure to zero.

In Fig. 2, DRM reaction and CO_2 dissociation are compared under the condition of 80 Pa CO_2 and/or 80 Pa CH_4. The rates for Ni(110), (111) and Ru(001) surfaces are displayed as TOF in an Arrhenius plot. It is observed that CO_2 dissociation rate on Ni(110) surface is faster than that on Ni(111). From the slope of fitted straight line in Fig. 2, apparent activation energies of 31 and 68 kJ/mol are calculated for Ni(110) and (111) surfaces, respectively, which are well corresponding to the difference of work function between both surfaces. It is also clearly confirmed that CO_2 dissociation rates exceed those of CH_4 dissociation on the bare Ni(111) and Ru(001) surfaces reported in the literature [4], which are located in the middle between those for DRM reaction and CO_2 dissociation. It suggests that CH_4 activation will be a relevant step in CH_4 dry reforming reaction. It is consistent with the linear dependence of reaction rates on CH_4 pressure observed in the present study. As demonstrated in Fig. 2, it is revealed that the intrinsic reactivity for DRM reaction increases in the following order; Ru(001) > Ni(110) > Ni(111) where apparent activation energies of 83 and 88 kJ/mol are obtained for Ni(110) and (111) surfaces, slightly smaller than the activation energy of 110 kJ/mol on Ru(001) surface. These activation energies are in good agreement with those reported in the literature [1-2]. Taking the first order dependence of reaction rate on CH_4 concentration into consideration, it is most probably concluded that the rate-limiting step of DRM reaction is CH_4 dissociation on partly covered Ni surfaces by CO and oxygen species derived from CO_2 dissociation.

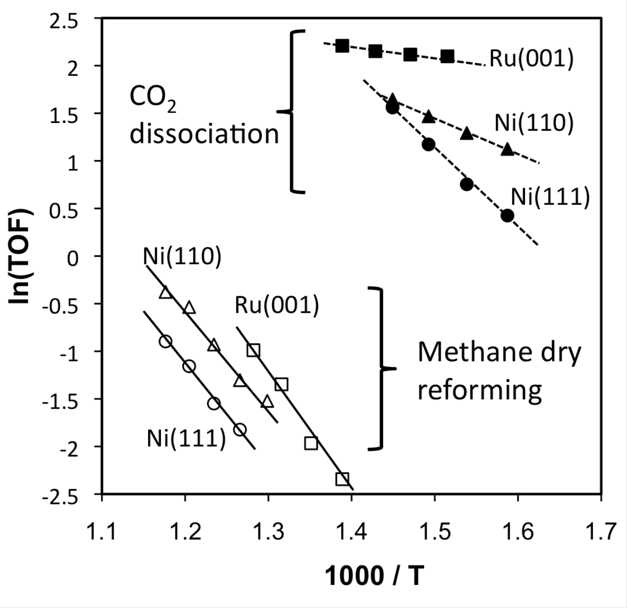

Figure 2. CO_2 dissociation and methane dry reforming rates on Ni(110),(111) and Ru(001).

4. Conclusions

Methane dry reforming on Ni(110) and (111) surfaces was investigated for temperatures between 770 and 870 K and under initial CH_4 and CO_2 pressures in a range of 50 to 240 Pa. In CH_4-CO_2 reaction, dry reforming (DRM) reaction proceeds accompanied with quasi-equilibrated reverse water gas shift (RWGS) reaction. The DRM reaction rates exhibited first order dependence on CH_4 pressure and almost independent of CO_2 pressure. The intrinsic reactivity for DRM reaction increases in the following order; Ru(001) > Ni(110) > Ni(111), giving the apparent activation energy of 83 and 88 kJ/mol for Ni(110) and (111) surfaces, respectively. These kinetic parameters are in good agreement with those reported on Ni supported oxide catalysts.

References

1. J.R. Rostrup-Nielsen, J-H. Bak Hansen, J. Catal. 144 (1993) 38.
2. Z. Zhang, X.E. Verykios. Catal. Lett., 38 (1996) 175.
3. C. Egawa, J. Catal., in press.
4. R.C. Egeberg, S. Ullmann, I. Astrup, C.B. Mullins, I. Chorkendorff, Surf. Sci., 497 (2002) 183.
5. H. Iwai, T. Umeki, M. Yokomatsu, C. Egawa, Surf. Sci., 602 (2008) 2541.