Ammonia Decomposition on Co/Mo(112) Model Surface

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As a model surface of Co-Mo alloy catalysts for ammonia decomposition, Co deposited Mo(112) surface has been investigated by XPS, UPS, LEED, and kinetic measurement using a high-pressure reactor. Co deposition on Mo(112) surface followed by annealing at 1000 K shows a (1×1) LEED pattern with the split along the [111] direction and a characteristic emission at −2.9 eV for Co-Mo d-band hybridization. The decomposition of ammonia on Co/Mo(112) surface proceeds accompanied by nitride formation. The reaction rate exhibits half order dependence on ammonia pressure with an activation energy of 101 kJ/mol, which is in good agreement with the results on alumina supported Co-Mo alloy catalysts. [DOI: 10.1380/ejssnt.2018.115]

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I. INTRODUCTION

Recently, hydrogen has attracted a lot of attention as a clean energy source in the future, only producing H2O to the environment. There are several practical methods to produce hydrogen. For example, methanol reforming is one of representative reactions in which partial oxidation using oxygen and steam reforming by water are so far well investigated. However, these reactions are accompanied by co-production of CO, which is a notorious impurity because it causes the poisoning of Pt electrodes by preferential adsorption to prevent hydrogen dissociation. Therefore, CO free hydrogen is desirable for the application in a proton exchange membrane fuel cell to avoid the poisoning problem. In this respect, the supply of hydrogen by ammonia decomposition is expected to be one of promising methods.

Volcano-type relationship is well known for ammonia decomposition and reverse synthesis reaction where the abscissa is related to adsorption energy of nitrogen on transition metal surfaces and the ordinate represents the reaction rates as log-scaled. Since the decomposition of ammonia is kinetically controlled by the recombinative desorption of nitrogen atoms from the metal surfaces, the most active catalyst is reported to be based on ruthenium with moderate strength of metal-nitrogen bonding. In the relationship, Co metal is classified as less stable nitrogen bonding group, while strong bonding is formed on Mo metal. However, according to Boisen et al. [1], Co-Mo bimetallic systems are predicted to locate closely to Ru catalysts having an optimum reactivity in the volcano curve. Hence fundamental understanding of cobalt-based catalysts is required for future development of Ru replaced systems, but previous studies indicate that the catalytic activity of cobalt-based catalysts depend on the metal dispersion and metal particle size as well as the interaction with oxide supports [2]. In order to obtain the intrinsic reactivity, surface science research based on a suitable model surface of Co-Mo catalysts is essentially indispensable. Recently it is suggested that the presence of highly energetic sites such as steps on Mo supported catalysts is vital for the reactivity [3]. We have also confirmed that the stepped structure on Ru(1,1,10) surface is effective for the scission of N-H bond [4]. In the present study, a model surface of Co-Mo catalysts is prepared by the deposition of Co metals on Mo(112) surface having furrows along [111] direction.

II. EXPERIMENTAL

The experiments have been performed in an ultra-high vacuum (UHV) chamber equipped with facilities for X-ray photoelectron spectroscopy (XPS) and ultra-violet photoelectron spectroscopy (UPS), low-energy electron diffraction (LEED), and temperature-programmed desorption (TPD) [5]. A Mo(112) 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 Mo(112) crystal was cleaned by repeated Ar+ sputtering and annealing at 1300 K until no impurities were observed by PES. The deposition of Co was carried out by evaporation of Co wire surrounded by a W filament. 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 NH3 (5.0% diluted in Ar) was introduced to 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 of 120–320 Pa. NH3 decomposition reaction was monitored by a quadruple mass spectrometer (QMS). Reaction rates were calculated based on the QMS intensities normalized by Ar intensity, taking QMS sensitivity toward H2, NH3, and N2 against Ar as a pressure calibration into consideration.

Co and Mo supported catalysts were prepared by incipient wetness impregnation using Co(NO3)2 and (NH4)6Mo7O24 as metal precursor on alumina support and calcination in air at 800 K. Before reaction, these catalysts were reduced under H2 and NH3 mixture at 800 K. Ammonia decomposition reactions were carried out in a flow reactor with 50 mg of catalyst. Reactant ammonia (5.0% diluted in Ar) flow rate of 25 mL/min at a gas pressure of 1 bar was controlled with a mass flow controller. During each catalytic study, the reaction temperature was
ramped from 300 K to 800 K at 10 K/min. The outlet flow of the reactor was continuously analyzed using QMS.

III. RESULTS AND DISCUSSION

Since there are a limited number of studies reported for the reactivity of Co-Mo catalysts, the catalytic ammonia decomposition over Co-Mo catalysts was examined as a function of Co and Mo loadings supported on aluminas. Figure 1 displays a typical result of temperature-programmed ammonia decomposition on Co(5 wt%)-Mo(8 wt%) alloy catalyst supported on Al$_2$O$_3$ showing best catalytic performance. The ordinate displays the relative QMS intensity to Ar included as an internal standard. It is observed that the Co-Mo alloy catalyst decomposes ammonia at temperatures above 600 K and ca. 60% conversion of ammonia is achieved at 800 K. Similarly, the decomposition reaction was studied on Co/Mo(112) surface at a temperature range from 680 K to 760 K. As depicted in a ball model inserted in Fig. 2, the structure of Mo(112) surface indicated as dark balls with a white rectangle unit cell consists of furrows parallel to [111] direction which is considered to be a kind of most densely packed stepped structures. Accordingly, it is expected that adsorption of Co atoms leads to the formation of atomic chains aligned along the furrows, resulting in a p(1×1) structure at a monolayer coverage as shown in the model as bright balls. After 10 min Co deposition on Mo(112) surface at 300 K, however, a broad (1×1) LEED pattern is observed with high background intensity, indicating that the Co overlayer is essentially disordered. Annealing the Co deposited Mo(112) sample at 1000 K greatly reduces the background in the pattern and additional splits of the reflections along the [111] direction are observed as shown in Fig. 2, which continues until 40 min of deposition. The completion of Co monolayer coverage is estimated to be accomplished at 15 min evaporation, giving a Co 2p/ Mo 3d XP intensity ratio of 0.3. On the contrary, annealing the Mo(112) surface after 40 min Co deposition at 1000 K reduced the XP intensity ratio to 0.25 slightly smaller than that expected for Co monolayer, implying the occurrence of inter-diffusion of Co atoms and/or mutual mixing between Mo substrate and Co overlayer. The ball model also displays a complex overlayer structure with a (n×1) rectangle unit cell (n > 12) for a second layer correlated to the appearance of splits along [111] direction. It suggests that the distance between adjacent atoms of the forming Co rows approaches the value close to Co bulk, which by ca. 8% contracts the distance along [111] direction in the Mo substrate, contrary to the observation of 5% elongated Ag rows on Mo(112) [6].

The modification of valence band structure upon Co-Mo alloy formation is considered to influence on the strength of metal–nitrogen bonding. Figure 3 shows detailed change in the valence band structure measured by He I UPS. In the UP spectrum (a) of the clean Mo(112) surface, three peaks mainly due to 4d-states appear in the valence band region from the Fermi level to ~6 eV which are in good agreement with the literature [7] and similar valence band structures are reported for W(112) and Ta(112) surfaces [8]. On the contrary, two intensity maxima at ~0.35 eV and ~0.1 eV were observed in the energy distribution curves obtained from fcc Co(100) surface [9]. The Co deposition at 300 K, however, changes slightly the UP spectrum of Mo(112) surface. In accordance with the appearance of well-ordered LEED pattern after annealing at 1000 K procedure, a characteristic sharp peak emerges at ~2.9 eV in the valence region as shown in Fig. 3(b),
FIG. 4. Ammonia decomposition on Co/Mo(112) at 700 K under $P_{\text{NH}_3}$ of (a) 5.8 Pa, (b) 8.3 Pa, and (c) 16.5 Pa, respectively.

FIG. 5. Arrhenius plot of ammonia decomposition rates on Co-Mo catalysts. Filled circle: Co/Mo(112), open circle: Co-Mo alloy on Al$_2$O$_3$.

which progressively increases simultaneously with the unstructured band spread from the Fermi level to $\sim$1.0 eV upon Co deposition further until 40 min [Fig. 3(c, d)]. These two valence band states can be interpreted to be attributed to the bonding and antibonding states upon hybridization of Co 3d and Mo 4d states.

Thus, for the well-characterized Co/Mo(112) model surface, the decomposition of ammonia is followed by QMS every 5 min at 700 K under ammonia pressures from 5.8 Pa to 16.5 Pa. Hydrogen is accumulated along with the progress of reaction as shown in Fig. 4. The accumulation curves are simulated by broken lines based on half order kinetics, because the dependence toward ammonia pressure is obtained to ca. 0.5 from the log-log plot between ammonia pressure and reaction rate. The fractional reaction order is consistent with stable metal-nitrogen bonding in the volcano-type relationship. Then, after cooling down the sample temperature in the reactant gas followed by evacuation, surface electronic states are measured for Co/Mo(112) surface. A dominant emission due to nitride around $\sim$5 eV appears with a small peak at $\sim$9 eV assignable to NH species, while the Co-Mo derived valence band states are completely lost by nitride formation. The nitride grown on Co-Mo alloy surface during ammonia decomposition is stable up to 1000 K. It suggests the recombinative desorption step of adsorbed nitrogen determines the reaction rate.

Generally, supported metal catalysts possess various sizes and shapes of metal particles influenced by catalyst preparation methods and hence their surface structures and compositions often change depending on the reaction conditions, leading to deviation from bulk chemical compositions. Actually for the Co-Mo alloy catalyst mentioned in Fig. 1, the degree of Co atoms exposed at the surface is limited to only 3.8%. Under these circumstances, kinetic measurements such as activation energy and turnover frequency (TOF) on well-defined surfaces provide fundamental insights for understanding of the intrinsic reactivity of supported metal catalysts. In this sense, the decomposition reaction is further examined at a temperature range from 680 K to 760 K and the rates of ammonia decomposition as TOF are displayed in a form of Arrhenius plot in Fig. 5. From the slope of line fitted to the data, the activation energy is obtained as 101 kJ/mol, which is slightly smaller than the activation energy of 106 kJ/mol derived from the open circles corresponding to the results of Co-Mo alloy supported catalyst as shown in Fig. 1. These two lines are closely depicted each other. It indicates that the Co/Mo(112) model surface represents satisfactory the reactivity of Co-Mo alloy supported catalysts.

IV. CONCLUSION

In the present study, the intrinsic reactivity of model Co-Mo alloy surface for ammonia decomposition has been investigated by Co deposited Mo(112) surface using the high pressure reactor. The deposition of Co on Mo(112) surface followed by annealing at 1000 K shows a (1×1) LEED pattern with the split along the [111] direction and a sharp emission at $\sim$2.9 eV due to hybridization of Co 3d and Mo 4d bands. The latter is completely vanished by nitride formation during ammonia decomposition. The rate of reaction on Co/Mo(112) surface exhibits half order dependence on ammonia pressure with an activation energy of 101 kJ/mol, which is in good agreement with the results on alumina supported Co-Mo alloy catalysts.

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