COMBINATORIAL COMPUTATIONAL CHEMISTRY APPROACH TO THE DESIGN OF METAL SULFIDE CATALYSTS FOR CO HYDROGENATION PROCESS

Momoji Kubo[1], Changho Jung[1], Tsuguo Kubota[1], Kotaro Seki[1], Seiichi Takami[1], Naoto Koizumi[2], Kohji Omata[2], Muneyoshi Yamada[2], and Akira Miyamoto[1]

[1] Department of Materials Chemistry,
Graduate School of Engineering, Tohoku University,
Aoba-yama 07, Sendai 980-8579, Japan.
[2] Department of Applied Chemistry,
Graduate School of Engineering, Tohoku University,
Aoba-yama 07, Sendai 980-8579, Japan.

Introduction

Recently, computational chemistry made great impacts on the catalyst design and development. However, the computational chemistry is mainly employed to clarify the atomistic mechanism of the well-known catalytic reactions and to obtain the electronic information on the catalysts of which property and reactivity are well known experimentally. We suggested that such traditional computational chemistry can not contribute to the design and development of new catalysts at all. Hence, we recently introduced a concept of combinatorial chemistry used in the drug development to computational chemistry and proposed a new concept "Combinatorial Computational Chemistry" [1-3]. In this concept, the computational chemistry is employed to perform a high-throughput screening of the catalysts including active metals, supports, and additives.

On the other hand, the synthesis of the high-quality transportation fuels is expected in terms of the high-efficient utilization of the energy and low environmental impact. The development of high-active and high-selective catalysts with high-resistance to sulfur for methanol synthesis and Fischer-Tropsch synthesis is strongly demanded in order to advance the industry of the high-quality transportation fuels. Recently Koizumi and co-workers reported that a lot of metal sulfide catalysts have high activity for the CO hydrogenation process [4] and especially Rh sulfide has the highest activity and predominantly produces methanol [5]. Moreover, they found that the Rh sulfide catalyst is not deactivated by the H_2S, while regular methanol synthesis catalyst $Cu/ZnO/Al_2O_3$ is easily deactivated by the H_2S [5]. Moreover, they also reported that the products of the CO hydrogenation process are strongly depending on the metal species of the metal sulfide catalysts [4]. For example, Rh and Pd sulfides selectively produce methanol in the CO hydrogenation, while Re and Os sulfides predominantly produce hydrocarbons.

We have already applied our combinatorial computational chemistry approach to the design of the methanol synthesis catalysts based on the Cu/ZnO and the Fischer-Tropsch catalysts based on the supported Fe metals and have succeeded to propose new catalysts and additives [6-10]. Hence, we have confirmed the applicability of our combinatorial computational chemistry approach to the catalyst design.

In the present study, we applied our combinatorial computational chemistry based on the first-principles approach to the metal sulfide catalysts and investigated the dependency of the metal species in the metal sulfide catalysts to the CO hydrogenation process and its products on the electronic level.

Methods

Combinatorial computational chemistry based on the first-principles calculation [11] is performed by using ADF program [12-14] developed in Vrije University, Netherlands. In this program, linear combination of Slater-type atomic orbitals are used in the Kohn-Sham formulation. The structure optimization is carried out by local density approximation (LDA) with Vosko-Wilk-Nusair (VWN) functional [15]. The energy of the optimized structure is calculated by generalized gradient approximation (GGA) with Becke 88 and Perdew-Wang 91 functionals [16-17]. The triple-ζ basis sets extended by polarization functions are used. The Mulliken method is employed to perform the atomic population analysis [18].

Results and Discussion

Our combinatorial computational chemistry approach was applied to the CO adsorption on various metal sulfide catalysts. We also calculated the CO adsorption on various metal catalysts for the comparison, by using our combinatorial computational chemistry. The elongation of the C-O distance may lead to the formation of hydrocarbons, while the shrinkage of the C-O distance may lead to the formation of methanol. Hence, we paid attention to the C-O distance of the CO molecule adsorbed on the various metal and metal sulfide catalysts. The C-O distance of the CO molecule in the vapor phase is 0.113 nm. We found that the C-O distance of the CO molecule adsorbed on all the metal catalysts and metal sulfide catalysts is elongated, compared to the C-O distance in the vapor phase. It indicates that CO molecule on all the catalysts is activated by the adsorption. Moreover, the C-O distance was found to be strongly depending on the metal species. The C-O distance is shortened on the Co, Mo, Ru, Rh, and Ir sulfide catalysts compared to their metal catalysts. It indicates that these metal sulfide catalysts selectively produce methanol, which is in agreement with the experimental results by Koizumi and co-workers [4]. On the other hand, since the C-O distance is elongated on the Re and Os sulfide catalyst compared to their metal catalysts, these sulfides are suggested to be very effective catalysts to produce hydrocarbon selectively, which is also in good agreement with the experimental results by Koizumi and co-workers [4].

Moreover, we clarified that the Pd sulfide catalysts have the specific characteristics compared to the other metal sulfide catalysts. We suggested that the Pd sulfide has the highest selectivity of the methanol synthesis among all the metal sulfide catalysts, which is in agreement with the experimental result by Koizumi and co-workers [19]. CO molecule has the plus charge on the Pd sulfide catalysts, while CO molecule has the minus charge on the other metal and metal sulfide catalysts, as shown in Fig. 1. It was suggested that this difference is due to the different adsorption structure of the CO molecule on the Pd sulfide and the other metal sulfide catalysts as shown in Fig. 2. CO molecule adsorbs on the on-top site of the metal species in the case of all the metal sulfide catalysts except the Pd sulfide catalyst. Hence, electrons transfer from metal species to the CO molecule and then CO gains minus charge on the most metal sulfide catalysts. Similarly, CO molecule surely adsorbs on the metal species in the case of all the metal catalysts, and then electrons transfer from metal to the CO molecule and CO molecule gains minus charge. On the other hand, CO molecule adsorbs on the bridge-site of the Pd sulfide catalyst and contacts with both the Pd and sulfur on the Pd sulfide catalyst. Hence, electrons transfer from the CO molecule to the sulfur atom and CO gains plus charge. Fig. 3 shows the molecular orbital of the CO molecule. The lowest unoccupied molecular orbital (LUMO) and the second LUMO of the CO molecule are anti-bonding orbitals, and the electron has to be transferred to the above two orbitals of the CO molecule from catalysts, in order to dissociate the CO molecule. However, the CO molecule on the Pd sulfide catalyst has plus charge and then a large number of electrons have to be transferred to the CO molecule from the catalysts after the adsorption, in order to dissociate the CO

molecule. Hence, the dissociation of the CO molecule is much difficult on the Pd sulfide compared to the other metal sulfide catalysts. We suggested that this is the reason why the Pd sulfide catalyst has the highest selectivity of the methanol. Moreover, we proposed that the catalysts which realize the bride-site adsorption of the CO molecule has the high selectivity of the methanol. This proposed guidance to design the high-selective catalysts for methanol may be useful for the experiments.

In the previous papers [6-10], we have proved that our combinatorial computational chemistry approach is very effective to design new catalysts with high-activity and high-resistance to poisons. Moreover, we indicated that our combinatorial computational chemistry is also applicable to predict the catalytic selectivity and to design new catalysts with high selectivity. Hence, we concluded that our combinatorial computational chemistry approach is a powerful tool to design new catalysts.

Modelü @	Eads (kJ/mol)	CO Charge	CO Distance (nm)
Co-Co	-192.54	-0.115	0.1155
Co-S	-122.05	-0.064 ↓	0.1148 ↓
Mo-Mo	-111.48	-0.292	0.1172
Mo-S	-171.93	-0.204 ↓	0.1165 ↓
Ru-Ru	-216.94	-0.366	0.1183
Ru-S	-236.14	-0.122 ↓	0.1157 ↓
Rh-Rh	-253.55	-0.324	0.1176
Rh-S	-216.97	-0.115 ↓	0.1150 ↓
Ir-Ir	-187.79	-0.675	0.1181
Ir-S	-241.83	-0.396 ↓	0.1158 ↓
Pd-Pd	-314.23	-0.342	0.1172
Pd-S	-205.77	0.189 ↓	0.1178 ↑
Re-Re	-101.73	-0.315	0.1158
Re-S	-180.00	-0.322 ↑	0.1168 ↑
Os-Os	-172.36	-0.447	0.1161
Os-S	-237.84	-0.390 ↓	0.1164 ↑

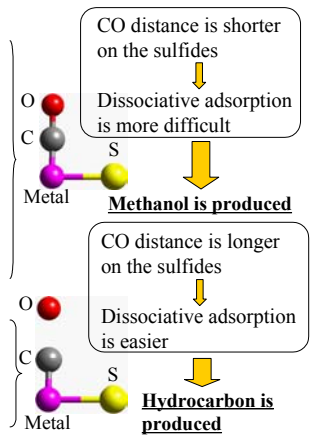

Figure 1 Adsorption energy, charge, and C-O distance of the CO molecule adsorbed on various metal catalysts and metal sulfide catalysts

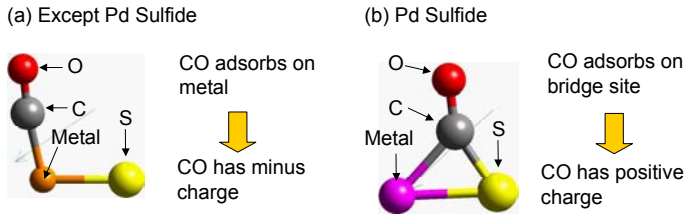

Figure 2 Adsorption structure of the CO molecule on the metal sulfide catalysts

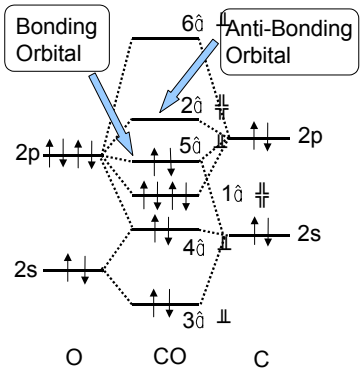

Figure 3 Molecular orbitals of the CO molecule

Conclusions

In the present paper, we have applied our combinatorial computational chemistry approach to the design of the metal sulfide catalysts for the CO hydrogenation process. We succeeded to clarify the dependence of the metal species in the metal sulfide catalysts to the products of the CO hydrogenation process. This result was in good agreement with the experimental results by Koizumi and co-workers. Moreover, we also propose that the Pd sulfide catalyst has the highest selectivity of the methanol from the CO hydrogenation process. This result strongly supports the experimental results by Koizumi and co-workers. Moreover, we propose that the catalysts which realize the bride-site adsorption of the CO molecule have the high selectivity of the methanol. This proposed guidance to design the high-selective catalysts for methanol may be useful for the experiments.

Finally, we concluded that our combinatorial computational chemistry approach is effective and useful to design new catalysts with high activity and selectivity. We are going to expand the application of our combinatorial computational chemistry to various catalyst systems.

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