Nitrogen and Hydrogen Gas Adsorption Properties of Microporous Ruthenium Coordination Polymers

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We investigated nitrogen and hydrogen gas adsorption properties of microporous ruthenium coordination polymers constructed from $\text{Ru}^{\text{II/III}}_2$ paddle wheel motif and dicarboxylic organic linkers such as terephthalic acid, fumaric acid, muconic acid and succinic acid. In nitrogen gas adsorption measurements, we calculated adsorption parameters such as surface area (Langmuir), pore volume and pore diameter. The relation between adsorption parameters and maximum amount of hydrogen uptake was discussed.

Key words: Microporous coordination polymer, Gas adsorption, mix-valence Ru complexes

Introduction

Microporous metal coordination polymers called metal organic frameworks (MOFs) have attracted a great deal of attention in the past decade because of their captivating structural diversities and intriguing potential applications, such as gas storage, separation, catalysis, and chemical sensing. The properties of gas-adsorption into MOFs were first found in the $[\text{Cu}_2(\text{TP})_2]_n$ (TP=terephthalic acid) by Mori and his co-workers[1]. Nowadays, many scientists have synthesized novel nano-porous crystals and their properties [2-4]. As known widely, Cu or Zn ions are useful as building blocks of MOFs. However, in the viewpoint of catalysis, their metal ions could not expect high catalytic performance. Therefore, in our laboratory, various metal coordination polymers incorporated with dinuclear paddlewheel motif such as Ru_2 , Rh_2 ions were also reported [5-11]. These materials were focused on not only gas-adsorption but also heterogeneous catalyst. For example, $[\text{Ru}_2(\text{TP})_2]_n$ was very useful for hydrogenation catalyst [5]. $[\text{Rh}_2(\text{TP})_2]_n$ and $[\text{Rh}_2(\text{FMA})_2]_n$ (FMA=fumarate) and $[\text{Rh}_2(\text{MTCPP})]_n$ ($\text{M}=\text{H}_2$, Cu, Pd and Ni; $\text{H}_2\text{TCCP}=4,4',4'',4'''$ -(21H, 23H-porphine-5,10,15,20-tetrayl) tetrakis benzoic acid) complexes have exhibited high catalytic activities for H-D exchange and hydrogenation of olefin (ethylene, propene, and butene) at 200K [6-7]. $[\text{Ru}_2(\text{H}_2\text{TCCP})\text{BF}_4]_n$ showed outstanding selectivity (>99%) for oxidation of primary aliphatic alcohols with air without any additives at room temperature[8]. Recently, we have been also reported the photochemical hydrogen production from water using these microporous ruthenium and rhodium coordination polymers [9-10]. Therefore, our reported ruthenium or rhodium coordination polymers are utility materials for heterogeneous catalyst and the development of more effective catalyst is desirable.

As above described, microporous ruthenium coordination polymers were especially promising materials for heterogeneous catalyst. Interestingly, the valence of dinuclear Ru_2 motifs took the mix-valence of

$\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ species. Therefore, according to choice of the counter-ion, several differential coordination polymers are obtained. As one example, we reported the microporous materials $[\text{Ru}_2(\text{L})_2\text{Cl}]_n$ (L=dicarboxylate) which have a three-dimensional jungle-gym-type structure, in which a two-dimensional square grid sheet composed of a dinuclear ruthenium (II, III) paddlewheel motif with a dicarboxylate organic linkers are bridged by halogen counterions to extend the two-dimensional structure into a three-dimensional structure [11]. (See Figure 1.)

Figure 1. Molecular structure of microporous ruthenium coordination polymers.

In order to develop the coordination polymer catalysts, it is important that adsorption properties of coordination polymers are closely investigated. In 2005, we reported the gas-adsorption properties and BET surface area of $[\text{Ru}_2(\text{L})_2\text{Cl}]_n$ [8]. Recently, Silva *et.al.* reported gas adsorption properties and adsorption parameters such as BET surface area, pore volume and pore diameters of same complexes [12]. However,

Silva's reported parameters are obviously incorrect, (1) micropore-filling of adsorption isotherm was not found, (2) pore diameter was obviously too large, (3) maximum amount of N_2 molecule was also too large. Therefore, in order to develop the ruthenium coordination polymers, it is required to correct the incorrect data to reliable data.

In this paper, we describe the gas adsorption properties of four microporous ruthenium coordination polymers $[Ru_2(L)_2Cl]_n$, which were constructed from $Ru^{II/III}_2$ paddle wheel motif and four dicarboxylate ligands, i.e. terephthalic acid (H_2TP), fumaric acid (H_2FMA), muconic acid (H_2MCA) and succinic acid (H_2SCA).

Results and Discussion

$Ru^{II/III}_2$ motifs were prepared by a procedure reported previously for $[Ru_2(L)_2Cl]_n$ [11]. N_2 or H_2 gas adsorption measurements were conducted by Shimadzu ASAP 2010 volumetric adsorption analyzer at the 77.35K and 760mmHg after vacuuming sample for eliminating solvent molecular in the pore. As shown Figure 2, in these complexes, N_2 gas isotherms show micro-pore filling at low pressure and the amount of N_2 gas adsorbed is increased slowly. At near the high pressure (760mmHg), large rise of N_2 gas adsorption depended on void space between particles is observed. These adsorption isotherms are typically a type I (Langmuir type) in the IUPAC classification. Langmuir surface area of $[Ru_2(TP)_2Cl]_n$, $[Ru_2(FMA)_2Cl]_n$, $[Ru_2(MCA)_2Cl]_n$ and $[Ru_2(SCA)_2Cl]_n$ calculated from these isotherms is 525.5m²/g, 470.3 m²/g, 645.4m²/g and 500.1m²/g, respectively. The surface area of $Ru^{II/III}_2$ motifs is good agreement with the order of the length of ligand ($H_2FMA < H_2SCA < H_2TP < H_2MCA$). Moreover, the maximum amounts of N_2 gas adsorbed are as followed: 170.1cm³/g by $[Ru_2(TP)_2Cl]_n$, 171.0cm³/g by $[Ru_2(FMA)_2Cl]_n$, 221.9cm³/g by $[Ru_2(MCA)_2Cl]_n$, 217.4cm³/g by $[Ru_2(SCA)_2Cl]_n$, respectively. Coordination polymers constructed from straight chain organic linker sometimes form interpenetrated frameworks. As an example of such interpenetrated frameworks, $Cu^{II/III}_2$ paddle wheel type coordination polymers selected H_2FMA ligand were reported previously [13]. Therefore, these $Ru^{II/III}_2$ motifs are much useful for the construction of microporous coordination polymers maintained high surface area. The pore diameter and pore volume are calculated by Harvovs- Kawazoe method [14]. The pore diameter of $[Ru_2(TP)_2Cl]_n$, $[Ru_2(FMA)_2Cl]_n$, $[Ru_2(MCA)_2Cl]_n$ and $[Ru_2(SCA)_2Cl]_n$ is 4.9 Å, 4.8 Å, 4.6 Å and 4.8 Å, respectively. The pore volume of $[Ru_2(TP)_2Cl]_n$, $[Ru_2(FMA)_2Cl]_n$, $[Ru_2(MCA)_2Cl]_n$ and $[Ru_2(SCA)_2Cl]_n$ is also good agreement with the order of surface area and is 0.265cm³/g, 0.151cm³/g, 0.265cm³/g and 0.150cm³/g, respectively.

H_2 gas adsorption isotherms are shown in Figure 3. The amount of H_2 gas adsorbed is 0.70wt% by $[Ru_2(TP)_2Cl]_n$, 0.50wt% by $[Ru_2(SCA)_2Cl]_n$, 0.73wt% by $[Ru_2(MCA)_2Cl]_n$, 0.54wt% by $[Ru_2(FMA)_2Cl]_n$, respectively. $[Ru_2(MCA)_2Cl]_n$ having the highest surface area shows high H_2 gas occupied performance. $[Ru_2(FMA)_2Cl]_n$ and $[Ru_2(SCA)_2Cl]_n$ are almost same. $[Ru_2(TP)_2Cl]_n$ exhibits similar gas adsorption amount compared with $[Ru_2(MCA)_2Cl]_n$, although surface area is

lower than that of $[Ru_2(MCA)_2Cl]_n$ and near to $[Ru_2(SCA)_2Cl]_n$. From these results, we assumed that benzene ring is effective for H_2 gas adsorption.

Figure 2 N_2 gas isotherm plot of $Ru^{II/III}_2$ motifs (● $[Ru_2(TP)_2Cl]_n$, ● $[Ru_2(FMA)_2Cl]_n$, ● $[Ru_2(MCA)_2Cl]_n$, ● $[Ru_2(SCA)_2Cl]_n$)

Figure 3 H_2 gas isotherm plot of $Ru^{II/III}_2$ motifs (● $[Ru_2(TP)_2Cl]_n$, ● $[Ru_2(FMA)_2Cl]_n$, ● $[Ru_2(MCA)_2Cl]_n$, ● $[Ru_2(SCA)_2Cl]_n$)

Conclusion

We demonstrated that gas adsorption property of four type $Ru^{II/III}_2$ microporous ruthenium coordination polymers constructed from $Ru^{II/III}_2$ paddle wheel motifs as building blocks and four dicarboxylic acid ligand as building units. From the N_2 gas adsorption measurement, the surface area of $Ru^{II/III}_2$ motifs is good agreement with the order of the length of ligand. The amount of H_2 gas adsorbed is non-relationship with surface area, and $[Ru_2(tp)_2Cl]_n$ shows high affinity concerning H_2 adsorption.

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