学 位 論 文 内 容 の 要 約

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学 位 論 文 題 名

Effective utilization of functional groups on micropore walls for designing materials with enhanced performances in catalysis and sorption

（向上した触媒および吸脱着性能を与える材料設計のためのミクロ細孔壁上の官能基の有効利用）

Porous materials are of great importance in modern science and technology owing to their fascinating properties, including high surface area, large accessible inner space, and variable chemical composition. These characteristics make them promising materials for a large variety of applications in gas adsorption and separation, catalysis, and biotechnology. In most of the applications, porous materials are designed based on the features of pores and channels, while in addition to these, the characteristics of regular structures of pore walls in crystalline porous materials, are one of the important features that need to be highlighted. Comparing to common amorphous porous materials, the crystallographically well-developed pore walls can provide uniformly distributed homogeneous sites with high stability and activity. Further investigation of these ordered crystalline walls will give us valuable information for the rational design of porous materials with enhanced adsorption ability and high catalytic performance. Given these, the present author worked on the utilization of the functional groups on pore walls in microporous materials to enhance the performance in catalysis and sorption in this thesis. Two kinds of microporous materials which were zeolite and metal-organic framework (MOF) were taken to introduce active metal species, and the catalysis and adsorption performance of the resulting materials were comprehensively investigated.

Initially, the amino functional groups on pore walls of an Al-based MOF (NH_2-MIL-53) were employed to introduce Pd for enhanced catalytic performance in nitrite reduction in water. MIL-53, which has a similar structure to NH_2-MIL-53 but without amino functional group, was also employed to introduce Pd for comparison. The MOF structure severely decomposed after the introduction of Pd via the conventional impregnation method. Therefore, a facile method that can readily prepare uniform Pd nanoparticles on NH_2-MIL-53 while maintaining the MOF framework structure was proposed. It was found that the amino groups on the pore walls of NH_2-MIL-53 played a critical role in introducing and dispersing Pd nanoparticles. Pd was successfully introduced into NH_2-MIL-53, but it was failed for MIL-53 by the equilibrium adsorption method. The precursor for the Pd nanoparticle, $(PdCl_3)^-$ in the acidic $PdCl_2$ solution, was electrostatically interacted with the protonated amino group in NH_2-MIL-53 to give $-NH_3^+$---$(PdCl_3)^-$ ion pair, resulting in the successful introduction of the precursor. Subsequential reduction with $NaBH_4$ gave uniformly dispersed Pd nanoparticles even with high Pd loadings. The resulting material, Pd@NH_2-MIL-53, prepared with different Pd loadings by this method, exhibited different Pd surface structures. A linear relation between specific activity per surface Pd site and the fraction of Pd(111) facet was observed. It was concluded that the Pd(111) facets on Pd@NH_2-MIL-53 exhibited high activity for nitrite reduction in water.

Meanwhile, the functional groups (cation exchange sites) on pore walls of microporous zeolites were utilized to introduce Ag^+ for enhanced performance in ethylene (C_2H_4) sorption. Systematical investigations of C_2H_4 adsorption on Ag^+-exchanged zeolites with different topology framework structures were carried out first. By performing adsorption isotherm measurements twice consecutively, chemical adsorption of C_2H_4 that could not be easily removed by vacuum treatment was confirmed for all the Ag^+-exchanged zeolites, while the parent Na^+-from zeolites only exhibited physical adsorption. The C_2H_4 chemical adsorption capacity was basically increased with the increase in Ag contents up to around 2 mmol g^{-1}. However, further increase in Ag contents did not bring about an improvement in C_2H_4 chemical adsorption capacity. Further investigation on the nature of Ag species in Ag^+-zeolites using the diffuse reflectance UV-vis spectroscopy and XAFS confirmed that large clusters or metallic Ag^0 nanoparticles were formed and became dominant when the Ag^+ contents became too high. These species did not act as adsorption sites for C_2H_4. Ag species dominantly presented as large clusters or metallic Ag^0 in A-type zeolite. While large clusters were also observed in X-type zeolite, more homogeneous Ag^+ was predominantly present in Y-type zeolite even with similar Ag contents. These results demonstrated that the nature of Ag species present in the Ag^+-exchanged zeolites was greatly influenced by the framework structure and composition (Si/Al ratio) of zeolites. This effect was presumably due to the different nature of functional groups on pore walls of zeolites, leading to the different interaction between these groups and the introduced Ag^+ ions. Ag_{36}-X (ion-exchange ratio of 36) and Ag_{62}-Y (ion-exchange ratio of 62) exhibit large C_2H_4 chemical adsorption capacity and strong C_2H_4 adsorption, making them promising C_2H_4 encapsulation materials.

Accordingly, investigations of C_2H_4 release behavior were conducted over Ag_{36}-X and Ag_{62}-Y, with Ag_{36}-A also included for comparison. Thermal desorption experiments revealed distinct desorption profiles for different zeolite samples, suggesting the presence of C_2H_4 adsorption sites with varying strengths in these materials. Isothermal dynamic release experiments associated with kinetic analyses demonstrated that Ag_{36}-A, Ag_{36}-X, and Ag_{62}-Y exhibited distinct release characteristics, with Ag_{36}-A showing comparable release kinetics to Ag_{36}-X but slightly lower than Ag_{62}-Y within the initial 2 h. Notably, despite possessing the same framework structure, Ag_{36}-X exhibited slower C_2H_4 release compared to Ag_{62}-Y, suggesting the variations in the interaction between C_2H_4 and the zeolite framework alters the release characteristic of Ag^+ sites. Release kinetic analyses revealed that Na^+-A with smaller pore size exhibited much slower release of C_2H_4 than Na^+-X and Na^+-Y with larger pore size, although they all had weak adsorption of C_2H_4, demonstrating that the pore size of the zeolites had great impact on release kinetics. Overall, Ag_{36}-X exhibits a comparable slow-release characteristic, along with its superior ethylene adsorption capacity, Ag_{36}-X shows promising potential for application as an ethylene controlled-release material.

From the results and findings obtained and revealed through the studies in this thesis, the present author concludes that the functional groups on the pore walls of microporous MOF and zeolite have great impact on tuning the nature of introduced active metal species, which can enhance the performance in catalysis and sorption. The methodology is quite general and effective and is appliable for different kinds of porous materials. Enhanced performance can be expected with the effective utilization of these functional groups on the pore walls, which will surely contribute to solving current and future global environmental problems such as environmental conservation and environmental issues.