A Novel Reaction Pathway in Olefin-Deuterium Exchange Reaction inside the Micropores of Rh(II) Dicarboxylate Polymer Complexes

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Three dimensional microporous polymers of Rh fumarate or Rh terephthalate complexes exhibited high catalytic activity for hydrogen exchange and hydrogenation of olefins at 200 K. The hydrogen exchange reaction takes place only inside the nanopores of the complexes without complete scission of C–H bond of olefin molecule.

Construction of microporous metal-organic frameworks by co-polymerization of organic molecules with metal ions is of great interest due to their intriguing structural diversity and their potential functions as microporous materials for molecular absorption, ion-exchange or catalysis.[1–3] Although a number of coordination polymers with new structural aspects is increasing, compounds that reveal such functional properties characteristic of their cavities and channels are still lacking.[4] In this paper, we report the first example of three dimensional microporous coordination polymers of Rh(II) carboxylates, which catalyze the dissociation of hydrogen molecules as well as the hydrogen exchange and hydrogenation of ethene, propene and butene.

Rh(II) fumarates (Rh(f)) and terephthalates (Rh(t)) polymer complexes were prepared by heating methanol solutions of Rh(II) acetate and organic ligands at 443 K, followed by filtration and evacuation at 373 K.[5] The color of the polymer complexes was light green (denoted as Rh(f)-A or Rh(t)-A). As shown in Figure 1, the complexes may possess two dimensional sheet structures, which construct nanoscale micropores with a three dimensional packing (pore size = 5.2 A for Rh(f) and 6.0 A for Rh(t) estimated from Ar adsorption at liq. N_2 temp) and occludes about 0.8 (Rh(f)) and 1.2 (Rh(t)) N_2 molecule per one molecule of Rh(II). By raising reaction temperatures from 443 K to 473 K, dark green color polymer complexes were obtained whose chemical composition was similar to the complex Rh(f)-A, but did not occlude N_2, maybe due to the incomplete packing of two dimensional sheets (denoted as Rh(f)-B). On the other hand at lower reaction temperatures of 413 K, the color of the obtained complex was pale green, whose pore size distribution was very broad (10–20 nm; denoted as Rh(f)-C).

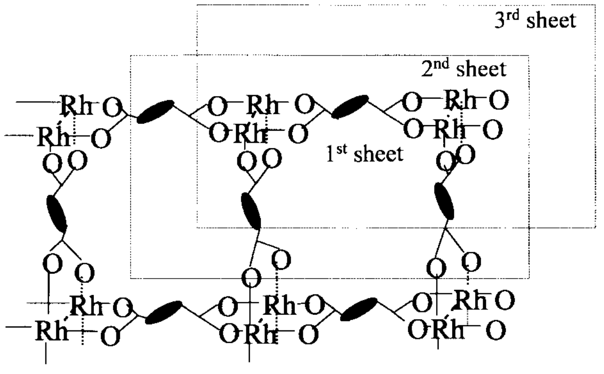

Figure 1. Schematic view of the structure of Rh(II) carboxylates.

The complexes were put into a reaction vessel, which was connected to a conventional closed gas circulation system. After evacuation at room temperature, Rh(f)-A and Rh(t)-A complexes exhibited high catalytic activity for H_2–D_2 exchange reaction even at 200 K. Moreover, hydrogen exchange of olefins such as ethene, propene and butene as well as their hydrogenation took place at 200 K. The composition of the gas phase was analyzed by mass spectra as well as gas chromatography with activated alumina column. The catalytic activity of these reactions was decreased gradually with the repeated runs, maybe due to the accumulation of hydrocarbon byproducts and re-activation of H_2 reduction at 373 K for 1 h was required to recover the original activity. Accordingly, we took this pretreatment condition for the study of catalytic behavior of these complexes.

Table 1. Initial rates of hydrogenation and hydrogen exchange reactions of propene over various Rh(f) complexes at 255K

Complexes	C_3H_6–C_3D_6(mol / s·g)	C_3H_6–H_2(mol / s·g)
Rh(f)-A	2.6×10^{-3}	2.4×10^{-5}
Rh(f)-B	0.0×10^{-3}	8.3×10^{-6}
Rh(f)-C 1st run	-	1.2×10^{-5}
2nd run	-	3.1×10^{-6}
3rd run	-	1.5×10^{-6}

Table 1 summarizes the initial rates of propane formation in C_3H_6–H_2 reaction as well as propene-d_1 formation in C_3H_6–C_3D_6 reaction over various polymer complexes. It is interesting to note that only the hydrogenation proceeded over the polymer complex Rh(f)-B but no hydrogen exchange reaction of olefin molecules. As mentioned already, Rh(f)-B did not occlude N_2 due to the incomplete packing of the sheets. This result suggests that the active sites for the hydrogen exchange of olefins may exist only inside the micropores of the polymer complexes, while hydrogenation of olefins takes place both inside and at the outer surface of the polymer complexes. In the case of Rh(f)-C complex both hydrogenation and hydrogen exchange reaction of propene took place with the slower rates than Rh(f)-A and deactivated rapidly after a few times of repeated reactions and was not recovered to its original activity even after 373 K reduction. The dependence of the initial rates of hydrogenation (hyd) and hydrogen exchange (exc) upon the sizes of the olefins and organic ligands was investigated by changing propene with ethene and butene, and also fumaric acid with terephathalic acid ligand. Figure 2 summarized the

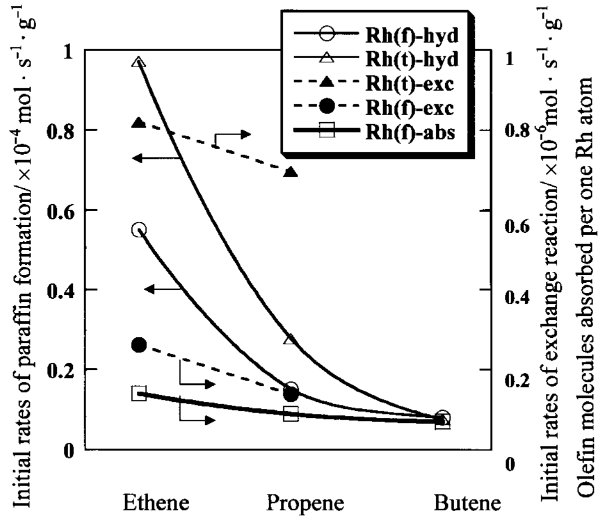

Figure 2. Initial rates of hydrogenation (255K) and hydrogen exchange reaction (194K) over Rh(f)-A and Rh(t)-A complexes, and absorbed amount of olefins at room temperature on Rh(f)-A complex.

results together with the amount of olefin molecules absorbed per one Rh atm (ads), estimated from the adsorption isotherms at room temperature. Smaller olefins and a larger ligand complex exhibited higher activities for hydrogen exchange and also larger olefin/Rh ratios, indicating that these reactions take place mainly inside the micropores of the polymer complexes.

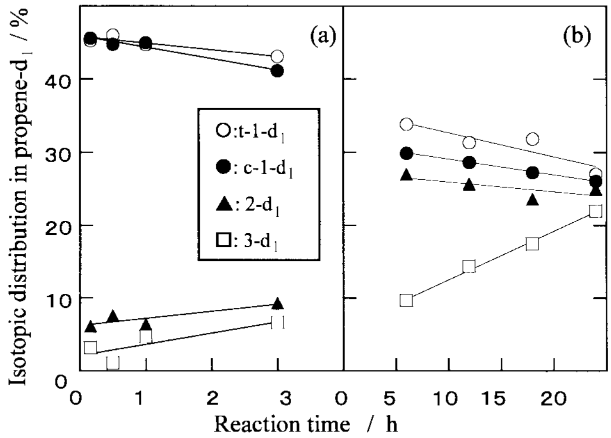

Figure 3. Time courses of (a) C_3H_6–C_3D_6 and (b) C_3H_6–D_2 reactions over Rh(f)-A complex at 194 K.

Figure 3(a) shows microwave spectroscopic analyses of the deuterium isotopic distribution of formed propene-d_1 during C_3H_6–C_3D_6 reaction over Rh(f)-A complex at 194 K, where cis- and *trans*- propene-1-d_1 were main products and the amount of propene-2-d_1 and 3-d_1 were very few. On the other hand, the exchange rate of C_3H_6–D_2 reaction was two orders of magnitudes smaller than that of C_3H_6–C_3D_6 reaction. Figure 3(b) shows the isotopic distribution pattern of this reaction, which was different from that of C_3H_6–C_3D_6 reaction, and 1,3- and 2,3-intramolecular hydrogen exchange processes operating.[6] To study the relationship between adsorbed hydrogen and propene, the initial rates of HD formation in H_2–D_2 and C_3H_6–H_2–D_2 reactions, and also initial rates of propene-d_1 formation in C_3H_6–C_3D_6 and C_3H_6–C_3D_6–H_2 reactions were compared over Rh(f)-A complex at 194 K. The initial rate of HD formation in H_2–D_2 and C_3H_6–H_2–D_2 reaction was comparable to each other, and one order of magnitude faster than that of propene-d_1 formation in C_3H_6–C_3D_6 reaction. On the other hand, the initial rate of propene-d_1 formation in C_3H_6–C_3D_6–H_2 reaction was identical with that of C_3H_6–C_3D_6 reaction with the same isotopic distribution. These results indicate that intermolecular hydrogen exchange between two propene molecules takes place independently from the dissociative adsorption of hydrogen molecules.

As discussed already, C_3H_6–C_3D_6 exchange reaction takes place only inside of the micropores of the complexes. The direct dissociative mechanism of propene C–H bond is not available for this exchange process, because no mixing was observed between hydrogen of propene molecules with dissociative hydrogen from gaseous hydrogen molecules. Accordingly we propose the following mechanism for this exchange process. When two propene molecules are put into the channel of the three dimensionally packed sheets, they may exchange their hydrogen without complete scission of C–H bond. Microwave spectroscopic analysis of propene-d_1 formed in this reaction indicates that only hydrogen atoms attached to the double bond carbons of propene are exchangeable and suggests the existence of an intermediate of a four centered carbon ring structure formed by two propene molecules We have already reported the existence of such novel exchange mechanism, which does not involve a complete C–H bond dissociation but intermolecular hydrogen shift between two adsorbed propene molecules over alumina supported $Os_3(CO)_{12}$ derived catalysts. Co-existing adsorbed CO modifies the electronic state of Os and makes the direct dissociation mechanism unfavorable, opening a new bimolecular pathway.[7] In the present study, special electronic structure of micropores as well as the restricted nano-space may play an important role for the operation of such a novel reaction pathway.

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