PREPARATION OF NOBLE METAL PARTICLES DISPERSED MESOPOROUS CARBONS AND THEIR CHARACTERISTICS

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Introduction

Mesoporous activated carbons are supposed to be useful for the adsorption of large molecules. We have already reported that highly mesoporous activated carbons can be obtained by steam activation of pitch containing rare earth metal complexes[1]. On the other hand, carbon materials have been used as a support for heterogeneous metal catalysts for various chemical reactions. Recently, we prepared simply noble metal particles dispersed activated carbons by activating pitch containing noble metal complexes such as Pt and Pd[2]. In this work, we attempted the simple preparation of noble metal particles dispersed mesoporous activated carbons by activating pitch containing both $Y(acac)_3$ and noble metal complexes such as Pt, Pd, or Rh, according to the procedure as shown in Fig. 1. In addition, the catalytic activities of these noble metal particles dispersed mesoporous carbons for hydrogenation of unsaturated compounds, e.g., methyl linoleate was investigated.

Experimental

Pitch containing noble metal complexes and $Y(acac)_3$ were prepared by mixing a THF solution of low softening point pitch with a solution of noble metal complexes and $Y(acac)_3$ and the removal of THF by flash distillation. Obtained pitch containing noble metal complexes and $Y(acac)_3$ were converted to high softening point pitch by heating in air at 360 ℃ and then activated by N_2 gas saturated with water vapor at 850-900℃.

BET specific surface area and pore characteristics were determined by N_2 adsorption using a Quantachrome Autosorb-6. Metals in carbons were characterized by XRD and electron probe microanalyses(EPMA).

Catalytic activities of noble metal particles dispersed mesoporous carbons for the hydrogenation of unsaturated compounds such as 1,3-cyclooctadiene and methyl stearate were determined.

Results and Discussion

Table 1 shows the pore characteristics, BET surface areas, mesopore surface areas and mean pore sizes of activated carbons obtained from pitch containing of noble metal complexes and $Y(acac)_3$. The content of Y was 2.0 wt% in pitch and The concentration of noble metals in pitch was changed from 0.5 ~ 2.0 wt%.The activated carbons obtained were highly mesoporous (>60%), although BET specific surface area is not necessarily high (~200m^2/g). XRD analyses indicated that noble metal compounds are reduced to metal and are contained as metal fine particles. EPMA showed that noble metals in carbons were homogeneously dispersed in activated carbons.

Catalytic activities for hydrogenation of 1,3-cyclooctadiene and methyl linoleate were tested. Fig.2 shows the conversion curves of methyl linoleate to methyl oleate and methyl stearate by Pt particles dispersed mesoporous activated carbon (AC-Y2/Pt1), and Fig.3 shows the conversion of 1,3-cyclooctadiene to cyclooctene and cyclooctane by Rh particles dispersed mesoporous activated carbon (AC-Y2/Rh1). In both cases, the formation of monoene and saturated compounds was observed at initial steps of reactions and finally they were converted to cyclooctane and methyl stearate.

The initial catalytic activities were calculated from the conversion of 1,3-cyclooctadiene and methyl linoleate with time shown in Figs. 2 and 3. The initial catalytic activities of these noble metal particles dispersed mesoporous activated carbon are summarized in Table 2. The initial catalytic activities of commercial noble metals supported on carbons are also shown in Table 2. Noble metal dispersed mesoporous activated carbons obtained in this work exhibited high catalytic activities, although these values were slightly lower than those of commercial ones. The specific surface areas of activated carbons obtained in this work are lower than those of commercial activated carbons. Catalytic activities of noble metal supported on activated carbons for

reactions of large molecules are supposed to be affected by surface area in addition to pore size of activated carbon.

Acknowledgments

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References

1. Tamai H, Kakii T, Hirota Y, Kumamoto T and Yasuda H. Synthesis of extremely large mesoporous activated carbon and its unique adsorption for giant molecules. Chem. Mater. 1996; 8:454-462.
2. Tamai H, Kataoka Y, Nishiyama F, and Yasuda H. Characteristics and catalytic activity of carbons obtained from pitch containing noble metal complexes. Carbon 2000; 38:899-906.

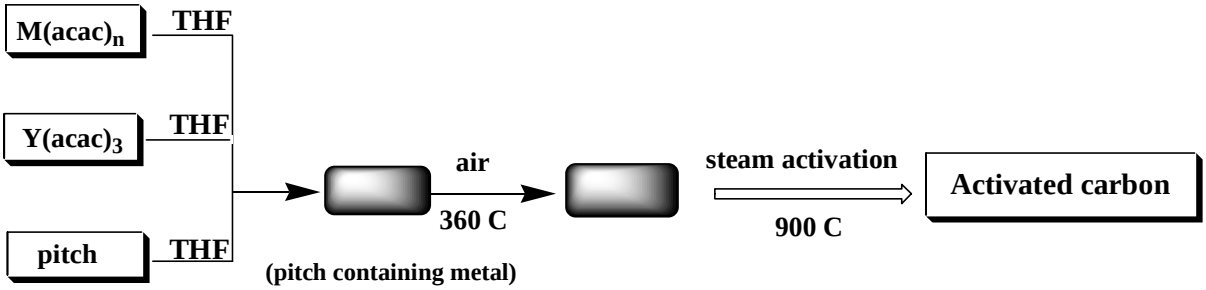

Fig.1 Preparation of activated carbon

Table 1 Activated carbons from pitch containing both $Y(acac)_3$ and noble metal complex

Sample	Activation time (min)	Yield (%)	BET surface area (m^2/g)	Mesopore surface area (m^2/g)	Mesopore ratio (%)	Pore size (nm)
Ac-Y2/Pd0.5	9	27.1	175	144	82.4	6.3
Ac-Y2/Pd1	9	34.4	143	63	43.9	4.6
Ac-Y2/Pd2	9	38.9	120	48	39.8	4.9
Ac-Y2/Pt0.5	9	21.1	169	79	46.9	7.7
Ac-Y2/Pt1	9	26.1	171	171	100	10.3
Ac-Y2/Pt2	9	22.3	169	169	100	10.2
Ac-Y2/Rh0.5	9	26.7	229	59	25.7	4.7
Ac-Y2/Rh1	9	36.5	128	53	41.4	4.9
Ac-Y2/Rh2	9	33.3	158	52	32.9	4.7

Activationtemp.:900 C

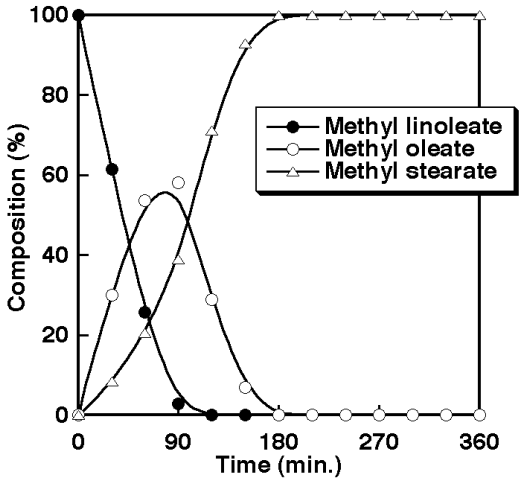

Fig. 2 Catalytic activity of AC-Y2/Pt1 9min for hydrogenation of Metyl linoleate

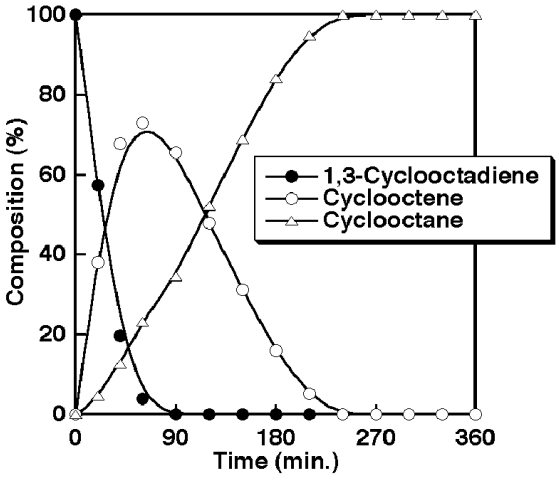

Fig. 3 Catalytic activity of AC-Y2/Rh1 9min for hydrogenation of 1,3-cyclooctadiene

Table 2 Catalytic activity of activated carbon obtained from pitch containing both Y(acac)3 and noble metal complex

Sample	BET surface area (m2/g)	Mesopore ratio (%)	Metal content in AC (wt%)	Initial activity (mol/mol-metal h)
AC-Y2/Pd0.5	175	82.4	1.89	6.0
AC-Pd5(std)	566	34.0	5.0	>375.0
AC-Y2/Pt0.5	169	46.9	1.82	0
AC-Y2/Pt1	171	100	2.63	93.8
AC-Y2/Pt2	169	100	4.42	20.0
AC-Pt5(std)	496	19.5	5.0	>375.0

Reaction temp.: 40 C