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PREPARATION OF NOBLE METAL PARTICLES DISPERSED MESOPOROUS CARBONS AND THEIR FUNCTIONS

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We report the simple preparation of noble metal particles dispersed in highly mesoporous activated carbons. The activated carbons were prepared by activating pitch containing rare earth metal complex and rare metal complexes by steam. The activated carbons obtained showed the high catalytic activities for the hydrogenation of unsaturated compounds of large size such as methyl linoleate and 1,3-cyclooctadiene.

Keywords: activated carbon; mesopore; metal particle; catalytic activity

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 [1,2]. Moreover, carbon materials have been used as a support for heterogeneous metal catalysts for various chemical reactions. In this work, we attempted the simple preparation of noble metal particles dispersed mesoporous activated carbons by activating pitch containing both yttrium acetylacetonate ($Y(acac)_3$) and noble metal complexes such as Pt, Pd, or Rh, according to the procedure as shown in Figure 1. In addition, the catalytic activities of these noble metal particles dispersed in mesoporous carbons for hydrogenation of unsaturated compounds, e.g., methyl linoleate and 1,3-cyclooctadiene were investigated.

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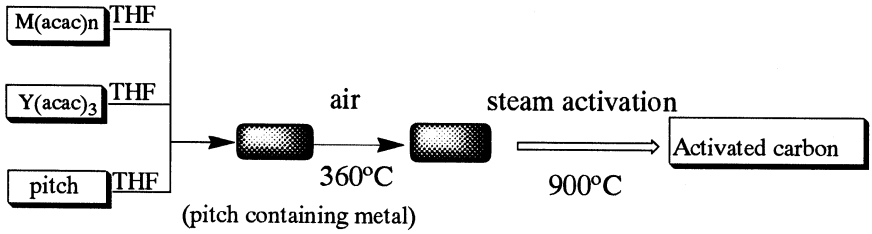

FIGURE 1 Preparation of activated carbon.

EXPERIMENTAL

Pitch containing noble metal complexes and $Y(acac)_3$ was 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 activated by steam in N_2 gas at 850–900°C.

BET specific surface area and pore characteristics were determined by N_2 adsorption using a Quantachrome Autosorb-6. Catalytic activities of noble metal particles dispersed in mesoporous carbons for the hydrogenation of unsaturated compounds such as 1,3-cyclooctadiene and methyl linoleate were measured by the reaction in the solutions containing activated carbon and sabstrates under H_2 gas.

RESULTS AND DISCUSSION

Preparation of Activated Carbons

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 $\sim$ 2.0 wt%. The activated carbons obtained were highly mesoporous (>60%), although BET specific surface area is not necessarily high ($\sim$200 m^2/g). This is remarkable in the system of Y and Pt complexes and the resulting activated carbon exhibited about 100% of mesopore ratio. In the case of Pd complex, mesopore ratio decreased with increasing Pd content. Regarding metal compounds formed by activation, XRD analyses indicated that noble metal compounds are reduced to metal and are contained as metal fine particles. Yttrium oxide(Y_2O_3) are formed from $Y(acac)_3$. EPMA analyses showed that noble metals in carbons were homogeneously dispersed in activated carbons.

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

Activation temp.: 900°C.

Catalytic Activity

Catalytic activities for hydrogenation of 1,3-cyclooctadiene and methyl linoleate were tested. Figure 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 Figure 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

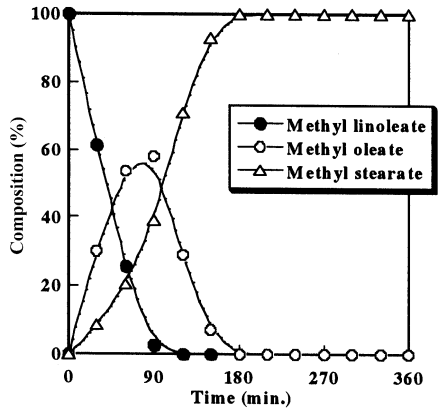

FIGURE 2 Catalytic activity of AC-Y2/Pt1 9 min for hydrogenation of methyl linoleate.

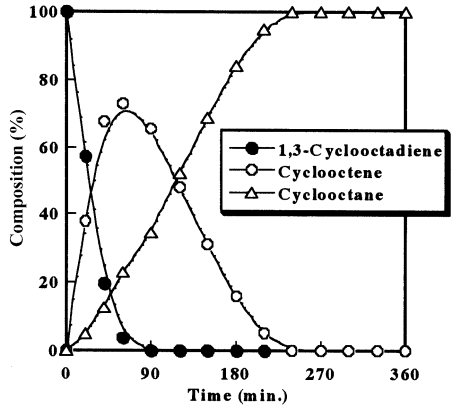

FIGURE 3 Catalytic activity of AC-Y2/Rh1 9 min for hydrogenation of 1,3-cyclooctadiene.

methyl stearate. On the basis of these conversion curves, we calculated the initial activities. Table 2 shows the initial activities for the hydrogenation of methyl linoleate. Activated carbons obtained from pitch containing $Y(acac)_3$ and Pt complex (AC-Y2/Pt1) showed the high catalytic activities, although their activities are slightly lower than that of commercial Pd or Pt supported carbons. These results suggest that mesopore in activated carbons plays an important role in hydrogenation of large size substrates. The lower activities of AC-Y2/Pt2 may be due to the larger particle size of Pt formed with long activation time. It is concluded that noble metal particles dispersed in mesoporous activated carbon are easily prepared by activating

TABLE 2 Catalytic Activity of Activated Carbons Obtained from Pitch Containing Both $Y(acac)_3$ and Noble Metal Complex

Sample	BET surface area (m^2/g)	Mesopore ratio (%)	Metal content in AC (%)	Initial activity (mol/mol-metal h)
AC-Y2/Pd0.5	175	82.4	1.9	6.0
AC-Y2/Pt0.5	169	46.9	1.8	0
AC-Y2/Pt1	171	100	2.6	93.8
AC-Y2/Pt2	169	100	4.4	20.0
AC-Y2/Rh0.5	224	21.5	1.8	38.8
AC-Pt1	53	40.8	2.9	1.2
Pd/C(std)a)	566	34.0	5.0	375
Pt/C(std)a)	496	19.5	5.0	375

Reaction temp.: 40°C a): commercial Pd or Pt supported carbon.

pitch containing rare earth metal complex and rare metal complex by steam.

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