

Regioselective hydrogenation of dienes catalyzed by palladium–aminosilane complexes grafted on MCM-41

Shogo Shimazu*, Noriyuki Baba, Nobuyuki Ichikuni, Takayoshi Uematsu

Department of Materials Engineering, Chiba University, 1-33 Yayoi, Inage, Chiba 263-8522, Japan

Received 2 July 2001; accepted 12 November 2001

Abstract

A palladium(II)–aminosilane complex supported on MCM-41 (Pd–AEAPSi/MCM (**1**)) was prepared by the complexation of palladium(II) acetate to 3-(2-aminoethyl)aminopropyl (AEAPSi) groups grafted on MCM-41. FT-IR and ^{13}C CP MAS NMR studies indicated that AEAPSi chelated to palladium(II) to form the Pd(II)–AEAPSi complex. Regioselective hydrogenation of dienes was carried out by the obtained **1** as a catalyst. Pd–AEAPSi/MCM exhibited remarkably high reaction rates for the dienes with a hydroxyl group such as geraniol and linalool, while for limonene without OH group the reaction rate was notably low. The MCM-supported catalyst also showed noticeably high regioselectivity in the hydrogenation of dienes with OH group. These results indicate that the hydrophilic interaction between the MCM-41 surface and the substrates plays an important role in the rate-determining step. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: MCM-41; Palladium(II) complex; Aminosilane; Hydrogenation; Regioselective

1. Introduction

The mesoporous silica compounds such as MCM-41 first prepared by Kresge et al. have high surface area and highly ordered mesopore of 2–10 nm [1]. The characteristic structure can provide the highly dispersed and relatively uniformed active sites for the various chemical reactions. Maschmeyer et al. first prepared the grafting Cp_2Ti -MCM-41 catalysts and used them for the shape selective epoxidation [2]. Jacobs and co-workers introduced the various functional groups such as sulfonic acid groups into MCM-41 [3]. Bruch et al. prepared the surface-grafted manganese-oxo species on MCM-41 [4]. In these studies, however, the catalytic reaction mainly took place at the introduced active sites, where the surface of the MCM-41 was not effectively utilized. We spec-

ulate that the hydrophilic surface caused by the silanol groups may assist the selective interaction between the active sites and the substrates, which enhances the catalytic activity and selectivity.

In this study, the syntheses and the characterization of the palladium complexes grafted on MCM-41 mesopore surface via silane coupling ligands (AEAPSi) and their catalytic behavior for the hydrogenation of dienes with/without a hydroxyl group are described.

2. Experimental

2.1. Preparation of AEAPSi/MCM

MCM-41 (500 mg, $1175\text{ m}^2\text{ g}^{-1}$) prepared by the Mobil's method [5] was placed in two-necked round-bottomed flask with a septum and reflux

* Corresponding author

condenser and dried in vacuo for 2 h at 473 K. 3-(2-Aminoethyl) aminopropyltriethoxysilane (AEAPSi) (1.5 ml) was added to the suspended solution of MCM-41 in THF (30 ml) under N₂ atmosphere and the mixture was refluxed for 12 h. After the filtration of the mixture, the white solid filtrate was washed with 10 ml of THF and dried in vacuo for 12 h. The obtained product was the MCM-41 modified with AEAPSi and was denoted as AEAPSi/MCM.

2.2. Preparation of Pd–AEAPSi/MCM (1)

AEAPSi/MCM (100 mg) was suspended in ethyl acetate (30 ml). [Pd(OAc)₂]₃ (38 mg) was added to the suspension and stirred for 24 h under N₂ atmosphere. After the filtration, the yellow solid was washed with 10 ml of ethyl acetate and dried in vacuo. The obtained product was denoted as **1**.

2.3. Preparation of Pd–AEAPSi/Me–MCM (2)

Compound **1** (200 mg) in a 30 ml round-bottomed flask was dried in vacuo at ambient temperature for 2 h. Methoxytrimethylsilane (0.2 ml) was added to **1** suspended in THF (15 ml) in N₂ atmosphere and stirred at ambient temperature for 6 h. After filtration, the brown solid was dried in vacuo. The obtained product was denoted as **2**.

2.4. Preparation of Pd–AEAPSi/SiO₂ (3)

Compound **3** was prepared in the similar manner as **1** by means of Aerosil 200 (200 m² g⁻¹) instead of MCM-41.

2.5. Quantitative analysis of OH group on MCM-41

All operations were performed under a nitrogen atmosphere. An MCM-41 sample in a vial equipped with a rubber septum was dried in vacuo at 473 K and dispersed with dried toluene. Excess methyl-lithium in diethyl ether was added to the MCM-41 sample via a syringe and was stirred for 1 h. The concentration of unreacted methyl-lithium was determined by the titration of aliquots of the supernatant liquid with *sec*-butanol in toluene solution using 1,10-phenanthroline as an indicator [6]. The repeated titrations gave $5.3 \pm 0.5 \text{ OH nm}^{-2}$ for the MCM-41

employed in the present paper. The obtained results are in good agreement with the results of silica described in [7].

2.6. Instruments

IR spectra of the catalysts were measured by a JEOL JIR-7000 spectrometer. XRD data were obtained by a MAC SCIENCE MPX³V powder diffractometer using Ni filtered Cu K α radiation. The loading amounts of AEAPSi and Pd(OAc)₂ were estimated from CHN analyses by a Perkin-Elmer-2400. Transmission electron microscopy (TEM) images of **1** were observed by a JEOL-4000 FX II with accelerating voltage at 200 kV. ²⁹Si (59.6 MHz) and ¹³C (75.5 MHz) CP MAS NMR spectra were recorded on a Bruker GSX-500 at ambient temperature.

2.7. Hydrogenation of dienes

In a 5 ml two-necked round-bottomed flask with septa, catalyst (10 mg for **1** or 5.6 mg for **3**) was dried in vacuo for 1 h at ambient temperature and then dried benzene (5.0 ml) was added by using a syringe. After the pretreatment of the catalyst under H₂ atmosphere (1.01×10^5 Pa) for 12 h at ambient temperature, 1.0 mmol of substrate was added to initiate the catalytic reaction with stirring under H₂ atmosphere (1.01×10^5 Pa).

The products were analyzed on gas chromatography (SHIMADZU GC-14A with Chromatopac C-6A integrator) with a glass column (3.2 mm \varnothing \times 3 m, PED-20M Chromosorb WAW-DMCS 10% 80/100 mesh). The authentic samples were used for determination of reactants and substrates.

3. Results and discussion

3.1. Characterization of the MCM-41-supported catalysts

From the chemical analyses, the loading amount of the AEAPSi group was 1.10 mmol g⁻¹ for **1** and 1.25 mmol g⁻¹ for **3**. The ratio of AEAPSi/Pd was 1.14 for **1** and 1.79 for **3**. From these results, it appears that the AEAPSi group was nicely dispersed on the MCM-41.

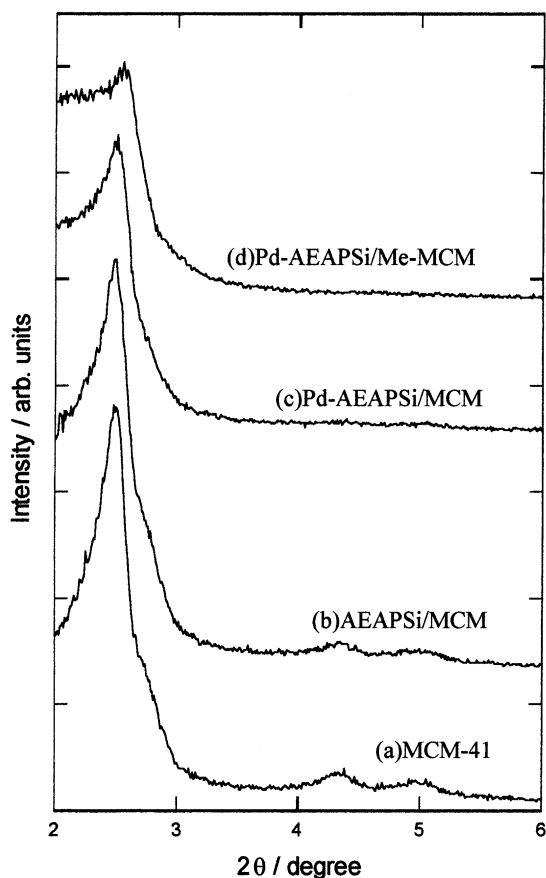


Fig. 1. XRD patterns for (a) MCM-41, (b) AEAPSi/MCM, (c) Pd-AEAPSi/MCM, and (d) Pd-AEAPSi/Me-MCM.

Fig. 1 shows the XRD patterns for the MCM-41 modified with AEAPSi group and the Pd complexes as well as the original MCM-41. Although the modification of AEAPSi group hardly changed the d_{100} peak intensity of the support, the coordination of $\text{Pd}(\text{OAc})_2$ decreased the crystallinity of MCM-41. However, the specific surface area of **1** was $600 \text{ m}^2 \text{ g}^{-1}$ which was still three times larger than that of **3**.

TEM image of **1** is shown in Fig. 2, in which the hexagonal structure is still detected although the crystallinity of MCM-41 support was decreased.

According to the IR spectra of **1** (Fig. 3(b)), acetate was observed at 1559 cm^{-1} for ν_{as} and 1412 cm^{-1} for ν_{s} . The difference between ν_{as} and ν_{s} ($\Delta\nu = 147 \text{ cm}^{-1}$) indicates that the acetate was ionic instead of the bridging coordination observed for $[\text{Pd}(\text{OAc})_2]_3$



Fig. 2. TEM image for Pd-AEAPSi/MCM (**1**).

($\Delta\nu = 231 \text{ cm}^{-1}$) [8]. These results suggest the strong coordination of AEAPSi to $\text{Pd}(\text{II})$.

In the ^{29}Si CP MAS NMR spectra (Fig. 4), each Q3 peak at -101 ppm for AEAPSi/MCM (Fig. 4(b)) and **1** (Fig. 4(c)) was remarkably decreased compared to that of the original MCM-41 (Fig. 4(a)) [1]. In contrast to the Q3 peak, the intensity of Q4 peak at -109 ppm increased for AEAPSi/MCM (Fig. 4(b)) and **1** (Fig. 4(c)). The peak at -58 ppm corresponding to T2 (schematized in Fig. 4) was mainly observed for AEAPSi/MCM and **1** [9]. These results confirmed the organofunctionalization of MCM-41 with AEAPSi groups.

Fig. 5 shows the ^{13}C CP MAS NMR spectra of the modified MCM-41 with AEAPSi and Pd complex. Table 1 summarizes the assignment of the chemical shifts for the carbon atoms in these modified MCM-41 compounds referred to the published papers [10,11]. The down-field shift was observed only for the C1, C2, and C3 resonances from AEAPSi/MCM

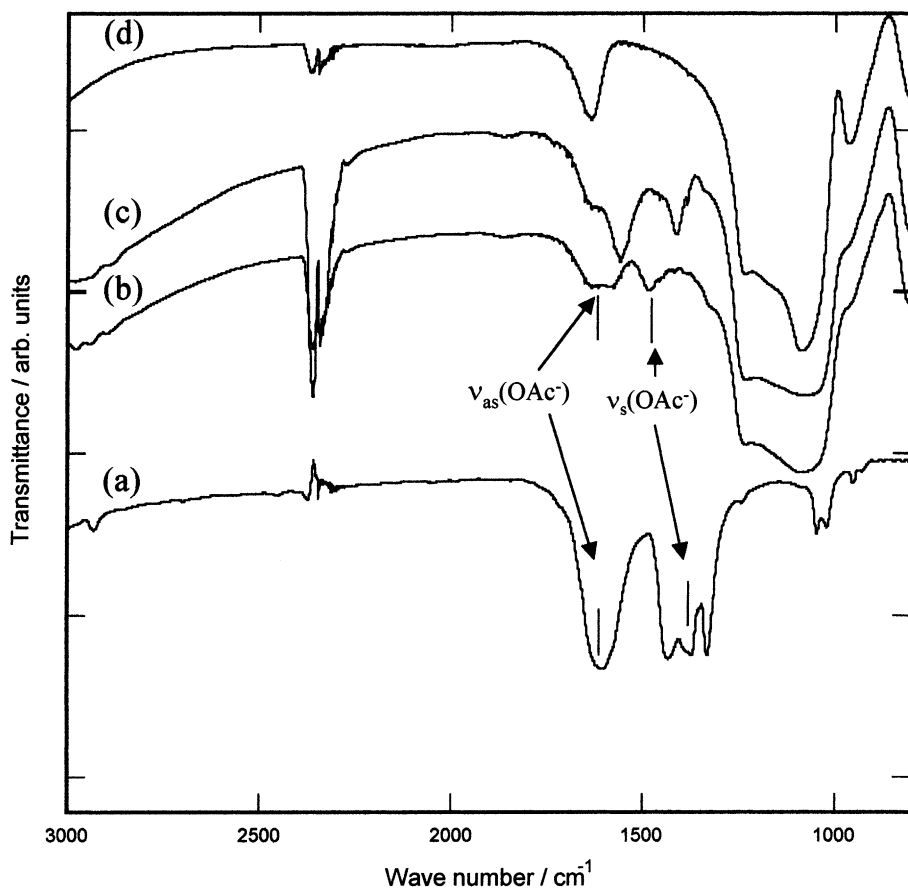


Fig. 3. IR spectra for (a) $[\text{Pd}(\text{OAc})_2]_3$, (b) Pd-AEAPSi/MCM, (c) AEAPSi/MCM, and (d) MCM-41. The peaks around 2400 cm^{-1} are attributed to CO_2 in the atmosphere.

Table 1

^{13}C CP MAS NMR spectra for the MCM-41 modified with AEAPSi and palladium acetate

Carbon ^a	Chemical shift δ (ppm)		
	AEAPSi/MCM	Pd-AEAPSi/MCM	Pd-AEAPSi/Me-MCM
C5	10.6	11.5	11.0
C6	17.2	17.4	17.4
C4, C7, C9	22.8 (C4)	22.1 (C4, C7)	22.1 (C4, C7, C9)
C3	40.2	46.8	46.8
C2	50.1	52.4	52.4
C1	58.4	59.2	59.2
C8	–	181.8	181.8
C10	–	–	–1.0

^a The numerical value of each carbon corresponds to that in Fig. 6.

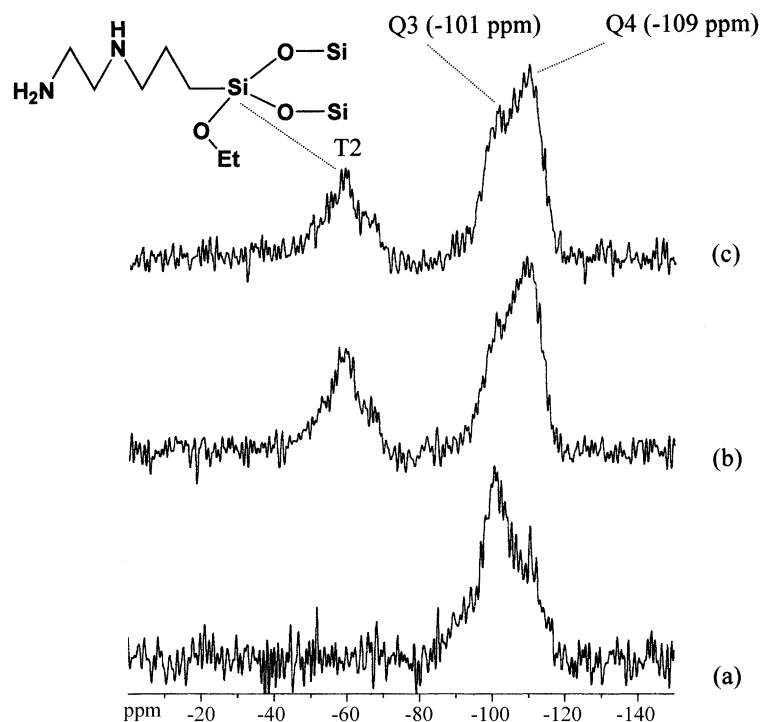


Fig. 4. ^{29}Si CP MAS NMR spectra for (a) MCM-41, (b) AEAPSi/MCM, and (c) Pd-AEAPSi/MCM.

(Fig. 5(a)) to **1** (Fig. 5(b)). This phenomenon clearly demonstrates the chelate coordination of AEAPSi to Pd(II) atom. The chelated structure of Pd(II)–AEAPSi complex moiety in the case of **2** is illustrated in Fig. 6, where acetate anions are present according to the FT-IR study described above.

3.2. Hydrogenation of dienes

Three reactants with two different C=C bonds were employed for the hydrogenation (Scheme 1). In order to evaluate the selectivity in the hydrogenation of the C=C bond near hydroxyl group against the C=C bond remote from hydroxyl group, the formation rate ratio (r_1/r_2) is summarized in Table 2, where r_1 is the formation rate of mono-olefin with C=C bond remote from hydroxyl group and r_2 is the formation rate of mono-olefin with C=C bond near hydroxyl group. The drastic change in the formation rate (r_1) was observed for the MCM-41 catalyst (**1**), i.e. **1** revealed noticeably higher reaction rate than **3** in the case of dienes

with OH group such as geraniol and linalool. On the contrary, the MCM-41 catalyst (**1**) exhibited remarkably low formation rate (r_1) of 1-*p*-menthene, while the SiO₂ catalyst (**3**) had still relatively high reaction rate for limonene. Another interesting observation should be mentioned for the MCM-41 catalyst, i.e. **1** preferably hydrogenated the C=C bond near OH group for geraniol. In the hydrogenation of linalool, both of **1** and **3** exclusively hydrogenated the C=C bond near OH group probably due to the sterically less hindered position (terminal). However, **1** showed 10 times larger activity than **3**. Regioselectivity was clearly observed for the MCM-41 catalyst.

We have speculated that the OH groups on the wall of MCM-41 involve the rate-determining step in the catalytic reaction. Thus, the remaining OH groups was calculated from the elemental analysis and the amount of OH groups on the original MCM-41 treated at 473 K. The amount of the unmodified OH groups was 7.7 mmol g⁻¹ for **1**, 6.5 mmol g⁻¹ for **2**, and 0.4 mmol g⁻¹ for **3**. It is clear that large amount

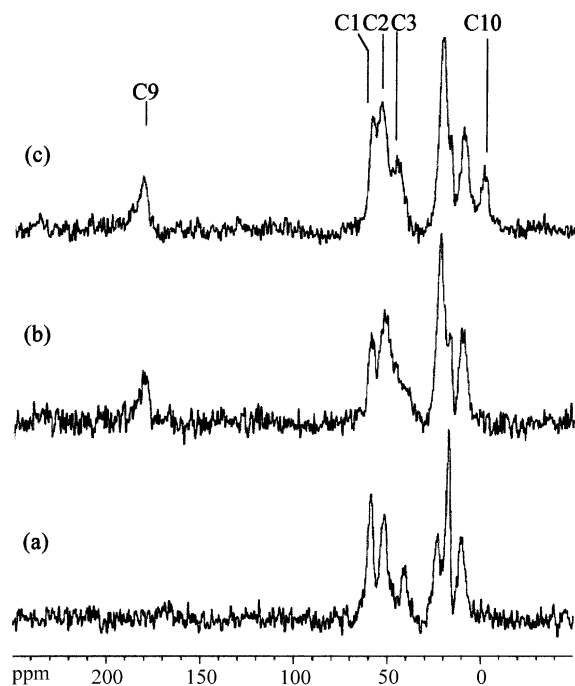


Fig. 5. ^{13}C CP MAS NMR spectra for (a) AEAPSi/MCM, (b) Pd-AEAPSi/MCM, and (c) Pd-AEAPSi/Me-MCM.

of OH groups are present on the surface of **1** and can readily interact with OH groups of geraniol and linalool in contrast to **3**. The activity of **2** for the hydrogenation of dienes was remarkably low compared with that of **1** even though only 16% of OH groups in **1** were capped by trimethylsilyl groups. It is specu-

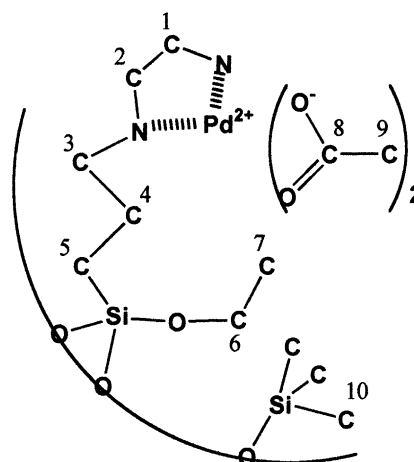


Fig. 6. Plausible structure of Pd-AEAPSi/Me-MCM (**2**).

lated that the low activity of **2** is due to the following two reasons: (a) the decrease of OH groups on the surface of MCM-41 and (b) the blocking of the neighboring OH groups by the bulky trimethylsilyl groups. The above results indicate that the capping of OH groups with even small amounts of bulky hydrophobic groups causes the drastic decrease in the catalytic activity. From these results, it can be concluded that the interaction between the surface OH and that of the substrates may enhance the activity and regioselectivity. For the SiO_2 catalyst, it is difficult to control the amount of organofunctional groups due to the small specific area.

Table 2

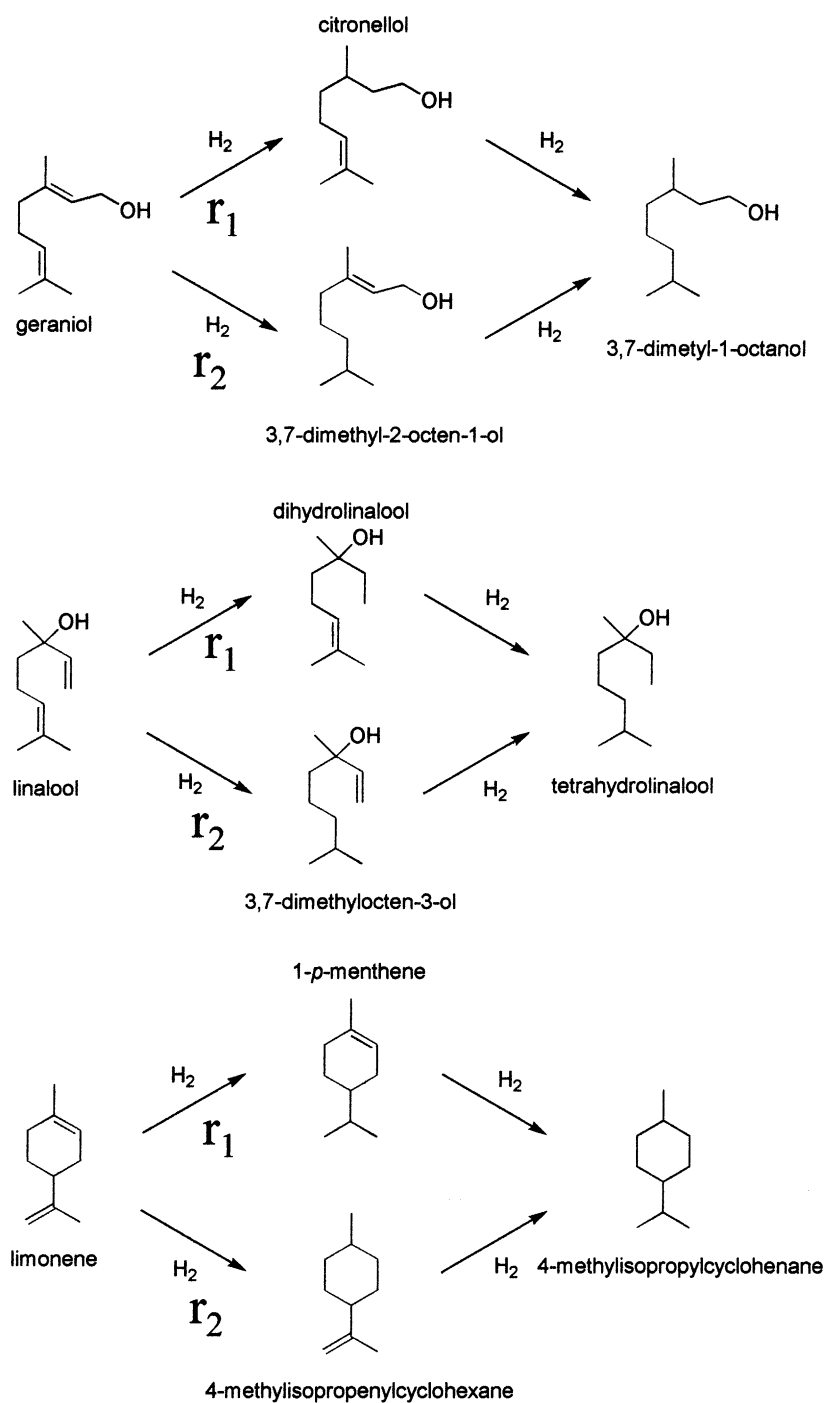
Hydrogenation of dienes catalyzed by Pd-AEAPSi/MCM (**1**) and Pd-AEAPSi/SiO₂ (**3**)^a

Run	Catalyst	Substrate	r_1^b (mol h ⁻¹ mol ⁻¹ Pd)	r_1/r_2^c
1	Pd-AEAPSi/MCM	Geraniol	68.0	2.86
2	Pd-AEAPSi/Me-MCM	Geraniol	2.81×10^{-3}	10.3
3	Pd-AEAPSi/SiO ₂	Geraniol	30.5	0.93
4	Pd-AEAPSi/MCM	Linalool	60.6	∞
5	Pd-AEAPSi/Me-MCM	Linalool	1.56×10^{-3}	∞
6	Pd-AEAPSi/SiO ₂	Linalool	6.19	∞
7	Pd-AEAPSi/MCM	Limonene	0.69	1.28
8	Pd-AEAPSi/Me-MCM	Limonene	0.33×10^{-3}	3.06
9	Pd-AEAPSi/SiO ₂	Limonene	30.7	1.55

^a Conditions: substrate, 1.0 mmol; catalyst, 5×10^{-3} mmol Pd; solvent, benzene 5 ml; H₂ pressure, 1.01×10^5 Pa; temperature, 303 K.

^b r_1 is the formation rate of mono-olefin where C=C bond near OH group is hydrogenated.

^c r_2 is the formation rate of mono-olefin where C=C bond remote from OH is hydrogenated.



Scheme 1. Hydrogenation of various dienes.

4. Conclusions

A MCM-41-supported palladium(II) complex catalyst was prepared by the functionalization with AEAPSi. The MCM-41-supported catalyst had a large amount of the unmodified OH groups in the mesopore as well as the AEAPSi functional group. The MCM-41-supported catalyst exhibited the high activity and the high regioselectivity in the hydrogenation of dienes with OH group.

Acknowledgements

This work was financed by the Ministry of Education, Culture, Sports, Science and Technology (Grant no. 09650972). We are grateful to Prof. Katsuyuki Ogura, Prof. Satoshi Sato, and Dr. Ryoji Takahashi for the use of the NMR spectrometer and for useful discussions.

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