Demethoxylation of hydrogenated derivatives of guaiacol without external hydrogen over platinum catalyst

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ABSTRACT

Selective deoxygenation of 2-methoxycyclohexanone, one of the hydrogenated by-products in guaiacol hydrodeoxygenation, to phenol, cyclohexanone and cyclohexanol was investigated over carbon supported noble metal catalysts without external H_2. Pt/C exhibited the best performance and the yield of target products reached 48% in water solvent at 493 K. This system can be applied to demethoxylation of 2-methoxycyclohexanol (49% yield). Demethoxylation of guaiacol is also possible under 0.1 MPa of H_2 (46% yield). The yield of the target demethoxylation products was strongly dependent on the catalyst amount; too much catalyst decreased the yield due to the over-reaction, while the reaction stopped before total conversion of intermediates when the catalyst amount was too small. Fresh Pt/C catalyst has activity in hydrodeoxygenation of the target products and the reusability test showed deactivation of Pt/C during reaction, suggesting that deactivation at appropriate reaction progress controlled by catalyst amount is a key to good yield of the target products. In contrast to other noble metal catalysts, Pt/C has activity in both dehydrogenation of cyclohexane ring and hydrogenolysis of C–O bond, both of which contributed to the conversion of 2-methoxycyclohexanone to target demethoxylation products, according to the reactions of cyclohexanone and cyclohexanol as model substrates.

1. Introduction

Amid the concern that petroleum, which is indispensable in modern society, will be depleted in the near future, biomass is attracting attention as a substitute for petroleum because biomass can be used not only for energy but also for production of chemicals [1–4]. Lignocellulose is inedible biomass, and one of its main components, lignin, possesses aromatic rings, so lignin is expected as renewable raw material of cyclic compounds [1,2]. Fast pyrolysis is a representative lignin conversion method and quickly produces liquid compounds (bio-oil) at high yield [1–3]. However, bio-oil contains more oxygen than petroleum. Therefore, researches on hydrodeoxygenation of bio-oil have been actively conducted using external H_2 [2,2,3,4]. In such researches, guaiacol (2-methoxyphenol) is widely used for substrate as a representative compound of bio-oil components [5–19] since guaiacol has three types of C–O bonds existing much in bio-oil: (1) C_{methyl}–$OC_{aromatic}$, (2) $C_{aromatic}$–OC_{methyl} and (3) $C_{aromatic}$–OH; order of bond energy: (1) < (2) < (3), Fig. 1 [3,4]. Typical hydrodeoxygenation systems such as NiMoS and CoMoS systems convert guaiacol to catechol (cutting at (1)) and phenol (cutting at (2)) first, and

next benzene (cutting at (3)) [6–8]. While phenol is more useful than others as a chemical feedstock because of the key compound for resin production, selective production of phenol is not easy; although catechol tends to be produced easily from guaiacol, selective conversion from catechol to phenol is difficult because catechol hydrodeoxygenation to phenol and phenol hydrodeoxygenation to benzene dissociate similar type of C–O bond (3). Severe reaction conditions (typically $T > 523$ K, $P_{H2} > 4$ MPa [5–7]) and sulfur contamination (in the case of sulfide catalysts) are another problems [2,7]. Many researchers have tried to develop the new catalytic system for selective production of phenol and its hydrogenated products (cyclohexanone and cyclohexanol used for nylon production as KA oil) from guaiacol [8,6–19]. Recently, our group reported that Ru/C + MgO [8] and Ru-MnOx/C [9] are effective demethoxylation catalysts, giving cyclohexanol in 81% yield at lower temperature and H_2 pressure (433 K, 1.5 MPa, Fig. 1). In this system, we obtained methanol as C1 product derived from the methoxy group in 86% yield, which is more useful than methane. There is one problem in this system that the ring-hydrogenation products, mainly 2-methoxycyclohexanol, are formed as by-products; hydrogenation tends to proceed easily at lower reaction temperature because
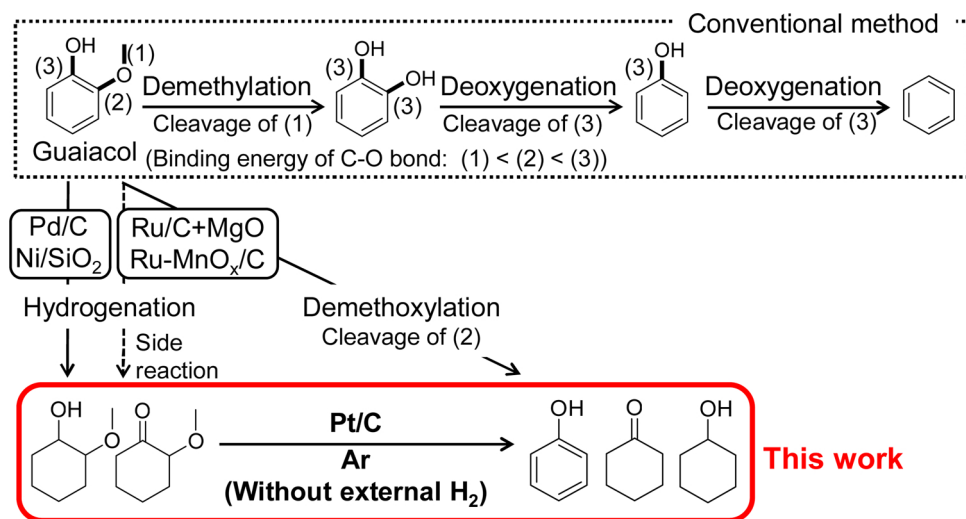
Fig. 1. Guaiacol deoxygenation using external H$_2$ and target reaction of this work.

of exothermic reaction. The demand of 2-methoxycyclohexanol is much lower than that of phenol or the hydrogenated products (cyclohexanone and cyclohexanol). On the other hand, 2-methoxycyclohexanol can be produced in high yield (> 99%) with a suitable catalyst by guaiacol hydrogenation (Fig. 1) [20,21]. Hydrogenation of guaiacol to 2-methoxycyclohexanone is also possible [22,23]. Moreover, production of cyclohexanones from cyclohexanols has been established [24–28]. Therefore, conversion of 2-methoxycyclohexanol or 2-methoxycyclohexanone to phenol or the hydrogenated products is desirable to be developed; however, these reactions have not been focused as the main target reactions in the literature.

In this paper, we investigated the conversion of hydrogenated derivatives of guaiacol (2-methoxycylohexanone and 2-methoxycyclohexanol, Fig. 1). The target products in this work are phenol, cyclohexanone and cyclohexanol. Since the conversion of 2-methoxycyclohexanol or 2-methoxycyclohexanone to phenol does not consume H$_2$, rather produces H$_2$, in reaction formulas (Eqs. (1) and (2)), we carried out the reaction without expensive external H$_2$. We explored these reactions with various noble metal catalysts. We found that Pt/C catalyst can convert 2-methoxycyclohexanone and 2-methoxycyclohexanol to target products. The catalytic behavior of each noble metal was also investigated in detail.

(1)

(2)
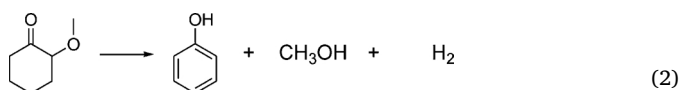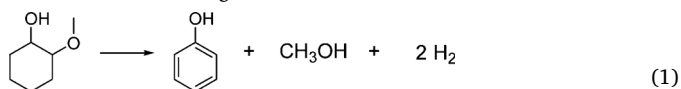
2. Experimental section

2.1. Catalysts and activity tests

Commercially available carbon-supported noble metal catalysts (FUJIFILM Wako Pure Chemical Corporation, Pt, Rh, Pd and Ru: 5 wt%) were used. The dispersion of metal particle on the catalysts was determined by CO adsorption and XRD, and they are shown in Table 1. The XRD patterns are shown in Fig. S1. Catalysts were reduced in H$_2$ flow (> 99.99% H$_2$, 30 mL min^{-1}) at 473 K for 30 min in a glass tube just before use. Activity tests were performed in a 190 mL stainless steel autoclave. The reduced catalyst (0.1 g), 2-methoxycyclohexaone (Tokyo Chemical Industry Co., Ltd., 5 mmol, > 95%), water (20 mL) and a magnetic spinner were introduced into an autoclave under N$_2$ atmosphere in order to avoid exposing the pre-reduced catalyst to air.

Table 1
Dispersion of noble metal catalysts in this study.

Catalyst	Dispersion /%		Particle size (XRD) /nm
	CO adsorption	XRD	
Pt/C	15	17	6.7
Rh/C	24	14	8.0
Pd/C	7.5	6.8	17
Ru/C	35	–[a]	–[a]

[a] XRD peaks due to Ru metal were not observed.

After sealing the reactor, the inner gas was purged by flushing five times with 3 MPa of high purity Ar (99.9999%) to remove residual H$_2$ used in the catalyst reduction completely. The autoclave was then heated to the reaction temperature for about 30 min and the temperature was monitored using a thermocouple inserted in the autoclave. When the temperature reached the target one, the time was defined as "0 h". During this experiment, stirring rate was fixed at 300 rpm. After an appropriate reaction time, the reactor was cooled down and the gases were collected in a gas bag. The autoclave contents were diluted with 2-propanol (FUJIFILM Wako Pure Chemical Corporation, > 99.7%) containing 2-methoxyethanol (FUJIFILM Wako Pure Chemical Corporation, > 99%) as an internal standard. The mixed solution was transferred to a vial, while the catalyst was separated by centrifugation and filtration. Analyses were conducted with GC and GC–MS. The used columns were MS-13X for H$_2$, Porapak N for methane, carbon dioxide and carbon monoxide, Rtx®-1 PONA for other gas components and catechol and benzene in liquid, and TC-WAX for other liquid components. Conversions, selectivity and carbon balance (C.B.) were calculated on carbon basis (Eqs. (3)–(5)). Amount of "others" included the products that cannot be detected by GC, and the amount was calculated by the difference between the carbon amounts of introduced substrate and the total carbon amounts of the detected products.

$$\text{Con version}(\%) = \left(1 - \frac{\text{Amount of detected 2- methoxycyclohexanone [mol-C]}}{\text{Amount of introduced 2- methoxycyclohexanone [mol-C]}}\right) \times 100 \quad (3)$$

$$\text{Selectively}(\%) = \left(\frac{\text{Amount of each product [mol-C]}}{\text{Amount of converted substrate [mol-C]}}\right) \times 100 \quad (4)$$

Table 2

Reaction of 2-methoxycyclohexanone over various catalysts.

Catalyst	Blank			Pt/C			Rh/C			Pd/C			Ru/C		
Reaction time /h	1	3	24	1	3	24	1	3	24	1	3	24	1	3	24
Conversion /%	14	23	75	97	99	100	69	91	98	50	82	97	49	75	99
Carbon balance/%	104	98	93	90	82	81	95	98	88	96	99	96	97	94	80
H_2 amount /mmol (observed)	0.0	0.0	0.2	0.8	1.1	1.3	0.5	0.7	1.3	2.1	2.1	1.3	0.1	0.4	3.1
(calculated)[a]	0.0	0.0	0.1	0.5	1.0	1.5	0.2	0.3	1.0	1.8	2.0	0.7	−0.2	−0.1	3.7
C1 amount /mmol (observed)	0.5	1.0	2.9	2.8	3.3	4.1	1.9	2.5	4.0	0.6	1.1	2.0	1.4	2.0	3.1
(calculated)[b]	0.4	0.9	3.2	2.6	3.2	3.8	1.6	2.3	3.3	0.3	1.2	2.0	1.1	1.8	1.9
Selectivity /%															
Demethoxylation															
phenol	< 1	< 1	< 1	16	14	13	16	18	9	1	1	6	1	1	2
cyclohexanone	0	0	< 1	10	14	19	4	4	8	2	3	8	4	5	2
cyclohexanol	0	0	0	5	10	16	< 1	1	6	< 1	1	5	< 1	1	6
Hydrogenation															
2-methoxycyclohexanol[c]	0	0	1 (0.4)	28 (0.4)	11 (0.4)	2 (0.4)	34 (0.5)	40 (0.5)	20 (0.4)	26 (0.6)	33 (0.6)	35 (0.4)	32 (0.4)	38 (0.4)	34 (0.4)
Dehydrogenation															
guaiacol	0	0	0	3	1	< 1	11	6	< 1	49	39	18	0	< 1	0
Demethylation															
2-hydroxycyclohexanone	84	78	74	2	2	< 1	8	5	2	9	5	2	39	26	5
1,2-cyclohexanediol[c]	0	0	1 (0.0)	3 (0.1)	5 (0.3)	1 (0.2)	4 (0.3)	5 (0.3)	4 (0.1)	0	4 (0.4)	5 (0.1)	4 (0.2)	11 (0.4)	9 (0.7)
catechol	0	0	0	8	5	1	1	3	0	0	5	3	0	1	0
Deoxygenation															
cyclohexane	0	0	0	1	2	5	0	< 1	2	0	< 1	< 1	0	0	2
benzene	0	0	0	4	6	5	1	5	17	< 1	< 1	1	< 1	< 1	1
C1															
methanol	16	15	11	3	3	1	8	7	9	3	4	5	8	6	1
CH_4	0	0	0	3	3	5	< 1	< 1	< 1	< 1	0	< 1	0	< 1	1
CO_2	0	< 1	< 1	2	4	6	< 1	1	3	< 1	< 1	2	1	2	7
Others	0	7	12	12	21	26	12	6	20	10	5	11	9	9	31
(cyclopentanone[d])	0	0	0	0	< 1	4	3	3	5	0	3	4	0	0	3

Reaction conditions: 2-methoxycyclohexanone 5 mmol, water 20 mL, M/C 0.1 g, P_{Ar} 1 MPa, 493 K.

[a] Calculated formation amount of H_2: (phenol) – (cyclohexanone) – (cyclohexanol) × 2 – (2-methoxycyclohexanol) + (guaiacol) × 2 + (catechol) × 2 – (1,2-cyclohexanediol) – (cyclohexane) × 3 + (cyclopentanone) × 2 + (cyclopentanol) – (n-hexane) × 4 + (anisole) – (methoxycyclohexane) × 2 – (methane) + ((CO_2 production amount) – (cyclopentanone) – (cyclopentanol)) × 3.

[b] Calculated formation amount of C1: (Demethoxylation products) + (Total deoxygenation products) + (Demethylation products) + (Decarboxylation products (cyclopentanone + cyclopentanol)).

[c] The *cis/(cis + trans)* is shown in the parentheses.

[d] C5 products are included in "Others".

Carbon balance(C.B.)(%)

$$= \left(\frac{\text{Amount of all detected compounds[mol-C]}}{\text{Amount of introduced 2-methoxycyclohexanone[mol-C]}} \right) \times 100$$

(5)

The method of catalyst reuse was as follows. First, we conducted normal activity test with fresh catalyst. Next, we collected all the reaction mixture using 2-propanol as a dilution solvent. The used catalyst was recovered by centrifugation and washed with 30 mL of water (3 times). These recovery and washing processes were operated in glove bag to avoid exposure of the catalyst to air. About 90% of the catalyst was recovered in this method and the obtained catalysts were used for next reaction.

Reactions of other substrates were carried out by using guaiacol (Tokyo Chemical Industry Co., Ltd., > 98%), 2-hydroxycyclohexanone dimer (Sigma-Aldrich, > 97%), *trans*-1,2-cyclohexanediol (Tokyo Chemical Industry Co., Ltd., > 99%), catechol (Tokyo Chemical Industry Co., Ltd., > 99%), phenol (FUJIFILM Wako Pure Chemical Corporation, > 99%), cyclohexanone (Tokyo Chemical Industry Co., Ltd., > 99%), cyclohexanol (FUJIFILM Wako Pure Chemical Corporation, > 98%), and methanol (Kanto Chemical Co. Inc., > 99.8%). 2-Methoxycyclohexanol was obtained by hydrogenation of guaiacol (reaction conditions: guaiacol 5 g, tetrahydrofuran (FUJIFILM Wako Pure Chemical Corporation, > 99.5%) 20 mL, Pd/C 1 g, 438 K, 72 h) and tetrahydrofuran used as a solvent was removed by distillation. The purity of the obtained 2-methoxycyclohexanol was 98% and the *cis/(cis + trans)* ratio was 0.33 on GC area basis.

2.2. Characterization

Catalysts used for conversion of 2-methoxycyclohexanone were recovered as the samples of the characterization measurements by the following method. First, we conducted the activity tests under standard reaction conditions (2-methoxycyclohexanone 5 mmol, catalyst 0.1 g, water 20 mL, P_{Ar} 1 MPa, 493 K, 24 h). Next, we collected all the reaction mixture using 2-propanol as a dilution solvent. The catalysts were collected by centrifugation and heated at 383 K for 12 h.

X-ray diffraction (XRD) patterns were recorded by a Rigaku MiniFlex 600 diffractometer. Cu Kα (λ = 0.154 nm, 40 kV, 15 mA) radiation was used as an X-ray source. The samples were reduced under H_2 flow (30 mL min^{-1}) for 30 min at 473 K and passivated by 1%O_2/He flow (10 mL min^{-1}) for 30 min at room temperature before measurement for fresh catalysts.

Transmission electron microscope (TEM) images were taken with HITACHI HD-2700. Fresh catalysts after reduction under H_2 (30 mL min^{-1}) at 473 K were used as samples for the TEM observation. Supersonic waves dispersed the sample in ethanol. The samples were placed on Cu microgrids for TEM under air atmosphere. Average particle size was calculated by $\Sigma n_i d_i^3 / \Sigma n_i d_i^2$ (d_i: particle size, n_i: number of particles with size d_i).

Inductively-coupled plasma atomic emission spectrometry (ICP-AES, ThermoFisher iCAP6500) was carried out to measure the Pt amount in the solution after reaction and filtration.

The amount of CO chemisorption was measured by MicrotracBEL BELCAT II by a pulse adsorption method. The catalyst (0.05 g) in the measurement cell was reduced under flowing H_2 (30 mL min^{-1}) at

473 K for 30 min. After cooling to room temperature, 10% CO/He was introduced as pulse gas at 308 K. In the calculation of the dispersion of noble metals, one surface metal atom was assumed to adsorb one CO molecule (CO/M = 1).

TG-DTA was carried out with Rigaku Thermo Plus EVO-II instrument under N_2 flow (100 mL min^{-1}) using 0.01 g of sample at a heating rate of 10 K min^{-1}. Fresh catalysts were measured after heating at 473 K for 0.5 h under N_2 flow (30 mL^{-1}) to remove water contained in the catalysts.

3. Results and discussion

3.1. Optimization of catalyst and reaction conditions

The reactions of 2-methoxycyclohexanone were carried out at 493 K in water solvent under Ar atmosphere (Table 2). Without catalyst, 2-methoxycyclohexanone was converted slowly (14% conversion at 1 h), and 2-hydroxycyclohexanone was mainly produced. As a C1 product, methanol was produced almost stoichiometrically with 2-hydroxycyclohexanone, which means that 2-hydroxycyclohexanone was produced by hydrolysis of 2-methoxycyclohexanone (Eq. (6)). The target products (demethoxylation products: phenol, cyclohexanone and cyclohexanol) were hardly produced.
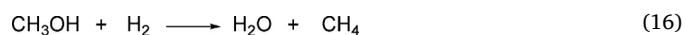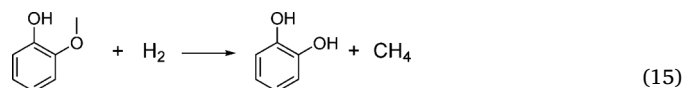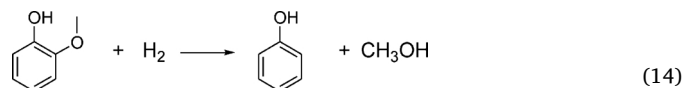
$$\text{2-methoxycyclohexanone} + H_2O \longrightarrow \text{2-hydroxycyclohexanone} + CH_3OH \tag{6}$$
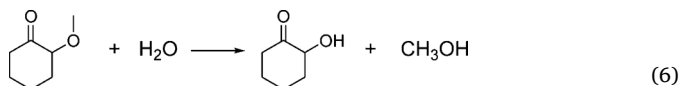
In the presence of noble metal catalysts, conversion was increased, and the selectivity was also changed. Formation of H_2 was observed, and possible formation route of H_2 included dehydrogenation of cyclohexane ring (Eqs. (7) and (8)) and aqueous phase reforming (APR) of methanol (eq. (9)).

$$\text{2-methoxycyclohexanone} \longrightarrow \text{guaiacol} + 2\,H_2 \tag{7}$$

$$\text{2-hydroxycyclohexanone} \longrightarrow \text{catechol} + 2\,H_2 \tag{8}$$

$$\text{2-hydroxycyclohexanone} \longrightarrow \left(\ \text{1,2-cyclohexanedione} + H_2 \longrightarrow \text{cyclopentanone} + CO + H_2\ \right) \xrightarrow{+H_2O} \text{cyclopentanone} + CO_2 + 2\,H_2 \tag{17}$$

$$CH_3OH + H_2O \longrightarrow CO_2 + 3\,H_2 \tag{9}$$
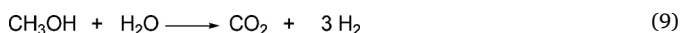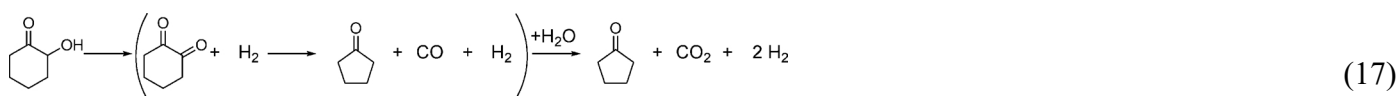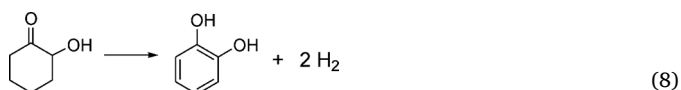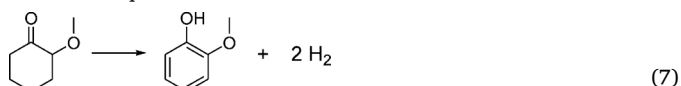
When Pt/C was used for the reaction, 2-methoxycyclohexanone was quickly reacted and conversion reached 97% at 1 h. The target demethoxylation products were observed significantly, and the total yield reached 48% (phenol 13%, cyclohexanone 19%, cyclohexanol 16%) at 24 h. Other identified products were 2-methoxycyclohexanol (a hydrogenation product, Eq. (10)), guaiacol (a dehydrogenation product, eq. 7) 2-hydroxycyclohexanone and its hydrogenation/dehydrogenation products (demethylation products, Eqs. (6), (11) and (8)), benzene and cyclohexane (total deoxygenation products, Eqs. (12) and (13)) and C1 products (methanol, methane and carbon dioxide). Anisol, methoxycyclohexane, C2-C5 hydrocarbons, *n*-hexane and cyclopentanone were detected a little and they were included in others. However, most of "others" were the undetected products by GC.

$$\text{2-methoxycyclohexanone} + H_2 \longrightarrow \text{2-methoxycyclohexanol} \tag{10}$$

$$\text{2-hydroxycyclohexanone} + H_2 \longrightarrow \text{1,2-cyclohexanediol} \tag{11}$$

$$\text{phenol} + H_2 \longrightarrow \text{benzene} + H_2O \tag{12}$$

$$\text{cyclohexanol} + H_2 \longrightarrow \text{cyclohexane} + H_2O \tag{13}$$
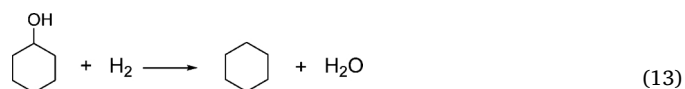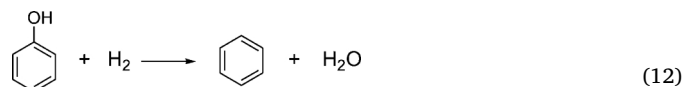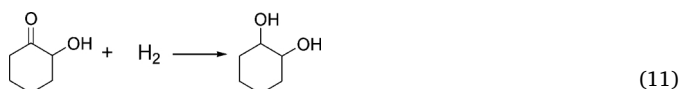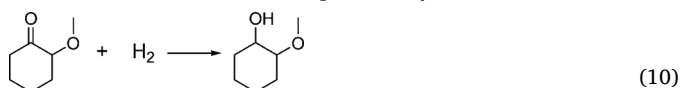
2-Methoxycyclohexanol, the hydrogenation product (Eq. (10)), was produced with 28% selectivity at 1 h and the amount was decreased after 1 h. Demethylation products (2-hydroxycyclohexanone (Eq. (6)),1,2-cyclohexanediol (Eq. (11)) and catechol (Eq. (8))) were also detected at first and then decreased. Considering that hydrolysis of 2-methoxycyclohexanone to 2-hydroxycyclohexanone and methanol (Eq. (6)) can proceed without a catalyst as described above, most demethylation products were probably formed via hydrolysis. Amounts of guaiacol (dehydrogenation product, Eq. (7)) and total deoxygenation products (benzene (Eq. (12)) and cyclohexane (Eq. (13))) were not large. Among C1 products, methanol was produced by hydrolysis (Eq. (6)); however, hydrogenolysis of R—OCH$_3$ bond (demethoxylation) can also give methanol (Eq. (14)). Hydrogenolysis of R—OCH$_3$ bond is a preferable reaction because it gives target demethoxylation products. Methane can be formed by hydrogenolysis of RO—CH$_3$ bond (Eqs. (15) and (16)) or hydrocracking of hydrocarbons. Carbon dioxide can be produced by aqueous phase reforming (APR) of methanol (Eq. (9)) or decarbonylation + water gas shift (Eq. (17)) [32]. Water gas shift reaction is another source of H_2.

$$\text{guaiacol} + H_2 \longrightarrow \text{phenol} + CH_3OH \tag{14}$$

$$\text{guaiacol} + H_2 \longrightarrow \text{catechol} + CH_4 \tag{15}$$

$$CH_3OH + H_2 \longrightarrow H_2O + CH_4 \tag{16}$$

After all, there may be many reaction routes in this 2-methoxycyclohexanone conversion; later we discuss the reaction scheme in detail. Here, the production amount of H_2 and sum of C1 was calculated based on Eqs. (6)–(17), and the values were compared with the actually observed ones (Table 2). The observed amount almost agreed with the calculated one for both H_2 and C1 in most runs. Next to Pt/C, Rh/C promoted 2-methoxycyclohexanone conversion and production of target demethoxylation products production. Pd/C and Ru/C gave much smaller amount of target demethoxylation products. When Pd/C was used, the main products were guaiacol (Eq. (7)) and 2-methoxycyclohexanol (Eq. (10)). Guaiacol/2-methoxycyclohexanol ratio was high at 1 h, and then decreased at longer reaction time. This trend indicates that Pd/C promoted dehydrogenation of 2-methoxycyclohexanone to guaiacol (Eq. (7)) and the hydrogenation of another 2-methoxycyclohexanone with produced H_2 (Eq. (10)). In the case of Ru/C, guaiacol was hardly produced, and the main products were 2-hydroxycyclohexanone (Eq. (6)) and 2-methoxycyclohexanol (Eq. (10)). 2-Hydroxycyclohexanone was probably produced by non-catalyzed hydrolysis (Eq. (6)). Ru/C seems to have little activity in dehydrogenation of 2-methoxycyclohexanone (Eq. (7)) but have activity in hydrogenation (Eqs. (10) and (11)) and APR (Eq. (9)). Regarding the production amount of H_2 and sum of C1 at long reaction time (24 h) over Ru/C, the observed C1 amount was larger than the calculated one and the observed H_2 amount was smaller. This difference is probably due to the hydrocracking. Anyway, Pt/C showed the highest selectivity to target
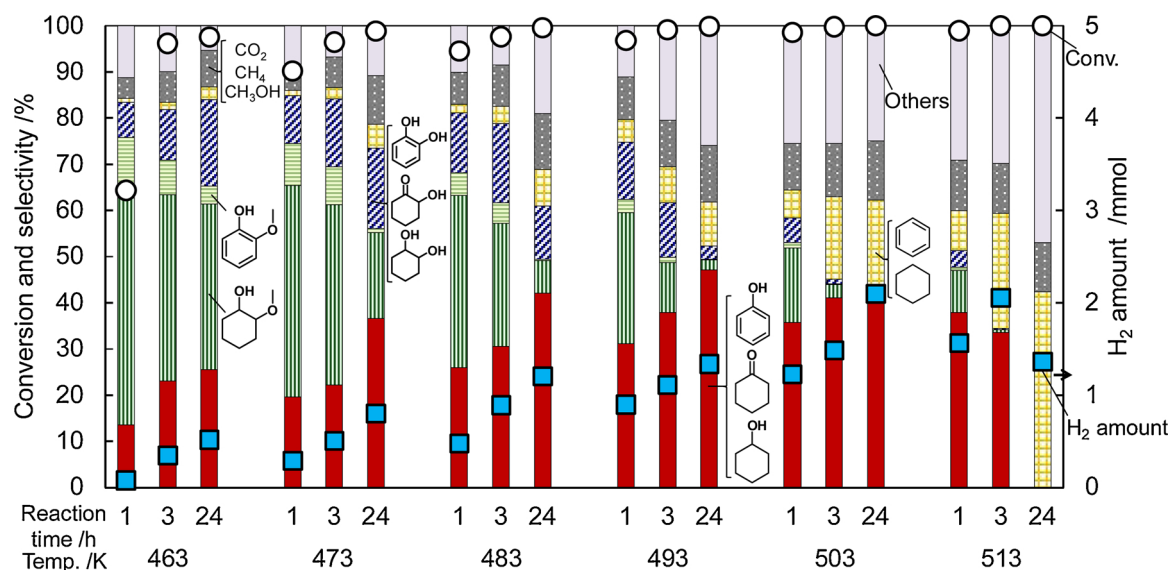
Fig. 2. Effect of reaction temperature on the reaction of 2-methoxycyclohexanone over Pt/C.
Reaction conditions: 2-methoxycyclohexanone 5 mmol, water 20 mL, Pt/C 0.1 g, P_{Ar} 1 MPa. Detailed data are shown in Table S1.

demethoxylation products, and we selected Pt/C as catalyst in the following study.

The effect of reaction temperature was investigated in the range of 463–513 K using Pt/C catalyst (Fig. 2). The detailed data are shown in Table S1. At low temperature such as 463 K, the main product is 2-methoxycyclohexanol, where H_2 can be supplied by the formation of guaiacol or phenol. At 483 or 493 K, the yield of target products become maximum (ca. 50%) at 24 h and the yield of 2-methoxycyclohexanol is rather small. At higher temperatures (503 and 513 K), the formation of total deoxygenation products was significant and the yield of the target demethoxylation products was lower than that at 493 K. The yield of "others" including undetected products by GC increased with higher reaction temperature and longer reaction time. Produced catechol and phenol, highly dehydrogenated compounds, may polymerize at high temperature [8,29–31]. As a result, we selected 493 K as the reaction temperature.

The effect of solvents was tested by using water, ethanol, n-dode-cane and toluene as well as none (solventless condition) (Table S2). Water solvent is by far better solvent to obtain target demethoxylation products. In the case of ethanol solvent, large amount of C1 products and H_2 were produced from ethanol and the main identified product from substrate was 2-methoxycyclohexanol, probably because of the large supply of H_2 from the solvent. In the cases of n-dodecane solvent, toluene solvent and solventless condition, the main products were 2-methoxycyclohexanol and guaiacol, and the produced H_2 was smaller than the case of water solvent. As mentioned before, H_2 was supplied to the system via dehydrogenation (Eqs. (7) and (8)) and APR of methanol (Eq. (9)) mainly, and APR of methanol only proceeds in water solvent. Because H_2 was needed for target demethoxylation, the smaller amount of H_2 in the non-water solvent systems except ethanol can limit the formation of the target demethoxylation products. Carbon monoxide which is detected in non-water solvent, especially ethanol, is another factor for suppressing the formation of the target products because carbon monoxide easily covers to the Pt metal surface. In water solvent, however, active Pt site can be regenerated by the conversion of adsorbed carbon monoxide and water to carbon dioxide and H_2, i.e. water gas shift reaction.

Fig. 3 shows the reaction results using different amount of Pt/C (0.02-0.20 g). The detailed data are shown in Table S3. When we used smaller amount of Pt/C, 2-methoxycyclohexanone reacted very slowly, and the yield of the target demethoxylation products did not increase even in 48 h reaction. On the other hand, when a large amount of Pt/C

was used, further deoxygenation of target demethoxylation products to cyclic hydrocarbons (i.e. over-reaction) significantly proceeded and decreased the yield of target products. In short, the reaction stopped before total conversion of intermediates with too small amount of catalyst, and too much catalyst promotes over-reaction of target products. Deactivation of the catalyst seems to be a key factor for this phenomenon: smaller the amount of catalyst is, faster deactivation occurs and reaction stops. Deactivation was investigated in the next section. Anyway, 0.1 g of Pt/C was found to be the best catalyst amount for this reaction. To summarize this section, the best catalyst is Pt/C and the best conditions are 493 K, water solvent and 0.1 g of catalyst (with 5 mmol 2-methoxycyclohexanone substrate.)

3.2. Performance of Pt/C

Fig. 4 shows the time course of reaction of 2-methoxycyclohexanone over 0.1 g of Pt/C at 493 K in water solvent. The detailed data are shown in Table S4. Conversion at 0 h means the reaction during the heating from room temperature to the target one which took about 30 min. The conversion increased rapidly to 99% and selectivity of target demethoxylation products also increased rapidly during 3 h. From 3 h to 24 h, the selectivity increased gradually, and highest yield of 48% (phenol 13%, cyclohexanone 19%, cyclohexanol 16%) was obtained at 24 h. Deoxygenation of target products and methanol to hydrocarbons proceeded slowly after 24 h.

Next, Pt/C catalyst was applied to related substrates (2-methoxycyclohexanol and guaiacol) and the results are shown in Table 3 and Table S5. In the case of guaiacol, small amount of H_2 was added to the gas phase because it is difficult to supply H_2, which is needed for hydrogenolysis, by dehydrogenation of guaiacol. The target demethoxylation products were obtained from both substrates in similar total yields: phenol 1%, cyclohexanone 15% and cyclohexanol 33% from 2-methoxycyclohexanol (Entry 4); phenol 41%, cyclohexanone 4% and cyclohexanol 1% from guaiacol (Entry 6). Pt/C is effective to demethoxylation of both guaiacol and hydrogenated guaiacol. The highest yield of target demethoxylation products from 2-methoxycyclohexanol was obtained at shorter time than the case of 2-methoxycyclohexanone (Entries 2 and 4). This trend suggests that 2-methoxycyclohexanol is an intermediate of demethoxylation. The reaction route will be discussed in detail in later section.

The reuse experiments were conducted to check the stability of Pt/C (Fig. 5 and Table S6). The used Pt/C was collected, washed with water
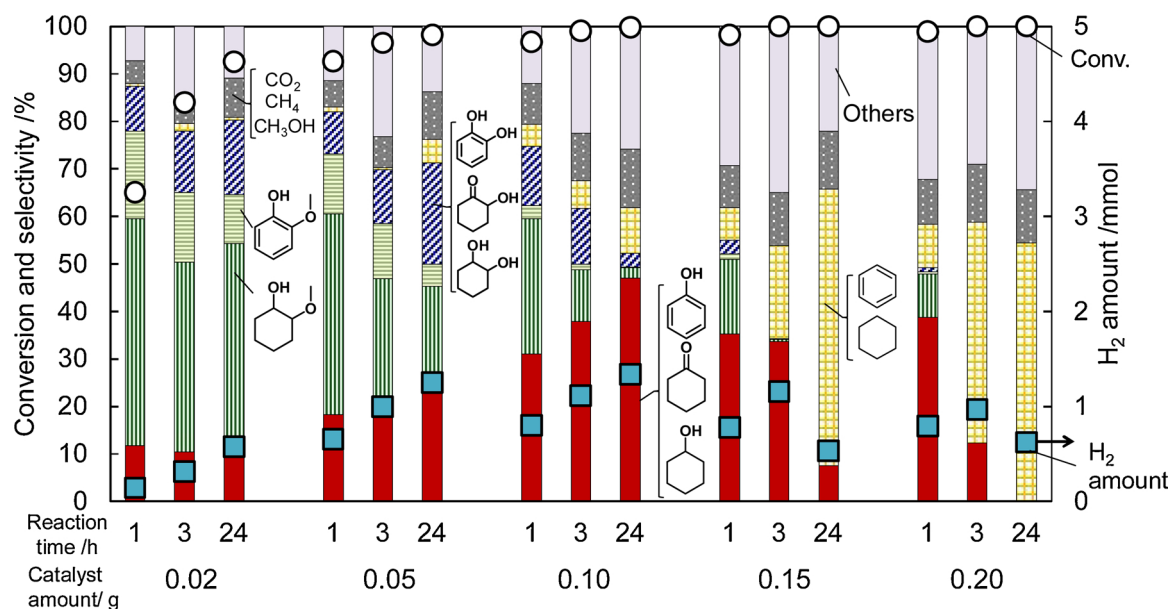
Fig. 3. Effect of catalyst amount on the reaction of 2-methoxycyclohexanone over Pt/C.
Reaction conditions: 2-methoxycyclohexanone 5 mmol, water 20 mL, Pt/C 0.02-0.2 g, P_{Ar} 1 MPa, 493 K. Detailed data are shown in Table S3.

and used for next reaction without exposure to air. The used catalyst showed good conversion, but selectivity of target demethoxylation products much decreased at first reuse, and further slightly decreased in subsequent reuses. In this reuse method, some amount of catalyst was lost during the recovery process, and 0.07 g catalyst remained after third reuse from initial amount of 0.1 g. About 10% of catalyst can be lost each use. Here, the performance of the reused catalyst is compared with the data for the effect of catalyst amount (Fig. 3). The performance in first reuse (ca. 20% yield of demethoxylation products) was similar to that of 0.05 g Pt/C, and that in third reuse (12% yield) was comparable to that of 0.02 g Pt/C. The comparison indicates that the catalyst was deactivated during the reaction.

The deactivation behavior and selectivity change were investigated in detail. Highly deactivated Pt/C gave much amount of 2-methoxycyclohexanol (Fig. 5). 2-Methoxycyclohexanol is the main product in very short reaction time under the standard reaction conditions using fresh catalyst (Fig. 4). In the reactions with a smaller amount of Pt/C (Fig. 3), the main product was also 2-methoxycyclohexanol and the reaction almost stopped at around 3 h. In the case of large Pt/C amount, cyclic hydrocarbons can be produced at 3 h. These data indicate that deoxygenation activity of Pt/C was lost during use (deactivation). Even in the standard run (0.1 g of Pt/C) the deactivation in deoxygenation proceeded to some extent. Moderate deactivation seems to be vital to obtain target demethoxylation products.

3.3. Characterization

Pt/C catalyst was characterized by XRD, TEM and CO adsorption. XRD patterns of Pt/C after reduction, after 24 h reaction and after third reuse are shown in Fig. 6. The sharp peaks at 39.8°, 46.3° and 67.5° can be assigned to Pt°. Pt particle size was estimated to be 6.7, 7.2 and 7.1 nm for the catalysts after reduction (a), after 24 h reaction (b) and after third reuse (c), respectively, by using Scherrer's equation. These values were similar, which indicates that the deactivation of Pt/C was not due to the change of particle size. The almost constant particle size during catalytic use was also confirmed by TEM analysis (Figs. 7 and S2): the average Pt particle size was 6.4 nm after reduction (a) and 6.7 nm after reaction (b). These values agreed with the XRD data.

ICP-AES showed that the leached amount of Pt to liquid phase during the 24 h reaction was < 0.1%, which indicates that leaching of

Pt is negligible.

The amount of CO chemisorption was measured to count the number of active surface metal atoms (Table 4). Pt dispersion of Pt/C after reduction was 12% while dispersion of Pt/C after reaction was 2%. On the basis that the particle size of Pt was almost constant during the reaction, the deactivation can be due to the coverage of Pt surface with some carbonaceous species such as polymeric by-products. Highly dehydrogenated compounds such as catechol, phenol and diketones can polymerize at high temperature [8,29–31]. The deposition of organic substance on the catalyst was investigated with TG-DTA. Although it is difficult to measure the amount of deposit accurately because the activated carbon support loses some weight by thermal decomposition, the weight loss of the used Pt/C was clearly larger than that of fresh Pt/C above 500 K (Fig. S3).

These characterization results can make the reason for the deactivation of Pt/C clear. The results of XRD and TEM indicate that the size of Pt particle size was unchanged during the reaction. So, aggregation is not the reason of the deactivation. ICP-AES showed leaching did not occur. On the other hand, the results of CO adsorption and TG-DTA show that organic compounds are deposited on the surface of used Pt/C. Carbon supported platinum catalyst is difficult to regenerate by calcination because of combustibility of carbon support. Catalysts with higher resistance to the deactivation and regeneration ability should be developed in future.

3.4. Formation route of the target products

To clarify the reaction route from 2-methoxycyclohexanone to target products (Fig. 8), we carried out the reaction tests of various related substrates (Table 5 (C7 compounds) and 6 (C6 compounds)). In order to discuss the selectivity in detail, the reaction time was set to be very short (0 h; only the heating to 493 K). The heating time was about 30 min for all runs. In 2-methoxycyclohexanone reaction, H_2 was absent at first but it was produced over time to about 1.3 mmol. Then, another type of initial gas conditions was applied to these experiments in order to evaluate the actual reactivity: a little amount of H_2 (0.1 MPa = ca. 7 mmol) in 0.9 MPa of Ar, in addition to Ar atmosphere (1.0 MPa) as usual.

When 2-methoxycyclohexanone was used as a substrate, the main products under Ar atmosphere were 2-methoxycyclohexanol, 2-
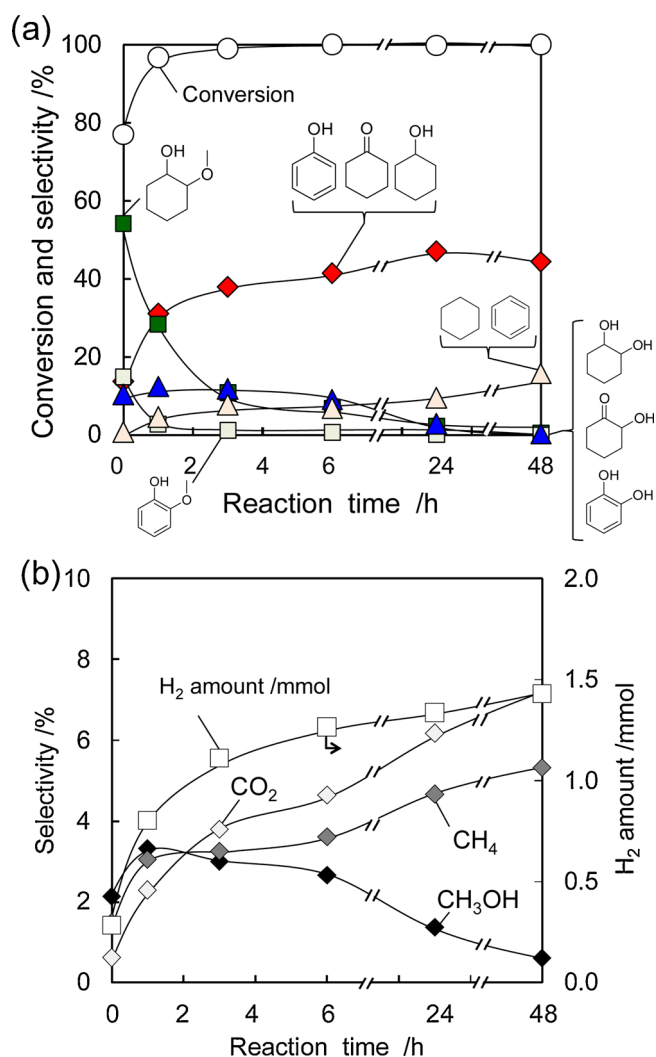
Fig. 4. Time course of reaction of 2-methoxycyclohexanone over Pt/C. (a) cyclic products, (b) C1 products and H_2.
Reaction conditions: 2-methoxycyclohexanone 5 mmol, water 20 mL, Pt/C 0.1 g, P_{Ar} 1 MPa, 493 K. Detailed data are shown in Table S4.
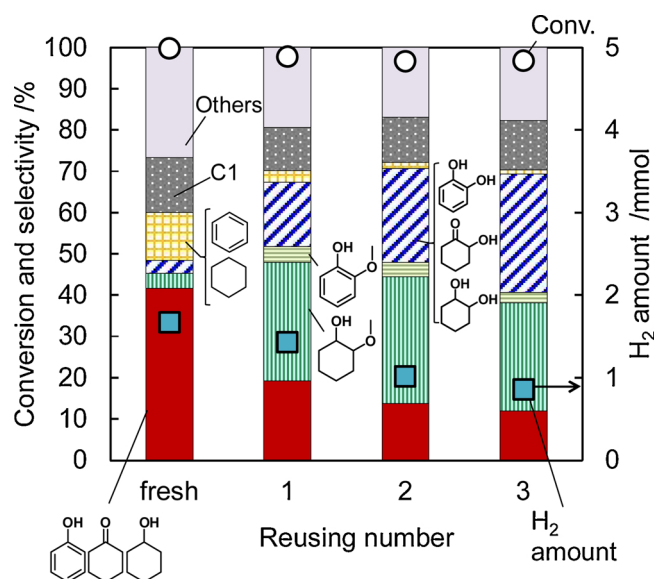

Fig. 5. Reuse of Pt/C in 2-methoxycyclohexanone conversion.
Reaction conditions: 2-methoxycyclohexanone 5 mmol, water 20 mL, Pt/C 0.1 g (fresh), P_{Ar} 1 MPa. 493 K. 24 h. Detailed data are shown are Table S6.

hydroxycyclohexanone and guaiacol (selectivities were 31%, 25% and 18%, respectively) (Table 5, Entry 1). 2-Hydroxycyclohexanone can be produced in two routes: (1) hydrogenolysis of C–O (Eq. (18)) or (2) hydrolysis (Eq. (6)).

$$\text{(structure)} + H_2 \longrightarrow \text{(structure)}OH + CH_4$$

(18)
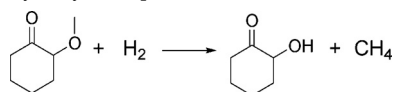
In the former route, methane is produced as C1 product while methanol is produced in the latter route. In fact, methanol was detected mainly and methane was hardly detected, which indicates that hydrolysis was the main route in 2-hydroxycyclohexanone production. Saying more about 2-hydroxycyclohexanone, it was produced under blank conditions along with methanol (Table 2). From these data, we can say that the first step of 2-methoxycyclohexanone conversion can be dehydrogenation and hydrolysis, and the produced H_2 by dehydrogenation was quickly consumed in hydrogenation.

Table 3
Reaction of guaiacol derivatives over Pt/C.

Entry	Substrate	Time /h	C.B.[c] /%	Conv. /%	Selectivity[d] /%							CH$_3$OH	CH$_4$	CO$_2$	H$_2$ amount /mmol
1		1	86	97	30	27 (0.4)	3	–	12 (0.1)	4	3	3	2	0.8
2		24	81	100	48	2 (0.4)	< 1	–	3 (0.2)	10	1	5	6	1.3
3[a]		1	90	40	38	- (0.4)	1	6	10 (0.0)	4	2	3	6	2.2[e]
4[a]		9	79	97	51	- (0.5)	0	< 1	0	12	1	3	7	0.0[e]
5[b]		1	80	94	43	1 (0.4)	–	1	17 (0.6)	5	4	6	1	0.7
6[b]		3	78	99	46	0	–	0	6 (-)	11	2	7	2	0.4

493 K. Full list of product compounds is shown in Table S4.
[a] Isomeric mixture (*cis*/(*cis* + *trans*) = 0.33) was used as substrates.
[b] Reaction conditions: substrate 5 mmol, water 20 mL, Pt/C 0.1 g, P_{Ar} 1.0 MPa or P_{total} 1.0 MPa (P_{H2} 0.1 MPa (7 mmol) + P_{Ar} 0.9 MPa).
[c] Carbon balance.
[d] The *cis*/(*cis* + *trans*) is shown in the parenthese.
[e] Included initial H_2.

Fig. 6. XRD patterns of Pt/C catalysts.
(a) After reduction, (b) after reaction (Table 2, Pt/C, 24 h reaction) and (c) after reuse for 3 time (Fig. 5).

Table 4
Characterization results of used Pt/C.

State	CO adsorption amount /$cm^3 g_{cat}^{-1}$	Dispersion /%		Particle size /nm	
		CO adsorption	XRD	XRD	TEM
After reduction	0.81	15	17	6.7	6.4
After reaction[a]	0.11	2.0	16	7.2	6.7

[a] Reaction conditions: 2-methoxycyclohexanone 5 mmol, water 20 mL, Pt/C 0.1 g, P_{Ar} 1 MPa, 493 K, 24 h (shown in Table 2).
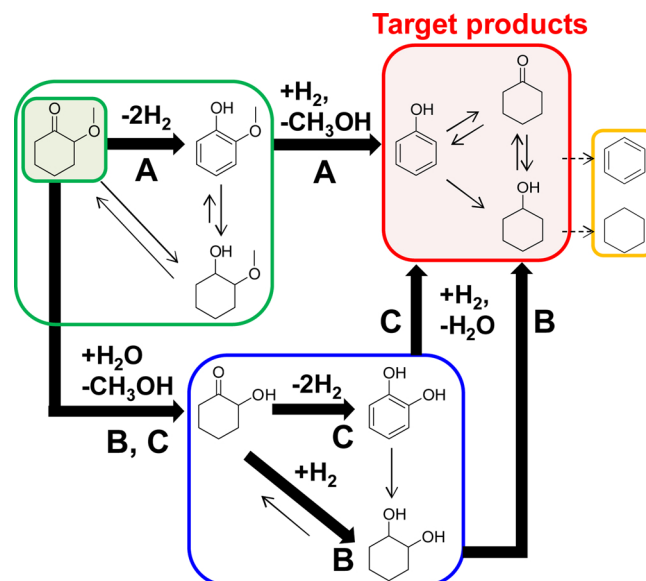

Fig. 8. Proposed reaction pathways of demethoxylation of 2-methoxycyclohexanone over Pt/C.

(19)

Fig. 7. TEM images of Pt/C catalysts.
(a) After reduction, (b) after reaction (Table 2, Pt/C, 24 h reaction). The histograms are shown in Fig. S2.

2-Methoxycyclohexanol conversion was slow and main products were guaiacol and 2-methoxycyclohexanone under Ar atmosphere (Table 5, Entry 3). Under H_2 containing conditions, little products were detected (Table 5, Entry 4). Only dehydrogenation seems to proceed from 2-methoxycyclohexanol. When guaiacol was used as a substrate, phenol and 2-methoxycyclohexanol were mainly produced under H_2 containing conditions (Table 5, Entry 6). Without initial H_2, the conversion of guaiacol was low (Table 5, Entry 5). From these data, one route from 2-methoxycyclohexanone to C6 products can be 2-methoxycyclohexanone → guaiacol → phenol (Eq. (19)).

Another route to C6 products is hydrolysis of 2-methoxycyclohexanone to 2-hydroxycyclohexanone which proceeds slowly in homogenous aqueous phase as discussed in Section 3.1.

Next, we investigated the route to target products (phenol, cyclohexanone and cyclohexanol) via 2-hydroxycyclohexanone. When 2-hydroxycyclohexanone was used as a substrate (Table 6, Entries 1 and 2), it was mainly converted to 1,2-cyclohexanediol and catechol which are hydrogenation (Eq. (11)) and dehydrogenation products (Eq. (8)), respectively. 1,2-Cyclohexanediol was converted to 2-hydroxycyclohexanone (a dehydrogenation product) and cyclohexanol (a deoxygenation product) (Table 6, Entry 3 and 4). Catechol was converted to 1,2-cyclohexanediol (a hydrogenation product) and phenol (a deoxygenation product) under H_2 containing conditions (Entry 6). From these data, the reaction routes from 2-methoxycyclohexanone to target products (phenol, cyclohexanone and cyclohexanol) include: 2-methoxycyclohexanone → 2-hydroxycyclohexanone → 1,2-cyclohexanediol → cyclohexanol (route B; hydrolysis + hydrogenation + deoxygenation, Eq. (20)) and 2-methoxycyclohexanone → 2-hydroxycyclohexanone → catechol → phenol (route C; hydrolysis + dehydrogenation + deoxygenation, Eq. (21)), as well as 2-methoxycyclohexanone → guaiacol → phenol route (route A; dehydrogenation + demethoxylation, Eq. (19)) as shown above (Fig. 8).

Table 5
Reaction of C7 intermediates over Pt/C.

Entry	Substrate	Gas condition	Conv.	Selectivity[b] /%												H₂ amount	C. B.[d]
				OH,O	OH,O	O,O	O,OH	OH	O	OH	(bicyclic)	CH_3OH	CH_4	CO_2		
1		Ar	15	31 (0.5)	18	–	25	4	5	0	< 1	8	< 1	1	0.1	102
2		H₂ + Ar	20	53 (0.6)	7	–	17	3	3	1	< 1	6	< 1	0	6.2[c]	100
3[a]		Ar	4	- (0.2)	17	60	1	5	6	5	1	1	2	1	0.4	110
4[a]		H₂ + Ar	< 1	- (0.3)	0	48	0	0	5	30	< 1	0	1	1	8.4[c]	105
5		Ar	4	0	–	0	0	0	0	0	0	0	0	0	0.0	96
6		H₂ + Ar	12	30 (0.6)	–	2	0	37	2	6	2	9	2	0	5.9[c]	95

Reaction conditions: substrate 5 mmol, water 20 mL, Pt/C 0.02 g, P_{Ar} 1.0 MPa or P_{total} 1.0 MPa (P_{H2} 0.1 MPa (7 mmol) + P_{Ar} 0.9 MPa), 493 K, 0 h.
[a] Isomeric mixture (*cis*/(*cis* + *trans*) = 0.3) was used as a substrate.
[b] The *cis*/(*cis* + *trans*) is shown in the parentheses.
[c] Including initial H₂ (7 mmol).
[d] Carbon balance.

$$\text{(20)}$$

$$\text{(21)}$$
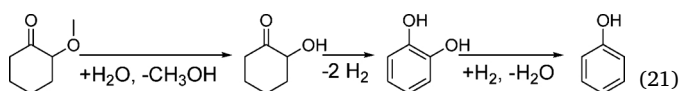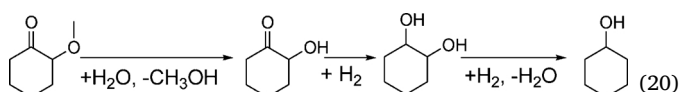
Table 7 shows the results of reactions of target products. In the case of phenol, the main reactions are hydrogenation to cyclohexanol and cyclohexanone, and in addition, C–O cleavage to benzene also proceeded (Table 7, Entry 1, Eq. (12)). Cyclohexanone gave phenol and cyclohexanol, and C–O cleavage products were hardly produced. Cyclohexanol gave C–O cleavage product (cyclohexane, Eq. (13)) as well as cyclohexanone when H₂ was present (Table 7, Entry 5). These data show that cyclic hydrocarbons such as benzene and cyclohexane are produced from phenol and cyclohexanol and not directly from cyclohexanone.

Now we discuss the formation of each C1 product. All the reaction routes (A (Eq. (19)), B (Eq. (20)) and C (Eq. (21)) produce methanol as C1 product. However methane and carbon dioxide were actually also produced in the reaction of 2-methoxycyclohexanone (Fig. 4(b)). The amount of methanol increased at first, but decreased gradually. Meanwhile, yields of carbon dioxide and methane remained to increase with time.

There are two formation route of carbon dioxide. One is

decarbonylation from C6 or C7 compounds (Eq. (17)). In fact, cyclopentanone, which is reported to be decarbonylation product of guaiacol [32–34], was detected a little (Table 2); however, the yield of cyclopentanone and its related compounds was much lower than the carbon dioxide yield in mol. The other route is aqueous phase reforming (APR) of methanol (Eq. (9)). In APR reaction, methanol and water are converted to carbon dioxide and H₂, and this reaction has been indeed reported to be catalyzed by Pt at 493 K [35–41]. In our system, water solvent was used in this 2-methoxycyclohexanone conversion. Besides, the time course data (Fig. 4 (b)) show that the decrease of methanol can be correlated with increase of carbon dioxide and H₂. Table 8 shows reactions using methanol as substrate. Carbon dioxide was produced much, in fact, especially in the case without H₂ (Entries 2 and 4). Therefore, the formation of carbon dioxide was mainly due to APR of methanol and the contribution of decarbonylation of C6 and C7 compounds was small.

For the formation of methane, there are three routes: demethylation (Eqs. (15) and (18)), hydrogenolysis of methanol (Eq. (16)) and cracking. As discussed above, the main reaction routes from 2-methoxycyclohexanone to demethoxylation products do not involve demethylation. Cracking produces methane from C6 ring moiety of the substrate, and when cracking is involved significantly, observed C1 amount will shift toward larger than converted methoxy group amount. As shown in Table 2, observed C1 amount was similar to that calculated by converted methoxy group over Pt/C catalyst, indicating that

Table 6
Reaction of C6 intermediates over Pt/C.

Entry	Substrate	Gas Conditions	Conv. /%	Selectivity[b] /%								H₂ amount /mmol	C. B.[d] /%
				O,OH	OH,OH	OH,OH	OH	O	OH	CH_3OH	CO_2		
1		Ar	69	–	55 (0.4)	32	9	3	< 1	0	0	0.0	97
2		H₂ + Ar	91	–	88 (0.4)	3	2	4	2	0	< 1	4.6[c]	84
3[a]		Ar	41	61	- (0.2)	6	9	13	8	1	< 1	1.1	97
4[a]		7H₂ + Ar	40	27	- (0.3)	0	0	14	53	1	< 1	7.5[c]	97
5		Ar	4	0	37 (1.0)	–	0	0	0	0	0	0.0	101
6		H₂ + Ar	30	10	31 (0.4)	–	37	10	8	0	< 1	6.7[c]	102

Reaction conditions: substrate 5 mmol, water 20 mL, Pt/C 0.02 g, P_{Ar} 1.0 MPa or P_{total} 1.0 MPa (P_{H2} 0.1 MPa + P_{Ar} 0.9 MPa), 493 K, 0 h.
[a] *trans*-1,2-Cyclohexanodiol was used as a substrate.
[b] The *cis*/(*cis* + *trans*) is shown in the parentheses.
[c] Including initial H₂ (7 mmol).
[d] Carbon balance.

Table 7
Reaction of target products over Pt/C.

Entry	Substrate	Gas condition	Conv. /%	Selectivity /%					H_2 amount /mmol	C.B.[b] /%
				OH (phenol)	O (cyclohexanone)	OH (cyclohexanol)	(benzene)	(cyclohexane)		
1	OH (phenol)	H_2 + Ar	70	–	33	44	12	3	4.6[a]	97
2	O (cyclohexanone)	Ar	52	41	–	55	2	2	0.4	88
3		H_2 + Ar	65	9	–	84	3	4	6.1[a]	90
4	OH (cyclohexanol)	Ar	14	2	84	–	< 1	2	0.5	108
5		H_2 + Ar	16	0	52	–	0	42	9.7[a]	93

Reaction conditions : substrate 5 mmol, water 20 mL, Pt/C 0.02 g, P_{Ar} 1.0 MPa or P_{total} 1.0 MPa (P_{H2} 0.1 MPa + P_{Ar} 0.9 MPa), 493 K, 0 h.
 [a] Including initial H_2 (7 mmol).
  [b] Carbon balance.

Table 8
Reaction of methanol over Pt/C.

Entry	Gas condition	Time /h	Conv. /%	Yield /%		H_2 amount /mmol	C.B.[b] /%
				CH$_4$	CO$_2$		
1	H_2 + Ar	1	25	0	6	6.5[a]	81
2	Ar	1	30	0	20		91
3	H_2 + Ar	24	80	2	51	15.5[a]	74
4	Ar	24	85	2	51	9.1	68

Reaction conditions : methanol 5 mmol, water 20 mL, Pt/C 0.1 g, P_{Ar} 1.0 MPa or P_{total} 1.0 MPa (P_{H2} 0.1 MPa + P_{Ar} 0.9 MPa), 493 K, 1 or 24 h.
  [a] Including initial H_2 (7 mmol).
  [b] Carbon balance.

cracking can be a minor route. As for hydrogenolysis of methanol in methane formation (Eq. (16)), methane was rarely observed in methanol conversion even in long time reaction as shown in Table 8. This indicates that hydrogenolysis of free methanol hardly proceeds. The involvement of methanation of carbon dioxide can be also ruled out since the selectivity to methane from methanol under H_2 + Ar was very small at long reaction time and that to carbon dioxide was high (Table 8, Entry 3). Then, the reaction results of related substrates (Tables 3 and 5) are closely re-considered. High selectivity to methane was observed when guaiacol was the substrate at longer reaction time (1 and 3 h; Table 3, Entries 5 and 6). On the other hand, selectivity to methane was much lower at short reaction time (0 h; Table 5, Entries 5 and 6). Considering that the reaction temperature for 0 h reaction was practically lower than longer reaction time runs, methane can be formed with demethylation of guaiacol at high reaction temperature; i.e. hydrogenolysis of adsorbed methanol produced by demethoxylation can proceed before the desorption [42].

3.5. Comparison with other noble metal catalysts in reactivity of related substrates

Model reactions over other noble metal catalysts were conducted in order to know the difference among noble metals in the performance for 2-methoxycyclohexanone conversion more clearly. In 2-methoxycyclohexanone conversion, dehydrogenation of cyclohexane ring and demethoxylation are revealed to be the key reactions. From the result of noble metals screening (Section 3.1, Table 2), Pt/C and Rh/C are good for demethoxylation, Pd/C is only active for dehydrogenation/hydrogenation (less active for C–O cleavage) and Ru/C has poor activity for dehydrogenation of cyclohexane ring. These data, however, were complex because many compounds were produced and the character of each noble metal was not clear. Here, the catalytic ability of each noble metal in dehydrogenation of cyclohexane ring and hydrogenolysis of
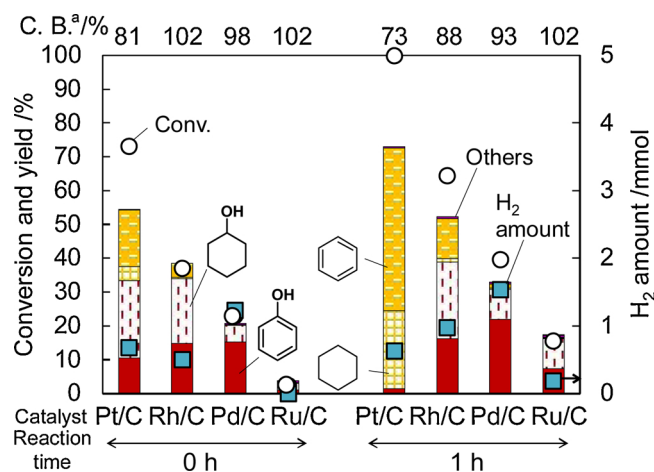

Fig. 9. Reaction of cyclohexanone under Ar atmosphere.
Reaction conditions: cyclohexanone 5 mmol, water 20 mL, M/C 0.1 g, P_{Ar} 1 MPa. Detailed data are shown are Table S7. [a]Carbon balance.

C–O bond was investigated by the reaction of cyclohexanone to phenol (under Ar atmosphere) and that of cyclohexanol to cyclohexane (under H_2 + Ar atmosphere).

As shown in Fig. 9 (and Table S7), cyclohexanone was converted to phenol over Pt/C, Rh/C and Pd/C but hardly converted over Ru/C. This trend clearly shows that Ru/C had little activity in dehydrogenation of cyclohexane ring. Pt/C catalyzed cyclohexanone conversion well, but the produced H_2 and phenol reacted additionally to give cyclohexanol (hydrogenation) or benzene (hydrogenolysis). Formation of benzene (and cyclohexane) was smaller over Rh/C and was negligible over Pd/C.

When cyclohexanol was used as substrate under H_2 + Ar atmosphere (Fig. 10 and Table S8), cyclohexane was produced over Pt/C, Rh/C and Ru/C by C–O hydrogenolysis, but Pd/C rarely catalyzes hydrogenolysis of cyclohexanol to cyclohexane, which indicates clearly that Pd/C had less activity for hydrogenolysis of C–O bond. The order of the ability of C–O cleavage is Pt/C > Rh/C > Ru/C > Pd/C. Ru/C gave some amount of C2-C5 hydrocarbons (cracking). The activity of Ru/C in cracking was also evident in the rise of C1 balance to C1 products in the conversion of 2-methoxycyclohexanone (Table 2). Ru° species was reported to have high catalytic activity for cracking [43,44]. We have reported the ability of (noble metal)/C catalysts in C–O cleavage of glycerol at 393 K: Ru/C and Rh/C showed significant activity; however, Pt/C and Pd/C showed very low activity [45]. The trend is due to the much high temperature in the present case (493 K).

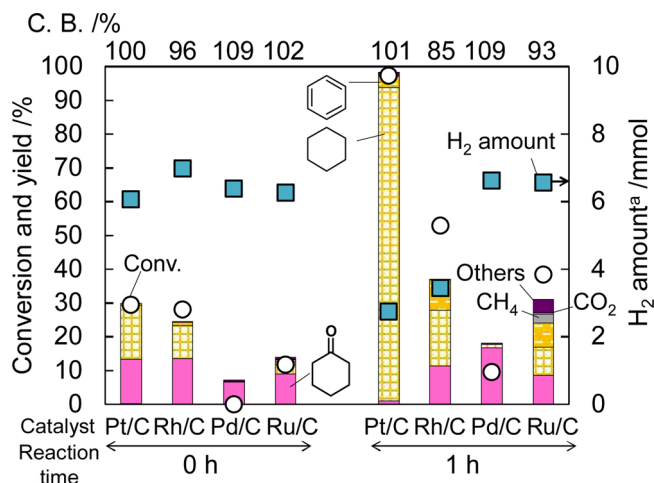After all, Pt/C and Rh/C have activity in dehydrogenation of

Fig. 10. Reaction of cyclohexanol under H_2 + Ar atmosphere. Reaction conditions: cyclohexanol 5 mmol, water 20 mL, M/C 0.1 g, P_{H2} 0.1 MPa (7 mmol) + P_{Ar} 0.9 MPa. [a]Included initial H_2. Detailed data are shown are Table S8. [a]Carbon balance.

cyclohexane ring and hydrogenolysis of C−O bond. High activity of both reactions can be connected to good yield of target products (phenol, cyclohexanone and cyclohexanol) from 2-methoxycyclohexanone. Ru/C has C–O hydrogenolysis activity, but the poor activity in dehydrogenation of cyclohexane ring inhibits the formation of target products. Pd/C has less activity for hydrogenolysis of C−O bond.

4. Conclusions

2-Methoxycyclohexanone conversion to phenol, cyclohexanone and cyclohexanol without external H_2 was achieved by using Pt/C catalyst (0.1 g) and water solvent at 493 K with 5 mmol of 2-methoxycyclohexanone. The yield of target demethoxylation products reached 48% (phenol: 13%, cyclohexanone: 19% and cyclohexanol: 16%). Pt/C can facilitate both dehydrogenation of cyclohexane ring to aromatic ring and hydrogenolysis of C−O bond well, both of which are important for this reaction. 2-Methoxycyclohexanol can be also used as a substrate over Pt/C, giving 49% yield of target products. Demethoxylation of guaiacol with a small amount of H_2 (0.1 MPa at room temperature) to target products over Pt/C also proceeds (46% yield). Produced target products are kept and are not converted to benzene or cyclohexane via over-hydrodeoxygenation in long time reaction under the appropriate conditions. This suppression of over-hydrodeoxygenation is related to deactivation of catalyst; too much amount of catalyst leads to formation of benzene and cyclohexane. Three routes exist in this reaction (Fig. 8): (A) dehydrogenation to guaiacol + demethoxylation (Eq. 19), (B) hydrolysis to 2-hydroxycyclohexanone + hydrogenation to 1,2-cyclohexanediol + deoxygenation (Eq. 20) and (C) hydrolysis + dehydrogenation to catechol + deoxygenation (Eq. (21)). H_2 was supplied by both dehydrogenation of cyclohexane ring and aqueous phase reforming of produced methanol.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.03.019.

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