## Hydrodechlorination of *para*-Chloroacetophenone in Water/Ethanol Mixtures Using Organosilane-grafted Rh/SiO<sub>2</sub> Catalysts

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Hydrodechlorination was performed in water/ethanol mixtures over organosilane-grafted Rh/SiO<sub>2</sub> catalysts. All catalysts in which organosilanes were covalently connected onto silica supports promoted hydrodechlorination, which may be attributed to the presence of a hydrophobic zone on the catalyst surfaces. Additional aromatic  $\pi$ - $\pi$  interactions between the 4tolylsilyl substituent in the catalyst and the aromatic ring of *p*-chloroacetophenone may be important for the activity of the most active Rh/SiO<sub>2</sub>-TS catalyst that was produced via silylation using trichloro-4-tolylsilane.

Catalytic hydrodechlorination (HDC) is expected to solve problems related to harmful organic chlorinated compounds by limiting the degradation costs and preventing the production of additional toxic by-products such as dioxins.<sup>1-3</sup> In particular, HDC systems using water-based solvents are now desirable to reduce the use of large amounts of organic solvents that release volatile or persistent organic substances into the environment. HDC attempts at dechlorinating chlorinated aromatics in water have involved directly modifying the surface functionalities of the catalyst support to increase the reactivity. These attempts include (i) using silicone polymers to coat Pd/Al<sub>2</sub>O<sub>3</sub> catalysts and/or fill their pores<sup>4-6</sup> and (ii) immobilizing Pd nanoparticles in amphiphilic copolymers.<sup>7–10</sup> In addition, when grafted to certain organosilyl derivatives, Pt/SiO2 was found to preferably catalyze the HDC of para-chloroacetophenone (CLAP) in a water/ethanol mixture.<sup>11</sup> Although all grafted Pt/SiO<sub>2</sub> catalysts showed the excellent HDC performance of CLAP, one drawback was found, i.e., the production of unpreferable by-product ethyl  $\alpha$ -methylbenzyl ether, which was caused by dehydration between ethanol in the solvent mixture and  $\alpha$ -methylbenzyl alcohol as one of the HDC products. To prevent the undesirable by-product formation, we developed new silica-supported rhodium catalysts. Here, the modified Rh/SiO<sub>2</sub> catalysts were found to promote this reaction in a water/ethanol mixed solvent, shedding light on the effect of organosilyl grafting reagents on silica supports.

The bare Rh/SiO<sub>2</sub> catalyst was prepared on silica by an ionexchange reaction (Supporting Information). Next, its surface was subjected to silylation using five types of organosilane reagents: butylchlorodimethylsilane (BDMS), chlorodimethyloctylsilane (DMOS), chlorodimethyloctadecylsilane (DMODS), trichloro-4-tolylsilane (TS), and chloro(3,3,4,4,5,5,6,6,7,7,8,8,8tridecafluorooctyl)dimethylsilane (TDFDMS). Silylation produced Rh/SiO<sub>2</sub>–BDMS, Rh/SiO<sub>2</sub>–DMOS, Rh/SiO<sub>2</sub>–DMODS, Rh/SiO<sub>2</sub>–TS, and Rh/SiO<sub>2</sub>–TDFDMS catalysts.

The catalyst (40 mg) in a 77-mL glass test tube was placed into a magnetically stirred batch autoclave, as described

previously,12 and reduced under a hydrogen flow of  $100 \text{ mL min}^{-1}$  under 0.5 MPa for 60 min at 473 K. Water (35 mL) was injected into the test tube at 373 K, and CLAP (2 mmol) in ethanol (5 mL) was introduced using 0.8 MPa hydrogen. The pressure was adjusted to 1.0 MPa, allowing the reaction to start. The products were periodically extracted from the reaction mixture through a pressure-resistant valve and quantitatively analyzed using a gas chromatograph (Shimadzu Co., GC-14A) equipped with a flame ionization detector. Toluene was used as an internal standard. The products were identified by gas chromatography-mass spectroscopy (Shimadzu Co., GCMS5050QA). The Brunauer-Emmett-Teller (BET) specific and metal surface areas were determined using a BELCAT-B instrument (Bell Japan Inc.). Elemental analyses were carried out using a JM10 apparatus (J-SCIENCE LAB Co., Ltd.). Thermogravimetry-differential thermal analysis (TG-DTA) profiles were acquired using a TG-DTA 2020s apparatus (MAC Science Co., Ltd.). Metal loading was measured by inductively coupled plasma mass spectrometry (Shimadzu Co., ICPS-8100) performed at Sumika Chemical Analysis, Ltd. Except for the BET specific surface area, all measurements were conducted under the same conditions as previously reported.<sup>11</sup>

Figure 1 shows the conversion and product yields for the HDC of CLAP, which was performed in the presence of the bare Rh/SiO<sub>2</sub> catalyst in 7:1 (v/v) water/ethanol for 60 min at 373 K. The detected products consisted of  $\alpha$ -methylbenzyl alcohol (MBA, 13% yield), ethylbenzene (EB, 9% yield), 4-chloro- $\alpha$ -methylbenzyl alcohol (CMBA, 3% yield), acetophenone (AP, 2% yield), 1-cyclohexylethanol (CHEL, 2% yield), acetylcyclohexane (ACH, 1% yield), ethylcyclohexane (ECH, 1% yield),



**Figure 1.** Product yields for the HDC reaction of CLAP over  $Rh/SiO_2$  catalyst in 7:1 (v/v) water/ethanol using 1 MPa hydrogen for 60 min at 373 K.



**Figure 2.** Product yields for the HDC reaction of CLAP over  $Rh/SiO_2$ -TS in 7:1 (v/v) water/ethanol using 1 MPa hydrogen for 60 min at 373 K.

(1-cyclohexenyl)-1-ethanol (CHEEL, <1% yield), and 4-chlorostyrene (CS, <1% yield) (Table S1, Supporting Information). Therefore, the reaction conversion and the overall dechlorinated product yield amounted to 31% and 28%, where the reaction conversion sums all product yields up, and the overall dechlorinated product yield means total amounts of the other products except for both CMBA and CS. Compared with the bare and modified Pt/SiO<sub>2</sub> catalysts,<sup>11</sup> the Rh/SiO<sub>2</sub> catalyst provided trace amounts of CHEEL and CS as new compounds, whereas the by-product ethyl  $\alpha$ -methylbenzyl ether was barely produced. This tendency shows a preferable catalytic activity for the HDC, indicating that ethanol does not react with MBA at all and promotes the HDC of CLAP on the Rh/SiO<sub>2</sub> catalyst.

As a representative example involving an organosilanegrafted catalyst, Figure 2 shows the conversion and product yields as a function of reaction time for the HDC reaction of CLAP over Rh/SiO<sub>2</sub>-TS. The results obtained for other organosilane-grafted catalysts are summarized in Table S1. A conversion of 62% was achieved in 60 min using the Rh/SiO<sub>2</sub>-TS catalyst. The detected products included MBA (27% yield), CHEL (15% yield), ACH (8% yield), CMBA (5% yield), EB (4% yield), AP (3% yield), CHEEL (1% yield), as well as trace amounts of ECH and CS, and their dechlorinated yields summed up to 58%. As well as the bare catalyst, the by-product ethyl  $\alpha$ -methylbenzyl ether was barely detected, although an improvement in the solid catalytic activity is generally liable to accompany with the undesirable subreaction. These increases in the reaction conversion and the overall dechlorinated product yield observed for Rh/SiO2-TS are consistent with the results obtained with the other modified Rh/SiO<sub>2</sub>. However, the overall dechlorination yields, which are indicators of catalyst activity, decreased in the order: Rh/SiO<sub>2</sub>-TS (58% yield) > Rh/SiO<sub>2</sub>-DMODS (44% yield) > Rh/SiO<sub>2</sub>-TDFDMS (40% yield)  $\approx$  Rh/  $SiO_2$ -BDMS (40% yield) > Rh/SiO\_2-DMOS (39% yield) > Rh/SiO<sub>2</sub> (28% yield).

The textural characteristics of the rhodium catalysts were investigated (Tables 1 and S2) to further evaluate their difference. Because both bare  $Rh/SiO_2$  and  $Rh/SiO_2$ -TS displayed a metal loading of 3 wt %, similar metal loading was used for their modified counterparts. First, the particle size of each rhodium catalyst increased upon silylation, meaning that the metal migrated and aggregated during the reaction, similar to previous

 
 Table 1. Turnover frequency (TOF) for the HDC reaction of CLAP over Rh/SiO<sub>2</sub> catalysts

Catalyst	TOF /min <sup>-1</sup>	Metal particle size <sup>a</sup> /nm	Organosilane number <sup>b</sup> /group nm <sup>-2</sup>
Rh/SiO <sub>2</sub>	6.2	3.7	_
Rh/SiO <sub>2</sub> -TS	19.7	6.7	2.3
Rh/SiO2-BDMS	10.2	5.5	0.6
Rh/SiO2-DMOS	9.8	5.1	0.4
Rh/SiO2-DMODS	18.2	7.8	0.3
Rh/SiO <sub>2</sub> -TDFDMS	7.5	4.8	0.3

<sup>a</sup>Calculated by carbon monoxide (CO) chemisorption. <sup>b</sup>Calculated by elemental analysis.



Figure 3. (a) TG and (b) DTA curves of bare and modified  $Rh/SiO_2$  catalysts.

results for Pt/SiO<sub>2</sub>–DMODS.<sup>11</sup> The number of organosilane groups per catalyst surface area unit was calculated using the methods by Helmy et al.<sup>13,14</sup> and Li.<sup>15</sup> This number was independent of the organosilane species but agreed well with the TG weight losses in air. Figure 3a shows the weight loss of Rh/SiO<sub>2</sub>–TS as a typical example. All the grafted catalysts showed exothermic peaks between 500 and 800 K, while the silica support and Rh/SiO<sub>2</sub> barely showed the peaks (Figure 3b), suggesting that the weight loss resulted from the pyrolysis of the organosilanes.

Turnover frequencies (TOFs) were calculated using the metal surface areas derived by carbon monoxide (CO) chemisorption. Here, it is noted that the amount of adsorbed CO may decrease due to the presence of organosilanes adjacent to Rh particles, thereby showing slightly higher TOFs for the grafted Rh/SiO<sub>2</sub> catalysts. Based on the reaction conversion at 10 min, all modified Rh/SiO<sub>2</sub> catalysts showed higher TOF than the bare Rh/SiO<sub>2</sub> catalyst (6.2 min<sup>-1</sup>). Rh/SiO<sub>2</sub>-TS exhibited the highest TOF  $(19.7 \text{ min}^{-1})$ , which was approximately 3.2 times that of bare Rh/SiO<sub>2</sub>. The TOF values of Rh/SiO<sub>2</sub>-BDMS  $(10.2 \text{ min}^{-1})$ , Rh/SiO<sub>2</sub>-DMOS (9.8 min<sup>-1</sup>), and Rh/SiO<sub>2</sub>-DMODS ( $18.2 \text{ min}^{-1}$ ) were inconsistent with their main carbon chain length, which contained 4, 8, and 18 carbons, respectively. Although  $Rh/SiO_2$ -DMODS (0.3 groups nm<sup>-2</sup>) displayed the lowest number of organosilane groups compared with the other two catalysts, its TOF was close to that of Rh/SiO2-TS, implying that long organosilane carbon chains were somewhat effective at enhancing the HDC activity. These results indicate that hydrophobic organosilane on the catalyst support effectively promote the HDC catalyst activity in the water/ethanol mixture. Here, the organosilane groups may create a hydrophobic zone that retains a large amount of CLAP close to the active sites, enhancing the catalytic activity. This tendency is similar to cases in which Pt/SiO<sub>2</sub> catalysts were grafted on BDMS, DMOS, and DMODS.<sup>11</sup> To verify this hypothesis, Rh/SiO<sub>2</sub> was grafted on TDFDMS, a fluorinated organosilyl reagent with a higher hydrophobicity. Contrary to expectation, the dechlorination activity and TOF of Rh/SiO2-TDFDMS amounted to 40% and 7.5 min<sup>-1</sup>, respectively. Therefore, low activity for the Rh/ SiO<sub>2</sub>-TDFDMS catalyst may stem from the lower organosilane density on the support  $(0.3 \text{ group nm}^{-2})$  and the considerable lipophobicity of the organofluorinated terminal configuration because of the hindered percolation of CLAP and ethanol near the metal active site in the organic zone. Therefore, an appropriate organosilyl reagent is required to promote the HDC reaction over organosilane-grafted Rh catalysts.

Rh/SiO<sub>2</sub>-TS showed the highest activity. This phenomenon may originate from its high organosilane number (2.3 groups  $nm^{-2}$ ), which facilitates the HDC reaction. To better understand this activity, the reaction intermediates CMBA, MBA, AP, and ACH were hydrotreated over Rh/SiO<sub>2</sub>-TS using 1 MPa hydrogen at 373 K for 60 min. Reaction conversions and product distributions are listed in Table S3 (Supporting Information). TOFs amounted to 18.9, 11.5, 36.7, and 1.1 min<sup>-</sup> for CMBA, MBA, AP, and ACH, respectively, clearly showing that the aromatic substrates (CMBA, MBA, and AP) smoothly converted to their hydrogenation and/or hydrogenolysis derivatives, whereas ACH barely reacted. Moreover, when cyclohexanol was hydrotreated over Rh/SiO2-TS under the same conditions, no conversion occurred. These results indicate that, in addition to a hydrophobic zone on the catalyst surface, the high activity of Rh/SiO<sub>2</sub>-TS depends on aromatic  $\pi$ - $\pi$  interactions between the 4-tolylsilyl substituent on the catalyst and the aromatic ring of CLAP. Also, the steric hindrance of the cyclohexyl ring might prevent ACH from approaching the hydrophobic zone.

Finally, the effect of the ethanol ratio in the solvent mixture on the HDC reaction was examined over Rh/SiO<sub>2</sub>–TS (Table S4, Supporting Information). When the ethanol composition increased to 3:1 (v/v) water/ethanol, all reaction conversions, overall dechlorinated product yields, and TOFs increased up to 72%, 68%, and 27.3 min<sup>-1</sup>, respectively. Yields for EB (9%) and ECH (5%) especially increased in the product distribution. On the other hand, for lower ethanol compositions (39:1 (v/v) water/ethanol), reaction conversions and TOFs decreased to 35% and  $11.6 \text{ min}^{-1}$ , respectively, which represents approximately half of the values obtained using 7:1 (v/v) water/ ethanol. Also, the overall dechlorinated product yields decreased to 20%, which correspond to one-third of those observed in 7:1 (v/v) water/ethanol. Therefore, ethanol in the solvent mixture plays a significant role in the HDC reaction. It (1) lowers the viscosity of the reaction mixture, (2) expands the hydrophobic zone, and (3) assists the percolation of substrates through the hydrophobic zone.

In conclusion, five different water-repellent rhodium catalysts were synthesized by attaching their organosilyl substituents to the silica support. All the modified catalysts successfully enhanced the HDC reaction in the water/ethanol mixture using 1 MPa hydrogen at 373 K. This improvement may stem from the hydrophobic zone created by the organosilyl substituents, retaining many CLAP molecules near the catalyst active sites. In particular, the Rh/SiO<sub>2</sub>-TS catalyst showed high performance in the HDC reaction. This behavior may also result from the (1) numerous 4-tolylsilyl substituents grafted on the support and (2) aromatic  $\pi$ - $\pi$  interactions between these 4-tolylsilvl substituents and the aromatic ring of CLAP. All organosilane-grafted catalysts prevented the by-product formation of ethyl amethylbenzyl ether from ethanol and MBA, meaning that overcame the weakness for the modified Pt/SiO<sub>2</sub> catalysts. Detailed studies are underway to uncover the mechanism involving this HDC catalyst.

Supporting Information is available electronically on J-STAGE.

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