Electronic Supplementary Information

for

“High density monolayer of diisocyanide on gold surface as a platform of supported Rh-catalyst for selective 1,4-hydrogenation of α,β-unsaturated carbonyl compounds”

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1. Preparation of high-density monolayer of Rh-diisocyanide on gold surface

Preparation of high-density monolayer of Rh-diisocyanide on gold surface was conducted via successive immersions of a gold surface in solutions of diisocyanide[1] and Rh precursor (Figure 2). Gold surfaces were prepared by successive vapor deposition of 5 nm thickness of titanium (99.5%, Nilaco) and 100 nm thickness of gold (99.99%, Tanaka Precious Metal) onto glass slides in a vacuum evaporator apparatus (ULVAC) with a diffusion pump. The pressure was maintained below 1×10^{-6} Torr and the temperature was kept at 300 °C. Deposition was carried out at constant rate of 0.01 nm/s. After annealing in a hydrogen-flame, a gold surface was immersed in a 1.0 mM CH_2Cl_2 solution of 4,4''-*p*-terphenyldiisocyanide (TPDI) for 24 h at room temperature.[1] Careful washing of the surface with CH_2Cl_2 to remove excess TPDI was followed by the immersion in a 5.0 mM benzene solution of $[Rh(CO)_2Cl]_2$ for 3 h at room temperature and washing with benzene as mentioned above.

2. Characterization of the monolayers on gold surface

Characterization of the monolayers on gold surface was conducted mainly by infrared reflection absorption spectroscopy (IR-RAS) and inductively coupled plasma - mass spectrometry (ICP-MS). IR-RAS data were collected on Perkin-Elmer Spectrum One equipped with MCT detector cooled by liquid nitrogen and with IR-RAS unit supplied from ST Japan. After purging the sampling room with enough flow of nitrogen gas, single power spectrum was obtained by acquisition of 1024 scans with 4 cm^{-1} resolution. An absorption spectrum was obtained by using a power spectrum of bare gold surface as a reference spectrum. ICP-MS measurement on ELAN DRC II (Perkin Elmer Co. Ltd.) was utilized to determine absolute amount of Rh immobilized on gold surface. A Rh-immobilized gold surface was dissolved into aqua regia. The solution thus obtained was evaporated by heating to afford the residue, which was then dissolved in 50 mL of 0.5 % nitric acid (Ultra analysis grade, Kanto) diluted with Milli-Q® water. The Rh concentrations in the samples were determined with calibration using a set of the Rh standard solutions.

3. Space-filling model of [Au]-TPDI-Rh (2)

Based on surface concentration of Rh (0.66 nmol from ICP-MS) and the assumption of perfect 1:1 complex formation between Rh and isocyanide, a space-filling model of [Au]-TPDI-Rh (**2**) can be drawn as shown in Figure S1. Considering the sizes of TPDI molecule and the Rh species, formation of the densely-packed monolayer in [Au]-TPDI (**1**) and complete Rh complexation in [Au]-TPDI-Rh (**2**) could be reasonable.

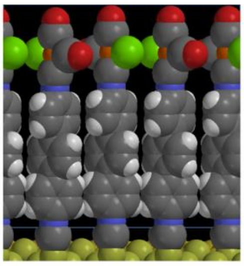

Fig. S1 (Space-filling model of [Au]-TPDI-Rh (**2**).

4. Typical procedure for catalytic reaction

A catalytic reaction was conducted by placing the glass chip typically in a dimension of 5×5 mm^2 with the Rh-immobilized surface in a Teflon cup in an autoclave together with an ethanolic solution of an α,β-unsaturated carbonyl compound under pressurized hydrogen. Gas chromatographic analyses were conducted using 1,4-diisopropylbenzene as an internal standard on a Shimazu GC-14B equipped with a capillary column HR-1 (I.D. 0.25 mm × 25 or 50 m) and a flame ionization detector. The peak assignments of products on GC analyses were confirmed by using authentic samples from commercial source or those synthesized according to the reported procedures. Identification of some of the products was further verified by GC-MS analysis on Shimazu GC-14B with a capillary column HR-1. A typical example of GC/MS analyses is shown in Fig. S2 and S3. Peak separation between cyclohexanone (4) and cyclohexanol (**5**) on GC column was confirmed by using a mixture of authentic samples (Fig. S2(a)). The peak assignments of **4** and **5**, whose retention times are close to each other, were further verified by comparison of the mass fragmentation patterns with the data in a commercialized database (Fig. S2(b)). Fig. S3 shows an example of GC-MS analysis of a reaction mixture after a catalytic reaction with almost perfect selectivity towards cyclohexanone (**4**), where single GC peak giving a mass fragmentation pattern perfectly corresponding to **4** was observed with no appearance of a GC peak corresponding to **5**. Quantification of the product was conducted by GC analyses based on the observed peak areas calibrated with peak areas of biphenyl (Fig S3) as internal standard.

XPS analysis suggested ca. 20% leaching of Rh after an initial run of a hydrogenation reaction.

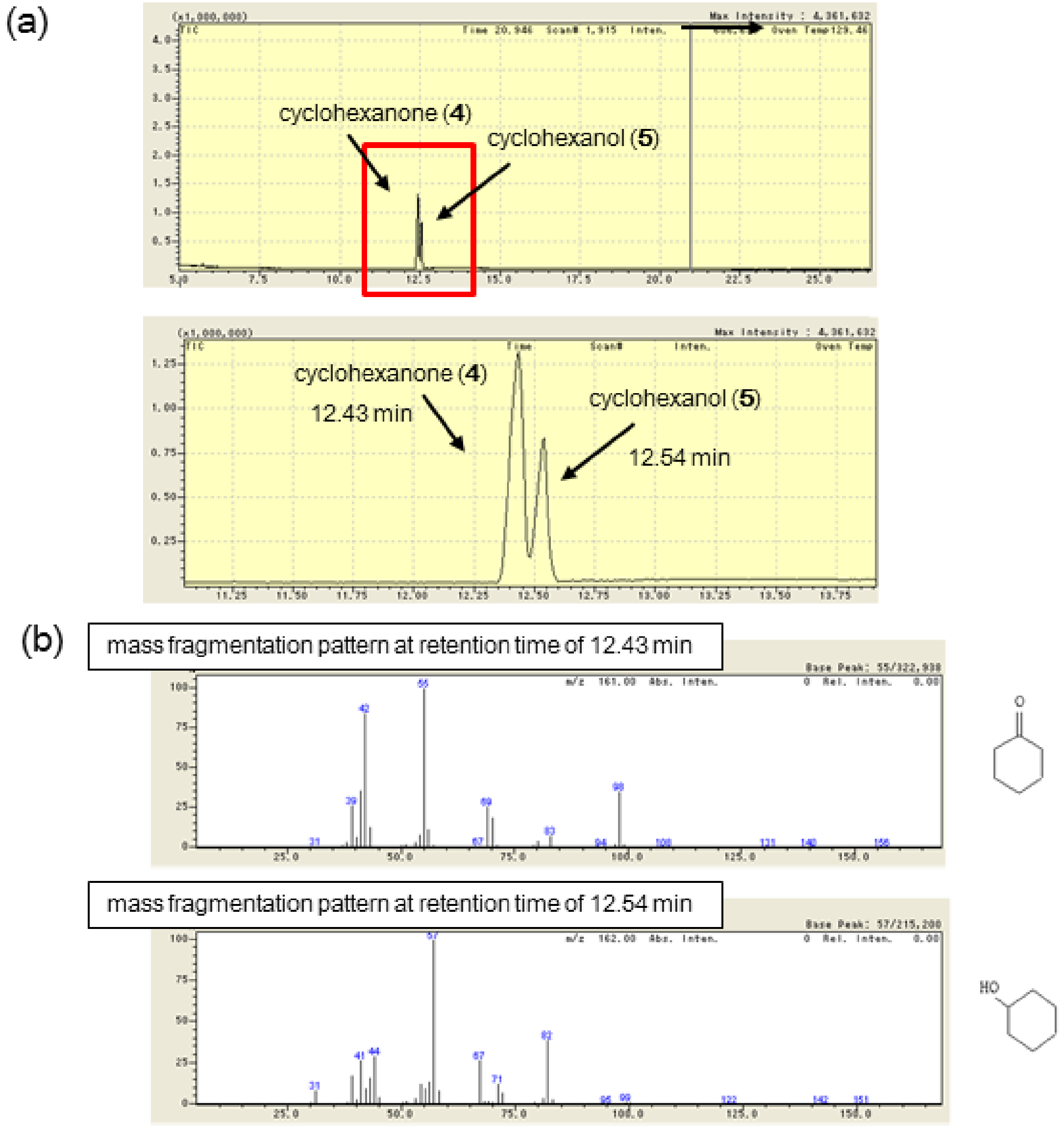

Fig. S2 (a) Peak separation between cyclohexanone (**4**) and cyclohexanol (**5**) on GC and (b) the mass fragmentation patterns of the observed GC peaks.

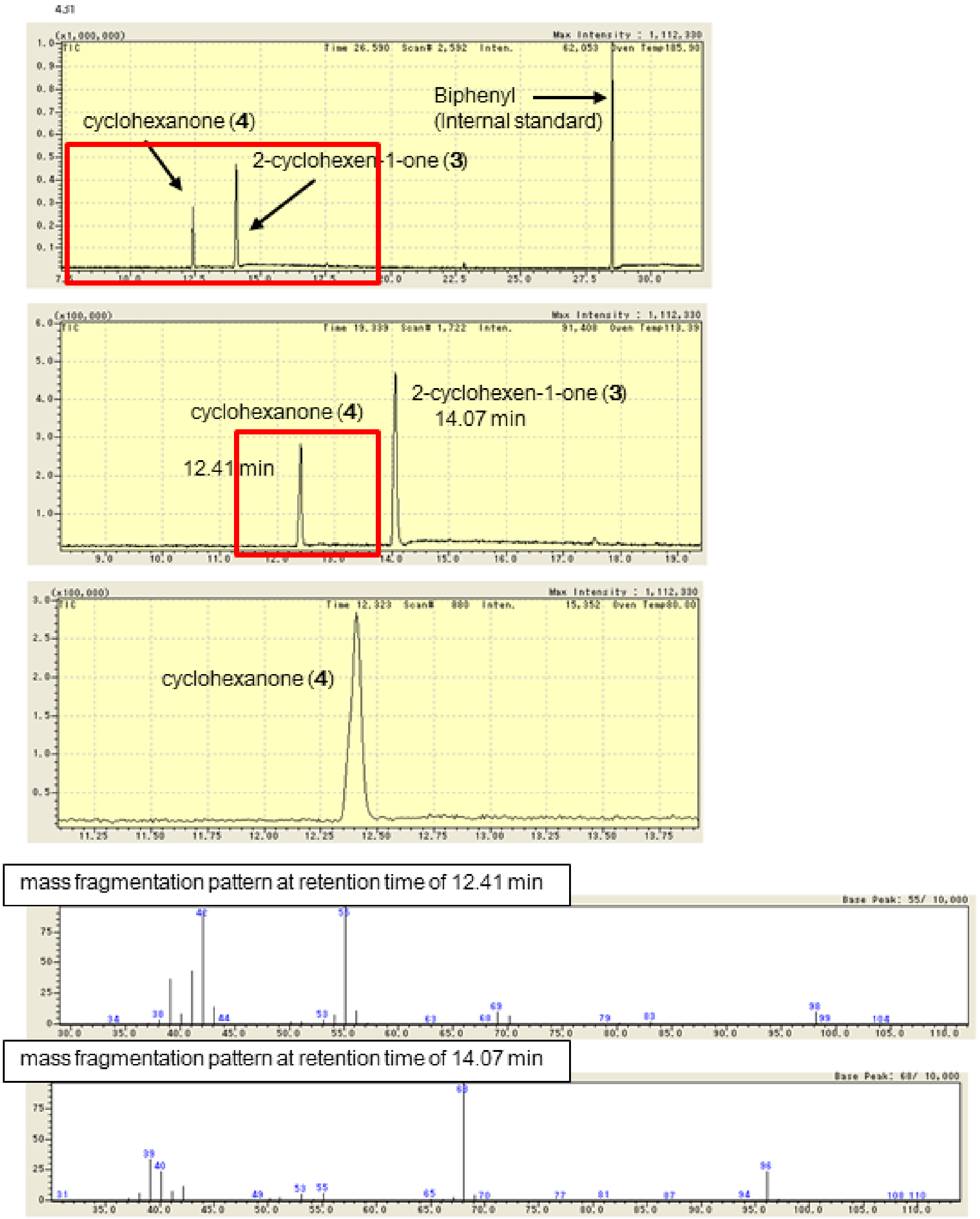

Fig. S3 An example of GC-MS analysis of a reaction mixture after a catalytic reaction with almost perfect selectivity towards cyclohexanone (**4**) and the mass fragmentation patterns of the observed peaks on GC.

Reference

1. J. I. Henderson, S. Feng, T. Bein and C. P. Kubiak, Langmuir 16 (2000) 6183.