Dehydrogenative Coupling of Alkanes and Benzene Enhanced by Slurry-Phase Interparticle Hydrogen Transfer

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ABSTRACT: The dehydrogenative coupling reaction of alkanes and benzene has attracted attention as a method of direct conversion of alkanes to raw materials for useful chemical products. Here, we report the first combined catalyst system composed of hydrotalcite-supported palladium and solid acid aluminum-exchanged montmorillonite for the direct alkylation of benzene promoted by slurry-phase interparticle hydrogen transfer at 150 °C. The combination of the two catalytic particles showed excellent activity and achieved the maximum benzene conversion of 21% and target product selectivity of 84% in the reaction of n-heptane and benzene. Our results, thus, provide a feasible strategy to design efficient liquid-phase reaction systems employing simple physical mixing of two catalytic particles.

KEYWORDS: alkane, benzene, dehydrogenative coupling, montmorillonite, hydrotalcite, palladium

Various solid catalysts have been developed and utilized for the production of a wide variety of chemicals: examples include acid, base, metal, and immobilized organic catalysts. Accumulation of two or more of such functionalities into one catalytic particle can be an interesting approach toward concerted catalysis.1−10 However, the properties of precisely constructed catalytic particles, such as zeolites and metal nanoparticles, typically deteriorate at the nanoscale because of the presence of additional functionalities and the synthesis of such catalysts is time-consuming. In contrast, physical mixing of two different catalytic particles becomes a simple and widely applicable way if interparticle transfer of atom and/or electron occurs for concerted catalysis.11−14 The catalytic applications of such interparticle hydrogen migrations have been limited to gas-phase reactions at high temperature.11,15−17

Dehydrogenative coupling of alkanes and benzene at low temperature is an efficient approach for the selective synthesis of alkylbenzenes with alkyl chains of the desired carbon number that produces only the hydrogen molecule as the byproduct, unlike the conventional system using a halide or an oxidizing agent.18 We reported that non-noble-metal solid acid, aluminum-exchanged montmorillonite (Al-mont) promotes liquid-phase dehydrogenative coupling between alkanes and benzene at 150 °C (Figure 1a).19,20 However, the yield was low, and a side reaction of cracking occurs with increasing benzene conversion. To increase the alkylation product yield and selectivity, incorporation of a noble metal such as Pt and Pd into the solid acid such as H-ZSM-5 has been studied,21−31 however, a high reaction temperature of >200 °C is still
necessary. The incorporation of the transition metal decreases the acidity of the solid acid.32

Herein, we report the first combined catalytic system for the direct alkylation of benzene promoted by slurry-phase interparticle hydrogen transfer at 150 °C (Figure 1b). We investigated a solid base-supported transition metal, such as palladium, which exhibits high activity in liquid-phase acceptor-less dehydrogenation reactions of polar molecules, such as alcohols and oximes,33−35 as a counterpart for the solid acid Al-mont.

Al-mont and Pd-grafted Mg−Al hydrotalcite (Pd/HT) were prepared according to previously reported procedures.19,44 The maintenance of layered structures of the prepared Al-mont and Pd/HT was confirmed by X-ray diffraction (XRD) analysis (Figure S1, S2). The almost same interlayered distance of Pd/HT and the parent HT indicates that Pd was located on the outer surface of HT. Pd K-edge X-ray absorption near edge structure (XANES) analysis indicated divalent Pd species on the outer surface of HT (Figure S3). In Fourier transform extended X-ray absorption fine structure (FT-EXAFS) analysis, the strong peak corresponding to the Pd−O bond was observed for Pd/HT at the same position and intensity as that for PdO, while the peak ascribed to the Pd−O−Pd bond was weaker than PdO (Figure S4). The FT-EXAFS spectrum of Pd/HT was fitted well with a coordination number (N) of 4 with a Pd−O bond distance of 2.02 Å (Table S2), suggesting dispersed PdO on the outer surface of HT.

We investigated the reaction of n-heptane and benzene at 150 °C for 16 h (Table 1). Both benzene conversion and selectivity of target products, alkylbenzenes with a carbon chain of 7 (Ph−C7), improved significantly on adding Pd/HT to Al-mont (Table 1, entry 1 vs 2). The formation of molecular hydrogen (H2) was detected by gas chromatography with a barrier discharge ionization detector (Figure S6). When only Pd/HT was used, biphenyl was the sole product (entry 3). The solid mixture of Al-mont and Pd/HT catalysts could be reused: high selectivity of Ph−C7 products (77−91%) and benzene conversion were maintained during four times of reuse. In addition, after optimization of the conditions, the combination of Al-mont and Pd/HT achieved 21% conversion and 84% Ph−C7 selectivity at 150 °C (entry 9). Compared to other combined systems of supported Pd catalysts with Al-mont, Pd/HT was found to be the best counterpart (entries 1 vs 13−18). Al-mont showed the highest performance with Pd/HT among other solid acids, such as H-mordenite and H-ZSM-5 (entries 19−22), while benzene conversion increased with Pd/HT in the cases of other solid acids.19 The reaction was barely accelerated with Pd salts, such as PdCl2 and Pd(NO3)2, indicating that only supported Pd catalysts promoted this reaction (entries 22−24).

The scope of alkanes for the direct alkylation of benzene using both Al-mont and Pd/HT is summarized in Table 2. The reaction of other linear alkanes, n-hexane and n-pentane, also proceeded with 13.7% and 8.3% benzene conversions, respectively, with high selectivity toward the corresponding alkylbenzenes. The main isomers were 2- and 3-phenyalkanes. In addition, cyclic alkanes could be used, and the target cyclic alkylbenzenes were obtained: for example, the reaction of cyclohexane occurred with 22% benzene conversion and 79% selectivity of the target product.

Table 1. Alkylation of Benzene with n-Heptane Using the Solid Acid and Supported Pd Combined Systems
a

| entry | solid acid | supported Pd | benzene conv/% | selectivity/% |
|-------|------------|--------------|----------------|--------------|
|       |            |              | Ph−C7 | Ph−C7 | Ph−Ph |
| 1     | Al-mont    | Pd/HT        | 6.8   | 82    | 10  |
| 2     | Al-mont    | Pd/HT        | 1.8   | 58    | 24  |
| 3     | Al-mont    | Pd/HT        | 0.4   | 0     | >99 |
| 4     | Al-mont (reuse 1) | Pd/HT (reuse 1) | 6.1   | 77    | 5   |
| 5     | Al-mont (reuse 2) | Pd/HT (reuse 2) | 5.7   | 88    | 3   |
| 6     | Al-mont (reuse 3) | Pd/HT (reuse 3) | 3.9   | 91    | 5   |
| 7     | Al-mont (reuse 4) | Pd/HT (reuse 4) | 8.0   | 82    | 6   |
| 8     | Al-mont    | Pd/HT        | 14.0  | 74    | 3   |
| 9     | Al-mont    | Pd/HT        | 21.0  | 84    | 7   |
| 10    | H-mont     | Pd/HT        | 2.7   | 77    | 12  |
| 11    | Pd-mont    | Pd/HT        | 1.6   | 65    | 2   |
| 12    | Na-mont    | Pd/MgO       | <0.1  |        |     |
| 13    | Al-mont    | Pd/TO2       | 3.3   | 80    | 13  |
| 14    | Al-mont    | Pd/Al2O3     | 2.6   | 70    | 18  |
| 15    | Al-mont    | Pd/Al2O3     | 1.9   | 57    | 23  |
| 16    | Al-mont    | Pd/SiO2      | 1.7   | 62    | 28  |
| 17    | Al-mont    | Pd/SmO2      | 1.7   | 59    | 33  |
| 18    | Al-mont    | Pd/CeO2      | 2.8   | 55    | 42  |
| 19    | H-mordenite| Pd/HT        | 3.9   | 79    | 3   |
| 20    | H-ZSM-5    | Pd/HT        | 3.7   | 80    | 16  |
| 21    | H-beta     | Pd/HT        | 4.6   | 80    | 3   |
| 22    | Al-mont    | PdCl2        | 1.8   | 40    | 38  |
| 23    | Al-mont    | Pd(NO3)2     | 0.6   | 72    | 12  |
| 24    | Al-mont    | Pd(OAc)2     | 2.3   | 57    | 11  |
| 25    | Al-mont    | HT           | 0.5   | 82    | 12  |

"Reaction conditions: solid acid (0.10 g), supported metal (0.10 g, metal: 0.05 mmol), n-heptane (1.0 mL; 6.8 mmol), benzene (1.2 mmol), 150 °C, 16 h. Yield and selectivity were determined by GC-FID. aAlkylbenzenes other than Ph−C7. bBiphenyl. c32 h. d64 h. eBenzene (0.6 mmol), 64 h. fPd/Carbon (Pd: 1 wt %) was used. gConversion without Pd/HT."
Table 2. Scope of alkanes for direct alkylation of benzene

| Al-mont + Pd/HT | 150 °C, 64 h | R + H₂ |
|-----------------|-------------|-------|
| conv. 21%       | conv. 14%   | conv. 8.3% |
| Ph-C7 sel. 84%² | Ph-C6 sel. 87%² | Ph-C5 sel. 51%³ |
| conv. 22%       | conv. 12.3% | conv. 6.2%⁵ |
| sel. 79%        | sel. 71%    | sel. 59%   |
|                 |             | C8 sel. 79% |

“Reaction conditions: solid acid (0.10 g), supported metal (0.10 g, metal: 0.05 mmol), n-heptane (1.0 mL; 6.8 mmol), benzene (0.6 mmol), 150 °C, 64 h. Yield and selectivity were determined by GC-FID. ²Ph-C7 selectivity: (2-:3-:4-:((methyl)cyclohexyl-others = 30:20:10:11:14). ³Ph-C6 selectivity: (2-:3-:cyclohexyl-others = 39:26:7:16). ⁴Ph-C5 selectivity: (2-:3-:others = 25:14:11). ⁵120 °C, 64 h. For detailed results such as isomer distributions in linear alkanes, see the Supporting Information.

A similar product distribution of the Ph-C7 isomer was observed when only Al-mont was used for the reaction or both Al-mont and Pd/HT were used (Table S3). Since almost no formation of 1-phenylheptane occurred in both cases, it can be said that the alkane activation and benzene alkylation step occurs by an acid-catalyzed carbocation mechanism even when Pd is added. The possibility of dehydrogenation of heptane by Pd/HT could be ruled out because the small amount of contaminated heptene in the raw n-heptane (0.10–0.31%) was not increase after the reactions with Pd/HT (Table S4). The alkylation rate was independent of the concentration of the contaminated heptene.

Figure 2a shows a time course for Ph-C7 and biphenyl formation with Pd/HT and Al-mont: biphenyl was initially observed, followed by the formation of Ph-C7. The catalyst mixture was recovered after the reaction, and its Pd K-edge XANES was acquired: the obtained spectrum was close to that of fresh Pd/HT or PdO (Figure 2b). This result indicates that the valence of the Pd on HT after the reaction was changed to zero from +2. FT-EXAFS analysis and transmission electron microscopy (TEM) of the recovered catalyst reveal the formation of Pd–Pd bonds and Pd²⁺ clusters, respectively (Figure S7 and S8). Sasson and co-workers reported a stoichiometric reaction between Pd²⁺ and benzene to Pd⁰ and biphenyl.55 Pd²⁺ on the HT surface was reduced to Pd⁰ along with the biphenyl formation, and then the newly formed Pd(0) nanoparticle accelerated the alkylation. This hypothesis is supported by the reuse experiment: no clear induction period was observed for alkylation in the second cycle (Figure S9), and the amount of biphenyl was 10 times lower than that of the first reaction at initial period (~60 min). The catalyst mixture during the alkylation reaction was also characterized. The Pd K-edge XANES spectrum of the catalyst during the reaction (1 h) indicates formation of Pd(0) nanoparticle as similar to the catalyst after the reaction (Figure S10). As shown in Figure 2, the target alkylated product, Ph-C7, rapidly increased after 1 h. These facts support that the Pd(0) species accelerates the alkylation reaction.

Then, we investigated an interparticle interaction between Al-mont and Pd/HT. The alkylation reaction was conducted under the conditions wherein two catalyst particles were separated by a filter (pore size = <1 μm), as shown in Figure 3.

A | B | Benzene Conv. (%) | Selectivity (%) |
|---|---|------------------|-----------------|
| Pd/HT | - | 8.1 | 61 | 4 | 35 |
| Al-mont | Pd/HT | 2.2 | 57 | 12 | 31 |
| Al-mont | - | 2.3 | 57 | 0 | 43 |

Figure 3. Effect of contact between Al-mont and Pd/HT on the alkylation reaction.

As a result, it was found that the alkylation reaction was not accelerated by the separated system, while the formation of biphenyl was observed which was not detected when using only Al-mont. The alkylation was accelerated by the physical contact between Pd/HT and Al-mont particles. No Pd was detected in the used Al-mont in the separated system by ICP analysis (Pd < 0.00 mmol/g), indicating no leaching of Pd from HT support. Scanning electron microscopy (SEM)-energy dispersive X-ray spectroscopy (EDS) and scanning transmission electron microscopy (STEM)-EDS analysis of the recovered catalyst mixture by the combined system (Table 1, Entry 1) was performed (Figure 4 and S). In the SEM-EDS image, the distribution of Pd is similar to that of Mg, which is the main constituent of HT, but differed from that of Si, a main constituent of mont (Figure 4). Similarly, the distributions of Mg and Pd also match in the STEM-EDS image (Figure Sb–d). The element count analysis implies that Pd was detected in the Mg-rich area (A) in Figure S5a, whereas Pd counts in the Si-rich area was under the detection limit (B) (Figure S5e). It is
suggested that Pd is maintained on HT during the reaction and participated in the alkylation catalytic cycle from the HT surface.

These investigations indicate that (i) the C–C bond formation occurs at Al-mont, (ii) Pd(0) nanoparticles on the HT surface enhances the benzene alkylation, and (iii) the contact between Al-mont and Pd/HT particles is mandatory. These results strongly imply that hydrogen transfer between Al-mont and Pd/HT particles occurs and H₂ generates on the Pd nanoparticle. The slurry-phase hydrogen migration was confirmed by a deuterium-labeling experiment. A deuterated HT (HT(D)) possessing the M-OD group and adsorbed D₂O was prepared by the treatment of the parent HT with D₂O, and it was dried under vacuum. The HT(D) and Al-mont were mixed in n-heptane solution and heated at 150 °C for 16 h. A 41% of an obtained isomer, 2-methylhexane contained deuterium, while no isomerization occurred with only HT(D) because of the lack of acidity (Scheme 1). The use of Pd/HT(D) instead of HT(D) also afforded a similar result (Scheme S1). These results clearly indicate that hydrogen migration between two catalyst particles occurs under the slurry-phase alkylation reaction conditions. H-D exchange and net migration of hydrogen are different phenomena; however, the surface environment of HT contains a large amount of water (∼5 wt %) and has a high hydroxyl (M−OH) density because of its clay nature and should support not only proton transfer but also hydrogen spillover. Similar to the interparticle hydrogen reverse spillover in gas-phase aromatization, abstracted protons and hydrides from an alkane and benzene at Al-mont are quickly transferred to Pd/HT particles and recombines to H₂ on a Pd nanoparticle. As shown in Table 1, HT showed the highest performance compared to other supports such as TiO₂ and CeO₂, while these reducible oxides are well-known as a good support medium for the hydrogen spillover. Similar Pd(0) particles on these oxide as HT are confirmed by Pd K-edge XAFS or TEM (Figures S7 and S8).

In the reaction using Pd/TiO₂ and Al-mont, the addition of a small amount of water enhances the alkylation reaction rate (Table S6). In the slurry-phase interparticle hydrogen transfer, the presence of adsorbed water and hydroxyl group on catalyst surface may play a pivotal role.

Furthermore, the effect of the weight of each catalyst on the alkylation rate was investigated. When 0.05 g or more of Al-mont was used with a fixed amount of Pd/HT, the rate became almost constant (Figure S12), while Ph–C₇ selectivity decreased as the amount of Al-mont increased because of cracking. This indicates that the alkylation rate is not mainly controlled by Al-mont: the carbocation formation rate and the C–C bond forming step of the alkylation are much faster among the other steps in the total catalytic cycle of the dehydrogenative coupling. In contrast, the reaction rate increased as the amount of Pd/HT in the reactor increased (Figure S12). Hydrogen transfer and/or recombination, which is a step involving Pd/HT, is potentially the rate-determining step. This kinetic result indicates that hydride species is

Figure 4. (a) SEM image of the used catalyst mixture containing Al-mont and Pd/HT, and EDS mapping result of elements: (b) Mg, (c) Si, and (d) Pd.

Figure 5. (a) Annular dark-field STEM image of used catalyst mixture of Al-mont and Pd/HT, EDS mapping results of elements (b) Mg, (c) Si, (d) Pd, and (e) element counts in two areas in (a). Scale bar is 200 nm.

Scheme 1. Deuterium-Labeling Experiment

| Catalyst | 150 °C, 16 h | D₂O |
|----------|-------------|-----|
| HT(D) 0.10 g + Al-mont 0.10 g | 41% deuterated |
| HT(D) 0.10 g | no reaction |

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maintained on the support surface or Pd nanoparticle during the alkylation reaction. After the alkylation reaction, small amount of indole was added to the reactor, then the reaction mixture was heated. As a result, hydrogenated product indoline was detected, while no such hydrogenation was observed with Al-mont or Pd/HT alone (Scheme S2). These phenomena strongly indicate hydrogen transfer from alkane to Pd through both surfaces of Al-mont and HT.

Dehydrogenative coupling of simple alkanes and benzene was, thus, successfully achieved by a simple approach: physical mixing of Al-mont and Pd/HT. Slurry-phase interparticle hydrogen transfer between the solid acid and supported Pd was key to accelerating dehydrogenative coupling. Given the possible various solid catalyst combinations, this finding provides a novel strategy for designing a combined catalytic system for liquid-phase organic synthesis including inert bond activation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.0c00070.

Detailed experimental procedures, detailed results of benzene alkylation including product selectivity, and catalyst characterization results including XAFS spectra, EXAFS curve-fitting analysis data, and TEM images (PDF)

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Notes

The authors declare no competing financial interest.

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Presence of Hydrogen Scavengers.

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