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Selective Alkylation of Benzene by Propane over Bifunctional Pd-Acid Catalysts

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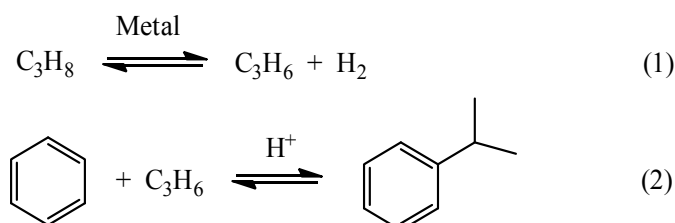
Received: 12 July 2017; Accepted: 8 August 2017; Published: 11 August 2017

Abstract: The alkylation of benzene by propane to yield isopropylbenzene (iPrPh) was studied using bifunctional Pd-acid catalysts, such as Pd-heteropoly acid and Pd-zeolite, in a fixed bed reactor at 300 °C and 1 bar pressure. Keggin-type tungstosilicic acid $H_4SiW_{12}O_{40}$ (HSiW) and zeolite HZSM-5 were used as the acid components in these catalysts. The reaction occurred most efficiently over 2%Pd/25%HSiW/SiO₂, giving iPrPh with up to 88% selectivity. The Pd-HSiW catalyst was more selective than the Pd-HZSM-5; the latter gave only 11–18% iPrPh selectivity. The reaction proceeded via a bifunctional mechanism including the dehydrogenation of propane to form propene on Pd sites, followed by the alkylation of benzene with the propene on acid sites. The effect of Pd loading in Pd-HSiW and Pd-HZSM-5 catalysts indicated that the first step reached quasi-equilibrium at 1.5–2% Pd loading and the second step became rate limiting. The addition of gold to Pd-HSiW enhanced the activity of this catalyst, although the Au-HSiW without Pd was inert.

Keywords: alkylation with alkanes; propane; benzene; isopropylbenzene; Pd-heteropoly acid; Pd-zeolite catalysts

1. Introduction

Acid-catalysed alkylation of benzene with alkenes is an established commercial process to produce a wide range of alkylbenzenes. The alkylation of benzene with ethene and propene is used to manufacture ethylbenzene (EtPh) and isopropylbenzene (iPrPh), which are the intermediates in styrene and phenol production, respectively [1]. It has been demonstrated that ethene and propene can be replaced by abundant and inexpensive alkanes, ethane and propane, which would lead to the more cost-effective and environmentally friendly production of these commodity chemicals [2–18]. The alkylation of benzene with light alkanes occurs in the gas phase in the presence of solid bifunctional metal-acid catalysts, which operate via a pathway, shown in Scheme 1, including the dehydrogenation of alkane on metal sites to form alkene and H₂ (step 1) followed by the alkylation of benzene with the alkene on acid sites (step 2).



Scheme 1. Alkylation of benzene with propane via a bifunctional pathway.

Pt-zeolite bifunctional catalysts have been shown to be the most active for benzene alkylation with ethane [2–17]. The best results have been attained using Pt-modified HZSM-5 zeolite to obtain >90% selectivity to EtPh at an almost equilibrium benzene conversion of 12% [6]. In contrast, the alkylation of benzene with propane has proved to be more difficult, giving only 32% iPrPh selectivity at 6.6% conversion using Pt/HZSM-5 [13]. The main product was nPrPh (50% selectivity) rather than iPrPh [13], which would be the favourable product from the carbenium ion mechanism. This may be due to the shape selectivity control imposed by the zeolite microporous environment [18]. A much more selective alkylation of benzene by propane (90–93% iPrPh selectivity) has been reported using a mesoporous silica-supported Pt-heteropoly acid catalyst, Pt/H₄SiW₁₂O₄₀/SiO₂, based on the Keggin-type 12-tungstosilicic acid H₄SiW₁₂O₄₀ (HSiW) [18]. Notably, HSiW is superior to its stronger analogue H₃PW₁₂O₄₀ in this reaction, probably due to its larger number of proton sites and better resistance to coking [18].

We now investigate the alkylation of benzene by propane using less expensive bifunctional catalysts based on palladium. Similar to platinum, palladium is an active catalyst for alkane dehydrogenation, and is hence capable of promoting the alkylation process. The bifunctional Pd catalysts under study comprise HSiW and HZSM-5 as the acid components. In general, regardless of their formulation, these catalysts are denoted herein as Pd-HSiW and Pd-HZSM-5, respectively. Both supported and physically mixed bifunctional catalysts are used in this work; the supported ones are denoted Pd/HSiW/SiO₂ and Pd/HZSM-5 and the mixed ones Pd/C + HSiW/SiO₂ and Pd/C + HZSM-5. Also, we looked at the effect of gold additives on catalyst performance by testing the corresponding AuPd-HSiW and AuPd-HZSM-5 bimetallic catalysts. It is demonstrated that in benzene alkylation with propane, the Pd-HSiW and Pd-HZSM-5 catalysts perform similarly to their Pt counterparts, Pt-HSiW and Pt-HZSM-5, as reported previously [18]. The addition of gold to Pd-HSiW is shown to enhance the activity of this catalyst, although the Au-HSiW without Pd is inert.

2. Results and Discussion

It is essential to compare the bifunctional Pd catalysts under study with previously reported Pt catalysts [18] under the same reaction conditions. Therefore, the Pd catalysts were tested in benzene alkylation with propane in the same system at 300 °C, contact time $W/F = 80 \text{ g h mol}^{-1}$ and $[C_6H_6]/[C_3H_8] = 1:9 \text{ mol/mol}$ without dilution of the gas feed with an inert gas, as described previously [18]. In such conditions, the equilibrium conversion of benzene to iPrPh has been reported to be 8.2% [18]. Information about the catalysts studied is given in the Materials and Methods (Section 3).

2.1. Alkylation of Benzene over Pd-HZSM-5

Representative results are given in Table 1. Monofunctional catalysts HZSM-5 and Pd/C + SiO₂ showed very low activity (entries 1 and 2). In contrast, bifunctional catalysts containing Pd and zeolite HZSM-5, both mixed and supported, were active in benzene alkylation with propane. This confirms the view that the reaction occurs through bifunctional metal-acid catalysis (Scheme 1). With mixed catalysts Pd/C + HZSM-5, the benzene conversion increased with Pd loading, levelling off at about 2% Pd loading (Figure 1; Table 1, entries 3–7). This indicates that the propane dehydrogenation step (1) reaches quasi-equilibrium at $\geq 2\%$ Pd loading, and the alkylation process becomes limited by the acid-catalysed step (2) of the benzene alkylation with propene (Scheme 1).

With Pd-HZSM-5 catalysts, the selectivity to the desired product iPrPh was 11–18%, the main reaction products being MePh, EtPh, and nPrPh. Similar results have been obtained previously with Pt-HZSM-5 [18]. The predominant formation of nPrPh rather than iPrPh, which would be the favourable product from the carbenium ion mechanism, has been explained [18] by the product shape selectivity control imposed by the HZSM-5 microporous environment. This implies that iPrPh, formed initially, could isomerize on HZSM-5 proton sites to form nPrPh, which possesses higher diffusivity in zeolite micropores. MePh and EtPh, which are thermodynamically more favourable products than iPrPh, probably arise from the cracking of nPrPh and iPrPh on zeolite acid sites [13].

Supported catalyst 2% Pd/HZSM-5 exhibited the best performance, giving 17.7% iPrPh selectivity at 19.5% benzene conversion (3.5% iPrPh yield) (Table 1, entry 8). This catalyst also showed good performance stability on stream (Figure 2). Its platinum counterpart, Pt/HZSM-5, gave similar results: 16.4% iPrPh selectivity at 19.9% conversion, i.e., 3.3% iPrPh yield [18]. Overall, in benzene alkylation with propane, Pd-HZSM-5 and Pt-HZSM-5 catalysts perform similarly regarding the selectivity to iPrPh.

It should be noted that the supported 2.0%Pd/HZSM-5 catalyst is twice as active as the Pd/C + HZSM-5 mixed catalyst (2.1% Pd loading) (Table 1, entries 7 and 8). Since the distances between metal and acid sites in these catalysts differ greatly (nanometre scale in the first one and micrometre scale in the second), this indicates that the reaction may be limited by the migration of alkene intermediates between the metal and acid sites within zeolite micropores. A different picture was observed in the case of mesoporous Pd-HSiW/SiO₂ catalysts (see below).

Table 1. Alkylation of benzene with propane over Pd-HZSM-5 catalysts.¹

Catalyst	Conversion ² (%)	Aromatic Selectivity (%) ³				
		MePh	EtPh	iPrPh	nPrPh	C ₉₊
(1) HZSM-5	0.2	25.5	22.8	14.2	24.6	12.9
(2) Pd/C + SiO ₂ (0.7%Pd) ⁴	0.6	88.7	0	0	0	11.3
(3) Pd/C + HZSM-5 (0.1%Pd) ⁴	1.1	19.3	31.6	15.0	28.9	5.3
(4) Pd/C + HZSM-5 (0.4%Pd) ⁴	2.5	25.2	23.9	16.4	28.2	6.4
(5) Pd/C + HZSM-5 (0.7%Pd) ⁴	3.8	27.9	20.8	14.2	25.6	11.6
(6) Pd/C + HZSM-5 (1.4%Pd) ⁴	9.2	34.9	21.8	12.0	19.2	12.2
(7) Pd/C + HZSM-5 (2.1%Pd) ⁴	10.9	35.6	21.1	10.7	19.1	13.6
(8) 2.0%Pd/HZSM-5	19.5	13.0	8.4	17.7	29.9	31.1

¹ Reaction conditions: 300 °C, 1 bar pressure, 0.20 g catalyst, inlet molar ratio C₆H₆/C₃H₈ = 1:9, 10 mL min^{−1} flow rate, W/F = 80 g h mol^{−1}; catalyst pre-treatment at 300 °C/1 h in H₂ flow, 10 mL min^{−1}. ² Benzene conversion at 3 h time on stream. ³ Selectivity to unidentified C₉₊ alkylbenzenes at 3 h time on stream. ⁴ Uniform physical mixture of 7.1% Pt/C with HZSM-5 or SiO₂.

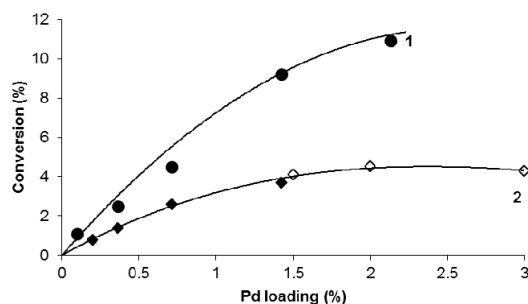


Figure 1. Effect of Pd loading on benzene conversion for benzene alkylation at 300 °C over (1) 7.1%Pd/C + HZSM-5 catalysts and (2) Pd-HSiW including physically mixed catalysts 7.1%Pd/C + 25%HSiW/SiO₂ (solid diamonds) and supported catalysts Pd/25%HSiW/SiO₂ (open diamonds) (for reaction conditions, see Tables 1 and 2).

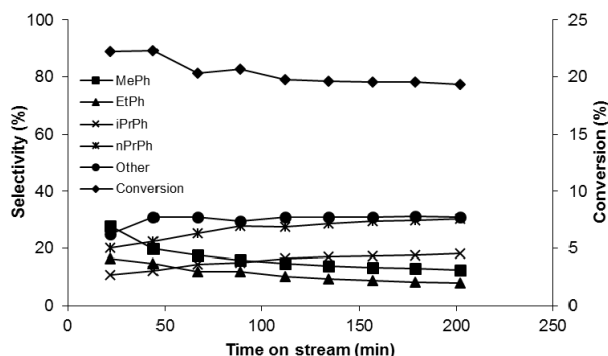


Figure 2. Time course for benzene alkylation by propane over 2% Pd/HZSM-5 (Si/Al = 10) (0.20 g catalyst, 1 bar pressure, inlet molar ratio $C_6H_6/C_3H_8 = 1:9$, 10 mL min^{−1} flow rate, W/F = 80 g h mol^{−1}; catalyst pre-treatment at 300 °C/1 h in H₂ flow).

Table 2. Alkylation of benzene with propane over Pd-HSiW catalysts.¹

Catalyst	Conversion ² (%)	Aromatic Selectivity (%) ³				
		MePh	EtPh	iPrPh	nPrPh	C ₉₊
(1) 25%HSiW/SiO ₂	0.2					
(2) Pd/C + HSiW/SiO ₂ (0.2%Pd) ⁴	0.8	0	5.9	44.3	18.8	31.0
(3) Pd/C + HSiW/SiO ₂ (0.4%Pd) ⁴	1.4	0	2.7	67.3	10.0	20.0
(4) Pd/C + HSiW/SiO ₂ (0.7%Pd) ⁴	2.6	3.6	1.4	69.6	6.4	18.9
(5) Pd/C + HSiW/SiO ₂ (1.4%Pd) ⁴	3.7	2.0	2.0	74.2	6.7	15.1
(6) Pd/C + HSiW/SiO ₂ (1.4%Pd) ⁵	5.2	4.4	3.1	70.6	15.9	6.0
(7) 1.5% Pd/25%HSiW/SiO ₂	4.1	0	0.8	86.3	3.0	9.9
(8) 2.0% Pd/25%HSiW/SiO ₂ ⁶	4.5	0	0.8	85.4	3.6	10.4
(9) 3.0% Pd/25%HSiW/SiO ₂	4.3	0	0.9	88.1	3.4	7.6
(10) 1% Pt/25%HSiW/SiO ₂ [18]	4.0	0	0.8	81.6	2.9	14.7

¹ Reaction conditions: 300 °C, 1 bar pressure, 0.20 g catalyst, inlet molar ratio $C_6H_6/C_3H_8 = 1:9$, 10 mL min^{−1} flow rate, W/F = 80 g h mol^{−1}; catalyst pre-treatment at 300 °C/1 h in H₂ flow, 10 mL min^{−1}. ² Benzene conversion at 3 h time on stream. ³ Selectivity to unidentified C₉₊ alkylbenzenes at 3 h time on stream. ⁴ Uniform physical mixture of 7.1% Pt/C with 25% HSiW/SiO₂. ⁵ Two catalyst beds: 7.1% Pd/C (0.04 g, top bed) and 25%HSiW/SiO₂ (0.16 g, bottom bed). ⁶ 2.1% coke content in the catalyst after reaction.

2.2. Alkylation of Benzene over Pd-HSiW

Silica-supported Pd-HSiW catalysts differ from Pd-HZSM-5 catalysts in two aspects: (i) they are mesoporous rather than microporous, and (ii) HSiW heteropoly acid possesses stronger proton sites than HZSM-5 [18]. Therefore, the Pd-HSiW catalysts can be expected to be much more selective to iPrPh than Pd-HZSM-5, similar to the previously reported Pt-HSiW catalysts [18].

The results for benzene alkylation with propane over Pd-HSiW are given in Table 2 for both the mixed Pd/C + 25% HSiW/SiO₂ and supported Pd/25% HSiW/SiO₂ catalysts. As expected, the 25% HSiW/SiO₂ acid catalyst in the absence of Pd was practically inert (entry 1), whereas the bifunctional Pd-HSiW metal-acid catalysts showed good activity in the alkylation reaction. In stark contrast to Pd-HZSM-5, the reaction with the Pd-HSiW catalysts occurred with high selectivity to iPrPh, up to 88.1% (entry 9), as anticipated for the alkylation unaffected by shape selectivity effects. The supported catalysts 1.5–3% Pd/25% HSiW/SiO₂ showed the best results to give 85–88% iPrPh selectivity at 4.1–4.5% benzene conversion (up to 3.8% iPrPh yield) (entries 8 and 9). Therefore, with comparable yields, the Pd-HSiW catalysts are much more selective to iPrPh than the Pd-HZSM-5 ones. It can be seen that Pd-HSiW and Pt-HSiW catalysts perform similarly (cf. entries 7 and 10), with the Pt catalysts predictably more active than Pd ones per metal loading. This, however, is compensated for by the lower price (by a factor of ~1.5) of Pd as compared to Pt.

Like with Pd-HZSM-5 catalysts, benzene conversion was found to increase with Pd loading in Pd-HSiW catalysts to level off at ≥1.5% Pd loading (Figure 1; Table 2, entries 2–5). This indicates that

the propane dehydrogenation step (1) reached quasi-equilibrium at ca. 1.5% Pd loading. A similar trend has been observed for Pt-HSiW [18].

Similar to the supported Pt-HSiW catalysts [18], the supported Pd-HSiW catalysts suffered from deactivation, as shown in Figure 3. This may be explained by catalyst coking (Table 2, entry 8). In contrast, the mixed and especially two-bed Pd/C + 25% HSiW/SiO₂ catalysts were more stable on stream (Figure 4), albeit with a lower *i*PrPh selectivity of 70–74% (Table 2, entries 4–6). A similar performance has also been observed for their Pt counterparts [18]. The high activity of both the mixed and two-bed catalysts indicates no reaction limitation by the migration of alkene intermediates between metal and acid sites within these mesoporous catalysts. This is different from the microporous Pd-HZSM-5 catalysts (see above). The better performance stability of these catalysts compared to the supported Pd/25%HSiW/SiO₂ catalyst may due to their better resistance to coking [18].

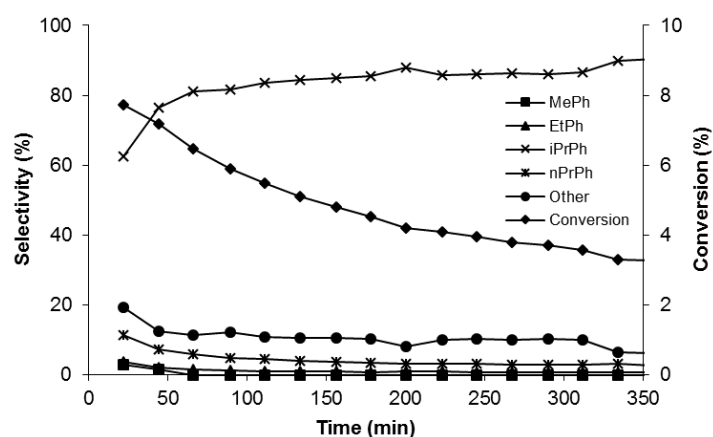


Figure 3. Time course for benzene alkylation by propane over 2% Pd/25% HSiW/SiO₂ (0.20 g catalyst, 300 °C, 1 bar pressure, inlet molar ratio C₆H₆/C₃H₈ = 1:9, 10 mL min^{−1} flow rate, W/F = 80 g h mol^{−1}; catalyst pre-treatment at 300 °C/1 h in H₂ flow).

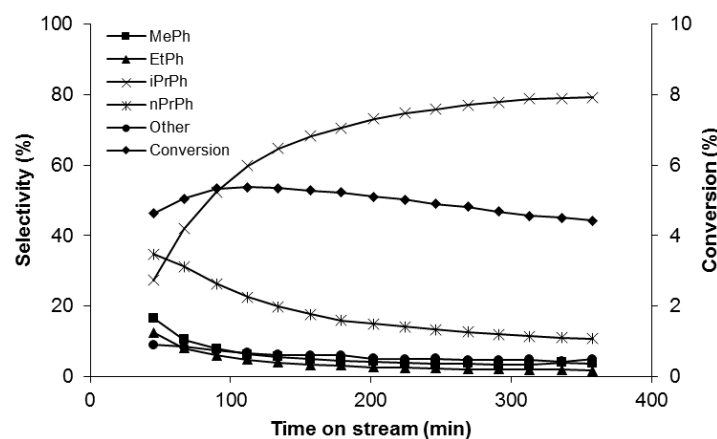


Figure 4. Time course for benzene alkylation by propane over two-bed catalyst 7.1% Pd/C (0.04 g, top bed) + 25%HSiW/SiO₂ (0.16 g, bottom bed) (0.20 g total catalyst weight, 1.4% Pd, 300 °C, 1 bar pressure, inlet molar ratio C₆H₆/C₃H₈ = 1:9, 10 mL min^{−1} flow rate, W/F = 80 g h mol^{−1}; catalyst pre-treatment at 300 °C/1 h in H₂ flow).

2.3. Effect of Gold Additives

Bimetallic AuPd and AuPt catalysts have attracted much interest because of their enhanced performance compared to monometallic counterparts ([19–29] and references therein), especially in hydrogenation [29], hydrodeoxygenation [20,26], hydrodesulfurisation [27,28], oxidation [21–23], and

other reactions (for review, see [19,24,25]). For example, the addition of gold to the bifunctional Pt/CsPW catalyst ($\text{CsPW} = \text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$) for the hydrodeoxygenation of 3-pentanone has been found to increase catalyst activity and catalyst stability to deactivation, whereas the Au itself was inert in this reaction [26]. Gold enhancement of catalyst performance is usually attributed to Au alloying through ensemble (geometric) and ligand (electronic) effects of the constituent elements [24,25]. Previously reported scanning transmission electron microscopy–energy dispersive X-ray spectroscopy (STEM-EDX) and X-ray diffraction (XRD) analyses of AuPt/CsPW catalysts show the presence of bimetallic particles with a wide range of Au/Pt atomic ratios in such catalysts [26].

Here, we looked at the effect of gold additives on the performance of Pd-HZSM-5 and Pd-HSiW catalysts in the alkylation of benzene by propane. The results, including benzene conversions and product selectivities, are shown in Table S1 in the Supplementary Material. Supported and mixed gold catalysts in the absence of Pd (0.5% Au/HZSM-5, 5% Au/C + HZSM-5 (2% Au) and 10% Au/C + HSiW/SiO₂ (2% Au)) showed very low activity (0.4–0.5% benzene conversion). No enhancing effect of gold was found in the case of the mixed Pd/C + HZSM-5 catalysts. Thus, Pd/C + HZSM-5 (1.4% Pd) and AuPd/C + HZSM-5 (1.2% Pd, 2% Au) gave similar benzene conversions of 9.2 and 8.8%, respectively, with the same product selectivity. In contrast, the HSiW-based mixed catalysts AuPd/C + HSiW/SiO₂ (1.2% Pd, 2.0% Au) showed a small enhancement of benzene conversion in comparison to Pd/C + HSiW (1.4% Pd) (Table S1). Even better activity enhancement was observed in the case of the two-bed catalysts AuPd/C + HSiW/SiO₂ (1.2% Pd, 2.0% Au) versus Pd/C + HSiW/SiO₂ (1.4% Pd) (5.8 and 5.2% conversion, respectively, with product selectivity unchanged) (Figure 5). Given the difference in Pd loading, the enhancement of benzene conversion amounts to about 20%. Similar results were obtained for the two-bed catalysts with lower metal loadings (Pd/C + HSiW/SiO₂ (0.71% Pd) and AuPd/C + HSiW/SiO₂ (0.60% Pd, 1.0% Au)).

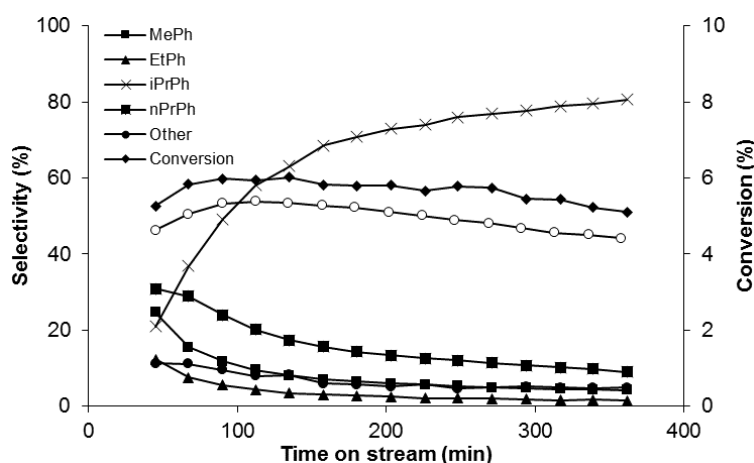


Figure 5. Time course for benzene alkylation by propane over two-bed catalyst 9.9% Au/6.0% Pd/C (0.04 g, top bed) + 25%HSiW/SiO₂ (0.16 g, bottom bed) (0.20 g total catalyst weight, 2% Au, 1.2% Pd, 300 °C, 1 bar pressure, inlet molar ratio $\text{C}_6\text{H}_6/\text{C}_3\text{H}_8 = 1:9$, 10 mL min^{−1} flow rate, $W/F = 80 \text{ g h mol}^{-1}$; catalyst pre-treatment at 300 °C/1 h in H₂ flow). Open circles show the conversion with Pd/C + 25% HSiW/SiO₂ (1.4% Pd) taken from Figure 4 for comparison.

Although clearly discernible, this Au enhancement is considerably smaller than that reported previously for the hydrodeoxygenation of octanoic acid (AuPd/SiO₂ catalyst) [20] and 3-pentanone (AuPt/CsPW catalyst) [26]. This may be explained by the reaction conditions of benzene alkylation. The relatively small Au effect on the dehydrogenation activity of Pd-HSiW catalyst can be attributed to the propane dehydrogenation step being close to equilibrium (Figure 1). Therefore, any enhancement of Pd activity would not cause a significant increase in benzene conversion.

3. Materials and Methods

3.1. Chemicals and Catalysts

Heteropoly acid hydrate $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (HSiW, 99.9%) containing 20–28 H_2O molecules per Keggin unit was from Sigma-Aldrich. The quantity of crystallisation water in HSiW was measured by thermogravimetric analysis (TGA). Zeolite NH_4^+ -ZSM-5 ($\text{Si}/\text{Al} = 10$, specific surface area $S_{\text{BET}} = 400 \text{ m}^2 \text{ g}^{-1}$) was from Zeolyst International. It was transformed into the H^+ form by calcination in air at 500°C for 6 h. Carbon-supported palladium 10%Pd/C was from Johnson Matthey (7.1% Pd content in dried catalyst from inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis). $\text{Pd}(\text{acac})_2$ and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ were purchased from Sigma-Aldrich. Aerosil 300 silica ($S_{\text{BET}} = 300 \text{ m}^2 \text{ g}^{-1}$) was from Degussa. Propane, N_2 and H_2 gases (all >99% purity) were from the British Oxygen Company. From GC analysis, the propane contained C_3H_8 (99.20%), C_2H_6 (0.76%), C_3H_6 (0.01%), C_4H_{10} (0.03%), and methane (0.004%).

Silica-supported HSiW catalysts were prepared by the impregnation of Aerosil 300 silica by an aqueous HSiW solution, which was then dried at $150^\circ\text{C}/10^{-3} \text{ kPa}$ for 1.5 h [30,31]. The integrity of the HSiW Keggin structure on the silica surface in fresh and spent catalysts was confirmed by infrared spectroscopy (Figure S1 in the Supporting Material). Pd/HSiW/ SiO_2 and Pd/HZSM-5 catalysts were prepared by the impregnation of 25% HSiW/ SiO_2 or HZSM-5 with 0.02 M $\text{Pd}(\text{acac})_2$ solution in benzene, followed by the slow rotoevaporation of benzene at room temperature, as described elsewhere [32]. The catalysts were dried under vacuum at $150^\circ\text{C}/10^{-3} \text{ kPa}$, then reduced in an oven by H_2 flow at 250°C for 2 h. The bimetallic 10% Au/6.0% Pd/C catalyst was prepared by the impregnation of 7.1% Pd/C with an aqueous solution of HAuCl_4 , followed by drying and reduction by H_2 flow at 250°C for 2 h. After reduction, Pd and Au loading in supported catalysts was confirmed by ICP-AES; this was in good agreement with the loading expected from the preparation stoichiometry (e.g., 10% Au/6.4% Pd/C from stoichiometry and 9.9% Au/6.0% Pd/C from ICP-AES analysis). Physical mixtures of 7.1% Pd/C with 25% HSiW/ SiO_2 or HZSM-5 containing a specified percentage of Pd were prepared by grinding mixtures of these components. Physical mixtures of 10% Au/6.0% Pd/C with 25% HSiW and HZSM-5 were prepared in the same way.

3.2. Techniques

The surface area, pore volume, and pore diameter of catalysts were determined from N_2 physisorption at -196°C using a Micromeritics ASAP 2010 analyser. The samples were outgassed at 240°C for 2 h. Nitrogen adsorption isotherms and pore size distribution for Pd-HSiW and Pd-HZSM-5 catalysts are shown in Figures S2–S5. ICP-AES elemental analysis was performed on a Spectro Ciros emission spectrometer. Powder X-ray diffraction (XRD) patterns of catalysts were recorded on a PANalytical Xpert diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$) and attributed using the JCPDS database. Diffuse reflectance infrared Fourier transform (DRIFT) spectra of catalysts were recorded on a Nicolet Nexus FTIR spectrometer using powdered samples of catalyst mixtures with KBr.

Average metal particle size, d , in supported catalysts was estimated from XRD using the Scherrer equation. Metal dispersion, D , defined as the metal (M) fraction at the surface, $D = M_s/M_{\text{total}}$, was calculated from the empirical equation $D = 0.9/d \text{ (nm)}$ [33]. XRD patterns of supported Pd and Au catalysts are shown in Figures S6–S8 in the Supplementary Material. Table 3 shows the texture and metal dispersion of the catalysts studied. The acid strength of heteropoly acids, including HSiW, has been characterised previously using ammonia adsorption microcalorimetry [18,31].

Table 3. Catalyst characterisation.

Catalyst	S_{BET}^1 ($\text{m}^2 \text{g}^{-1}$)	Pore Volume 2 ($\text{cm}^3 \text{g}^{-1}$)	Pore Diameter 3 ($\text{\AA}$)	d^4 (nm)	D^5
25% HSiW/SiO ₂	215	0.95	171		
2% Pd/25% HSiW/SiO ₂	189	0.75	159	5.0	0.18
HZSM-5	301	0.22	31		
2% Pd/HZSM-5	262	0.20	31	10	0.090
7.1% Pd/C				11	0.082
10% Au/C				89	0.010
9.9% Au/6.0% Pd/C				13 (Pd) 62 (Au)	0.069 (Pd) 0.015 (Au)

¹ BET surface area. ² Single point pore volume. ³ Average BET pore diameter. ⁴ Metal particle size from XRD. ⁵ Metal dispersion calculated from the empirical equation $D = 0.9/d$ (nm).

3.3. Catalyst Testing

The gas-phase alkylation of benzene by propane was carried out at 300 °C and an inlet C₆H₆/C₃H₈ molar ratio of 1:9 under ambient pressure using a quartz fixed bed reactor (9.0 mm i.d.) with online GC analysis (Varian 3800 gas chromatograph with a 30 m × 0.32 mm × 0.5 µm Zebron ZB-WAX capillary column and a flame ionisation detector), as described elsewhere [18]. The reactor was charged with 0.20 g catalyst powder with a particle size of 45–180 µm. The gas feed containing propane (90 kPa) and benzene (10 kPa) entered the reactor from the top with a 10 mL min^{−1} flow rate (space time $W/F = 80 \text{ g h mol}^{-1}$, where W is the catalyst mass and F is the benzene molar flow rate). Prior to reaction, the catalysts were pre-treated in situ in H₂ flow (10 mL min^{−1}) for 1 h at reaction temperature. The selectivity to alkylbenzenes was defined as moles of alkylbenzene formed per one mole of benzene converted and quoted in mole %. The mean absolute percentage error in product selectivity and conversion was ≤10% and the carbon balance was maintained within 95%.

4. Conclusions

It has been demonstrated that bifunctional Pd-acid catalysts (Pd-heteropoly acid and Pd-zeolite) are active in the alkylation of benzene by propane to yield isopropylbenzene (iPrPh). Keggin-type tungstosilicic acid H₄SiW₁₂O₄₀ (HSiW) and zeolite HZSM-5 were used as the acid components in these catalysts. The mesoporous catalyst Pd/HSiW/SiO₂ was much more selective to iPrPh (up to 88%) than the microporous catalyst Pd/HZSM-5, which gave only 11–18% iPrPh selectivity. The reaction proceeded via the bifunctional reaction pathway, including the Pd-catalysed dehydrogenation of propane to propene followed by the acid-catalysed alkylation of benzene with the propene thus formed. Evidence has been provided that the first step reached quasi-equilibrium at 1.5–2% Pd loading, and the second step became rate limiting. The addition of gold to Pd-HSiW has been found to slightly enhance the activity of this catalyst.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/7/8/233/s1, Figure S1: FTIR spectra of catalysts, Figures S2–S5: Catalyst texture, Figures S6–S8: XRD pattern of catalysts, Table S1: Alkylation over PdAu catalysts.

Acknowledgments: We thank Shaqra University, Shaqra, Saudi Arabia for PhD studentship (A. Alotaibi).

Author Contributions: I.K. and E.K. conceived and designed the experiments; A.A. and S.H. performed the experiments; I.K. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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