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Selective Alkylation of Benzene with Propane over Bifunctional Pt-Heteropoly Acid Catalyst

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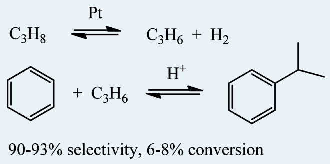
Ⓢ *Supporting Information*

ABSTRACT: The alkylation of benzene with propane to yield isopropylbenzene proceeds with high selectivity over bifunctional metal−acid catalysts comprising Pt and Keggin heteropoly acid in a fixed-bed reactor at 250−350 °C and 1 bar pressure. Most efficiently the reaction occurs over $Pt/H_4SiW_{12}O_{40}/SiO_2$ catalyst at 300 °C, giving isopropylbenzene with 90−93% selectivity at 6−8% benzene conversion, significantly exceeding the efficiency of previously reported Pt/HZSM-5 catalyst. The alkylation proceeds through bifunctional reaction pathway including dehydrogenation of propane to propene (1) on Pt sites followed by benzene alkylation with propene (2) on acid sites. At Pt loadings above 0.5%, step 1 is at fast quasi-equilibrium and step 2 is the rate-limiting one.



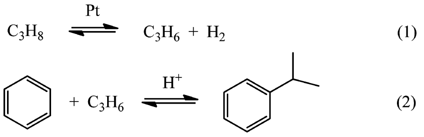
KEYWORDS: *alkylation with alkanes, benzene, propane, isopropylbenzene, Pt-heteropoly acid catalysts*

1. INTRODUCTION

Effective functionalization of light alkanes constituting natural gas, such as methane, ethane, and propane, has long been and still remains one of the greatest challenges for catalysis science.[1,2] Involving alkanes in reactions with other organic molecules, e.g., aromatic hydrocarbons, is important direction of light alkane utilization. The alkylation of benzene with ethane and propane to produce ethylbenzene (EtPh) and isopropylbenzene (iPrPh)) has attracted particular interest.[3] EtPh and iPrPh are the key intermediates in manufacturing styrene and phenol and produced commercially on a very large scale by the well-established acid-catalyzed alkylation of benzene by alkenes, viz., ethene and propene.[4] The replacement of ethene and propene by abundant and inexpensive alkanes would lead to more cost-effective and environmentally benign production of these commodity chemicals.[4]

Olah et al.[5] pioneered the alkylation of benzene with light alkanes in liquid superacid media to obtain EtPh and iPrPh in low yields (1.0 and 1.4%) at 25 °C in 24 h reaction time. Later more efficient and environment-friendly solid catalysts had been discovered for the alkylation of benzene with ethane[6−14] and propane[15−20] in the gas phase. These catalysts comprise zeolites modified with metals such as Pt, Pd, Re, Ga, or Zn and operate via bifunctional pathway, which includes alkane dehydrogenation on metal sites to form alkene and H_2 followed by benzene alkylation with the alkene on acid sites (Scheme 1).

Scheme 1. Alkylation of Benzene by Propane via Bifunctional Catalyzed Pathway



Best results have been achieved using Pt-modified HZSM-5 zeolites (MFI structure). Lukyanov et al.[9] have reported >90% EtPh selectivity at a close to equilibrium benzene conversion of 11.6% in the alkylation of benzene with ethane over 1%Pt/HZSM-5 (Si/Al = 36) at 370 °C, $[C_6H_6]/[C_2H_6]$ = 1:9 mol/mol, and 1 bar pressure. The yield can be further increased by adding a hydrogen acceptor to shift equilibrium in step 1; however, this effect decreases with time on stream due to saturation of acceptor capacity.[12]

The alkylation of benzene with propane, in contrast to the reaction with ethane, has proved to be more difficult to achieve high selectivity. Smirnov et al.[16] have studied this reaction with a range of Pt/HZSM-5 catalysts (Si/Al = 25−160) with and without addition of Zr_2Fe as a hydrogen acceptor to shift propane dehydrogenation equilibrium. In the presence of Zr_2Fe, iPrPh has been obtained with 32% selectivity at 14.4% conversion (4.6% yield) using 0.22%Pt/HZSM-5 (Si/Al = 160) as the catalyst at 350 °C, 1 bar pressure and $[C_6H_6]/[C_3H_8]$ = 1:1. In the absence of Zr_2Fe, the conversion dropped to 6.6%, with the selectivity unchanged (2.1% iPrPh yield). It should be noted that the main product was nPrPh (50% selectivity) rather than the favorable from the carbenium ion mechanism iPrPh. This points to the product shape selectivity control imposed by HZSM-5, i.e., iPrPh formed initially possibly isomerized on HZSM-5 proton sites to nPrPh possessing higher diffusion mobility within zeolite micropores. Other alkylation products such as MePh, EtPh, and unidentified C_9−C_{11} alkylarenes were also formed. MePh and EtPh are thermodynamically more favorable than iPrPh and probably arise from cracking reactions on zeolite acid sites.[16] It is likely, therefore, that the poor selectivity of benzene alkylation with propane on Pt/HZSM-5 is the result of the confinement of product molecules within

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zeolite micropores causing their isomerization and cracking to form primarily nPrPh together with the range of byproducts observed. In this regard, it is conceivable that bifunctional catalysts based on strong solid acids possessing larger pores could improve reaction selectivity.

In the past decade, we have investigated bifunctional heterogeneous catalysis by Keggin heteropoly acids (HPAs) modified with platinum group metals in a wide range of gas- and liquid-phase reactions.[21−24] HPAs are commercially available solid materials possessing very strong Brønsted acidity, stronger than zeolites and common mineral acids.[25,26] These have found many applications in catalysis, including several industrial processes.[26] Supporting HPA on oxide supports provides solid acid catalysts with wide range of pore geometries, e.g., SiO_2-supported HPAs possess both strong acidity and mesoporous structure.[26] Here we demonstrate highly efficient bifunctional catalysis by Pt-modified Keggin HPA $H_4SiW_{12}O_{40}$ for the alkylation of benzene with propane to give iPrPh with >90% selectivity.

2. EXPERIMENTAL SECTION

2.1. Chemicals and Catalysts. Heteropoly acid hydrates $H_3PW_{12}O_{40}$ (HPW, 99%) and $H_4SiW_{12}O_{40}$ (HSiW, 99.9%) containing 20−28 H_2O molecules per Keggin unit were purchased from Sigma-Aldrich. The amount of crystallization water in heteropoly acids was determined by TGA. Zeolite NH_4^+-ZSM-5 (Si/Al = 18, specific surface area S_{BET} = 400 m^2 g^{-1}) was from Zeolyst International. It was converted into the H^+ form by air calcination at 500 °C for 6 h. Carbon-supported platinum 10%Pt/C was from Johnson Matthey (7.0% Pt content in dried catalyst from ICP-AES analysis). $Pt(acac)_2$ and $Pt(NH_3)_4(NO_3)_2$ were purchased from Sigma-Aldrich. Propane, N_2 and H_2 gases (all >99% purity) were supplied by 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%).

Supported HPA catalysts were prepared by wet impregnation of oxide supports with an aqueous HPA solution and dried at 150 °C/10^{-3} kPa for 1.5 h.[27,28] The oxide supports P25 titania (anatase/rutile = 3:1) and Aerosil 300 silica (S_{BET} = 300 m^2 g^{-1}) were from Degussa. ZrO_2 and Nb_2O_5 oxides were prepared in-house[27,28] and calcined at 400 °C in air for 5 h.

Pt-HPA bifunctional catalysts were prepared by wet impregnation of acidic component, e.g., 25%HPA/SiO_2, with 0.02 M $Pt(acac)_2$ solution in benzene at room temperature for 1 h, followed by slow evaporation of benzene in a rotary evaporator at room temperature.[24] The catalyst was dried under vacuum at 150 °C/10^{-3} kPa and then reduced in oven by hydrogen flow at 250 °C for 2 h. 0.31%Pt/HZSM-5 was prepared by the literature procedure[22] involving adsorption of Pt(II) on to zeolite from 0.01 M aqueous solution of $Pt(NH_3)_4(NO_3)_2$ followed by washing with distilled water, air calcination at 450 °C for 2 h and reduction by H_2 at 400 °C for 2 h. The Pt loading quoted was determined by the ICP-AES analysis. Physical mixtures of 7%Pt/C with 25%HPA/SiO_2 or HZSM-5 containing 0.7% of Pt were prepared by grinding a 1:9 w/w mixture of these compounds.

2.2. Techniques. BET surface area and porosity of catalysts were determined from nitrogen physisorption measured on a Micromeritics ASAP 2010 instrument at −196 °C. Before measurement, the samples were evacuated at 250 °C for 2 h. Thermogravimetric analyses were carried out using a Setaram TG-DSC 111 differential scanning calorimeter. DRIFT (diffuse reflectance infrared Fourier transform) spectra of catalysts were recorded on a Nicolet Nexus FTIR spectrometer using powdered catalyst mixtures with KBr. Temperature-programmed reduction (H_2-TPR) of catalysts was carried out on a Micromeritics TPD/TPR 2900 apparatus equipped with a thermal conductivity detector. Catalyst samples (20−30 mg) were heated up to 800 °C at a rate of 10 °C min^{-1} in a H_2−N_2 (5:95) gas flow (60 mL min^{-1}). ICP-AES elemental analysis was carried out on a Spectro Ciros emission spectrometer. The amount of carbon deposited on postreactor catalysts was measured by combustion elemental analysis.

Pt dispersion, D, defined as the fraction of metal at the surface, $D = Pt_s/Pt_{total}$, was determined by pulse chemisorption of CO in He flow at 50 °C using Micromeritics TPD/TPR 2900 instrument (20 mg catalyst sample, 50 μL pulses of pure CO, adsorption stoichiometry Pt_s:CO = 1). The average diameter of metal particles, d, was calculated from the empirical equation d (nm) = $0.9/D$.[29] Table 1 shows the texture and Pt dispersion of the catalysts studied.

Table 1. Catalyst Characterization

catalyst	S_{BET}[a]	pore volume[b]	pore size[c]	D[d]	d[e]	ΔH[f]
	m^2 g^{-1}	cm^3 g^{-1}	Å	%	nm	kJ mol^{-1}
7%Pt/C				39	2.3	
25%HPW/SiO_2	198	1.00	203			
25%HSiW/SiO_2	191	0.84	177			
1%Pt/25%HPW/SiO_2	189	0.92	195	27	3.3	
1%Pt/25%HSiW/SiO_2	181	0.88	194	24	3.8	
0.31%Pt/HZSM-5	369	0.21	24	60	1.5	
15%HSiW/SiO_2	221	1.02	185			−154
15%HPW/SiO_2	202	1.00	169			−154
15%HPW/TiO_2	45	0.20	174			−143
15%HPW/Nb_2O_5	126	0.11	34			−132
15%HPW/ZrO_2	109	0.09	36			−121

[a] BET surface area. [b] Single point total pore volume. [c] Average BET pore diameter. [d] Pt dispersion in catalysts determined from CO chemisorption. [e] Pt particle size calculated from equation d (nm) = $0.9/D$. [f] Initial enthalpy of ammonia adsorption at 150 °C (±3 kJ mol^{-1}).[27,28]

2.3. Catalyst Testing. The alkylation of benzene with propane was carried out in the gas phase at 250−350 °C and an inlet C_6H_6/C_3H_8 molar ratio of 1:9 under atmospheric pressure in a quartz fixed-bed down-flow reactor (9.0 mm internal diameter) with online GC analysis (Varian 3800 instrument with a 30 m × 0.32 mm × 0.5 μm Zebron ZB-WAX capillary column and a flame ionization detector) (Figure S1, Supporting Information). For more accurate analysis of C_1−C_3 hydrocarbon products, a 60 m × 0.32 mm GS-GasPro capillary column was used, which allowed for complete separation of these hydrocarbons. The temperature in the reactor was controlled by a Eurotherm controller using a thermocouple placed at the top of the catalyst bed. Benzene was fed into the gas flow by passing propane flow controlled by a Brooks mass flow controller through a stainless steel saturator, which held liquid benzene at 20 °C to maintain the chosen reactant partial pressure of 10 kPa.[30] The downstream gas lines and valves were heated to 150 °C to prevent substrate and product condensation. The reactor was packed with 0.20 g catalyst powder of 45−180 μm particle size. The gas feed entered the

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reactor at the top at a flow rate of 10 mL min^{-1} (space time W/F = 80 g h mol^{-1}, where W (g) is the catalyst weight and F (mol h^{-1}) is the molar flow rate of benzene). Prior to reaction, the catalyst was pretreated in H_2 for 1 h at the reaction temperature. The downstream gas flow was analyzed by the online GC to obtain benzene conversion and product selectivity. The selectivity to alkylbenzenes was defined as moles of product formed per 1 mol of benzene converted and quoted in mole percent. The mean absolute percentage error in conversion and selectivity was ≤10%, and the carbon balance was maintained within 95%.

3. RESULTS AND DISCUSSION

3.1. Thermodynamic Analysis. The alkylation of benzene with propane via bifunctional pathway combines propane-to-propene dehydrogenation (1) and benzene alkylation with propene thus formed (2) (Scheme 1). Step 1 is thermodynamically unfavorable, whereas step 2 is a favorable one. Tungsten HPAs are active catalysts for the alkylation of benzene with propene (step 2)[31] as well as for the reverse reaction of iPrPh cracking.[32] Figure 1 shows the Gibbs free energy (ΔG) for these steps calculated from thermodynamic data[33−36] (see the Supporting Information (SI) for details). At 300 °C and 1 bar pressure, equilibrium conversion of propane in step 1 is only 0.55%. For benzene alkylation with propane, ΔG is positive at 30−35 kJ mol^{-1} in the temperature range of 25−800 °C. Equilibrium conversion of benzene at 300 °C and $[C_6H_6]/[C_3H_8]$ molar ratio of 1:1 is 2.8%. At the ratio $[C_6H_6]/[C_3H_8]$ = 1:9 applied in this work, it increases to 8.2% (Figure 1).

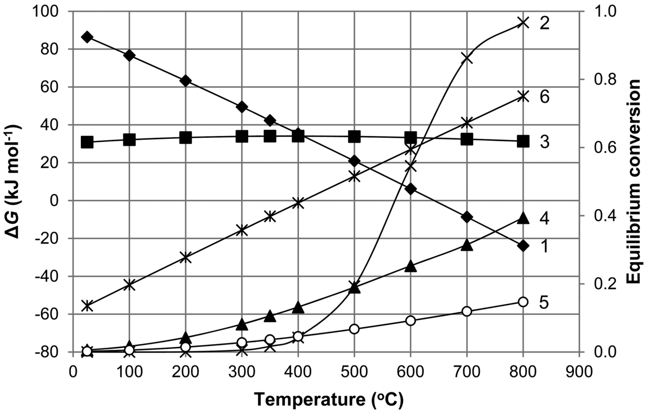

Figure 1. Gibbs free energy (ΔG) and equilibrium conversion (X) for dehydrogenation of propane (undiluted C_3H_8) and alkylation of benzene with propane as a function of temperature at 1 bar pressure: (1) ΔG and (2) X for $C_3H_8 = C_3H_6 + H_2$; (3) ΔG and (4) X at $[C_6H_6]/[C_3H_8] = 1:9$ and (5) X at $[C_6H_6]/[C_3H_8] = 1:1$ for $C_6H_6 + C_3H_8$ = iPrPh + H_2; (6) ΔG for $C_6H_6 + C_3H_6$ = iPrPh.

Table 2 shows the experimental conversion values for propane dehydrogenation (1) over bifunctional catalyst 1%Pt/25%HSiW/SiO$_2$ at 300−400 °C under typical reaction conditions applied for benzene alkylation in this work. It is evident that the experimental values of propane conversion are practically equal, within the accuracy of measurement, to the calculated equilibrium values, which indicates that the dehydrogenation reaction is fast in this system. On top of that, the amount of methane and ethane present in propane flow did not change hence propane cracking did not occur in this temperature range. Propane aromatization did not occur either, as no aromatic compounds were found among the products.

Table 2. Propane Dehydrogenation over 1%Pt/25%HSiW/SiO$_2$[a]

temperature (°C)	300	350	400
experimental propane conversion (%)[b]	0.48	1.93	4.56
calculated equilibrium conversion (%)	0.55	1.68	4.25

[a] Catalyst (0.20 g) pretreated in situ at 300 °C/1 h in H_2 flow, 10 mL min^{-1} propane flow rate, W/F = 80 g h mol^{-1}, 1 bar pressure, 1 h time on stream. [b] Inlet gas contained propane (99.20%), propene (0.01%), ethane (0.76%), butane (0.03%), and methane (0.004%); methane and ethane content did not change in the downstream flow.

3.2. Alkylation of Benzene over Pt/HZSM-5. It is essential to compare new Pt/HPA and previously reported Pt/HZSM-5 catalysts at the same reaction conditions. Therefore, first we tested Pt/HZSM-5 for benzene alkylation with propane in our system at 300 °C, contact time W/F = 80 g h mol^{-1} and $[C_6H_6]/[C_3H_8]$ = 1:9. Representative results are given in Table 3. Supported bifunctional catalyst 0.31%Pt/HZSM-5 gave 16.4% iPrPh selectivity at 19.9% conversion (3.3% benzene-

Table 3. Alkylation of Benzene with Propane via Bifunctional Catalyzed Pathway[a]

		aromatic selectivity (%)[c]				
catalyst	conversion[b] (%)	MePh	EtPh	iPrPh	nPrPh	C_{9+}
HZSM-5	1.1 (2)	25.5	22.8	14.2	24.6	12.9
25%HSiW/SiO$_2$	0.2 (2)	0	1.5	81.0	3.1	14.4
7%Pt/C+SiO$_2$[d]	0.1 (2)	0	0	37.2	54.6	8.2
0.31%Pt/HZSM-5	19.9 (8)	21.5	6.0	16.4	33.8	22.4
7%Pt/C+HZSM-5 (0.7%Pt)[d]	19.0 (6)	30.8	16.5	12.8	24.3	15.7
7%Pt/C+HZSM-5 (0.7%Pt)[e]	5.1 (7)	26.5	31.2	12.8	22.6	6.9
1%Pt/25%HPW/SiO$_2$	3.1 (3)	0	0.8	75.7	2.1	21.4
1%Pt/25%HSiW/SiO$_2$[f]	4.0 (3)	0	0.8	81.6	2.9	14.7
1%Pt/25%HSiW/SiO$_2$[g]	2.0 (3)	0	3.0	81.9	2.2	12.9
7%Pt/C+25%HPW/SiO$_2$ (0.7%Pt)[d]	3.8 (4)	0	1.6	85.7	2.6	10.2
7%Pt/C+25%HSiW/SiO$_2$ (0.7%Pt)[d]	5.5 (6)	0	0.5	89.2	2.4	7.8
7%Pt/C+25%HSiW/SiO$_2$ (0.7%Pt)[e]	7.6 (9)	0	0.5	90.4	3.0	6.0
7%Pt/C+25%HSiW/SiO$_2$ (0.7%Pt)[h]	6.2 (15)	0	0.7	92.6	2.7	4.2

[a] 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}; in situ catalyst pretreatment at 300 °C/1 h in H_2 flow, 10 mL min^{-1}. [b] Average conversion of benzene since steady state reached during time on stream (h) given in round brackets. [c] Selectivity to aromatic products including unidentified C_{9+} alkylbenzenes. [d] Uniform physical mixture 7%Pt/C (0.02 g) + HZSM-5, 25%HSiW/SiO$_2$, or SiO$_2$ (0.18 g). [e] Two catalyst beds: 7%Pt/C (0.02 g, top bed) and 25% HSiW/SiO$_2$ or HZSM-5 (0.18 g, bottom bed). [f] 1.2% coke content in the catalyst after reaction. [g] At 250 °C. [h] Two catalyst beds: 7%Pt/C (0.02 g, top bed) and 0.18 g 25%HSiW/SiO$_2$ (0.18 g, bottom bed) separated with ca. 1 mm SiO$_2$ layer.

based yield), with nPrPh (33.8%) and MePh (21.5%) formed as the main products. It should be noted that this catalyst showed stable performance for over 8 h on stream (Figure 2). In the absence of Pt, HZSM-5 gave only 1.1% benzene conversion with a similar iPrPh selectivity of 14.2%, which is in agreement with the previous report.[16] The reaction with Pt-free catalyst probably occurs through carbonium ion intermediate or transition state formed by propane protonation with the zeolite.[16] Uniform physical mixture 7%Pt/C + HZSM-5 (1:9 w/w) with 0.7% Pt content showed practically the same activity as the 0.31%Pt/HZSM-5 catalyst at 19.0% conversion and 12.8% iPrPh selectivity (Figure S2), with MePh (30.8%), nPrPh (24.3%) and EtPh (16.5%) formed as the main products (Table 3). This disagrees with the work of Smirnov et al.[16] who found a 4-fold decrease in catalyst activity when using a 1:1 w/w physical mixture of 0.3%Pt/CeO_2 and HZSM-5 (Si/Al = 25–160) instead of 0.22–0.29%Pt/HZSM-5 at 350 °C and $[C_6H_6]/[C_3H_8]$ = 1:1. At least partly, this may be explained by the decrease in Pt loading in the Pt/CeO_2 + HZSM-5 physical mixture in comparison with the supported Pt/HZSM-5 catalyst. Only when we used two catalyst beds, 7%Pt/C (top) and HZSM-5 (bottom) (1:9 w/w) separated by ~1 mm layer of silica, a 4-fold drop in benzene conversion was predictably observed, although the selectivity pattern did not change (Table 3, Figure S3). This supports the view that the selectivity of benzene alkylation with propane over Pt/HZSM-5 catalyst is controlled by acid-catalyzed transformations within zeolite microporous structure.

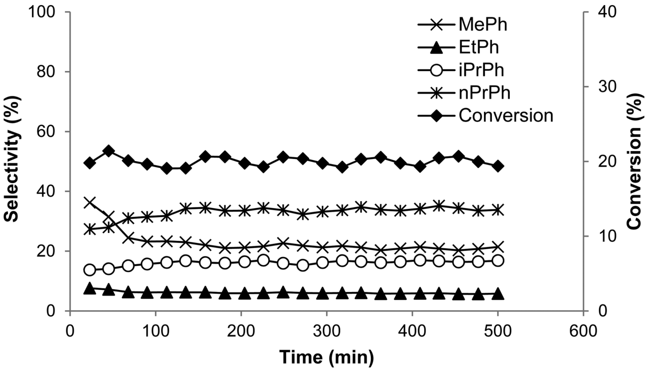

Figure 2. Time course for alkylation of benzene with propane over 0.31%Pt/HZSM-5 (Si/Al = 18; 0.20 g catalyst, 300 °C, 1 bar pressure, inlet molar ratio C_6H_6/C_3H_8 = 1:9, 10 mL min^{-1} flow rate, W/F = 80 g h mol^{-1}; in situ catalyst pretreatment at 300 °C/1 h in H_2 flow, 10 mL min^{-1}).

3.3. Alkylation of Benzene over Pt/HPA Catalysts. Bulk tungsten HPAs possess very strong proton sites.[25,26] The initial enthalpy of ammonia adsorption (ΔH) for bulk HPW and HSiW have been reported to be −197[27,28] and ≤−160[37] kJ mol^{-1}, respectively. The acid sites of MFI zeolites are weaker, ΔH = 131–150 kJ mol^{-1} (Si/Al = 20–70), from ammonia adsorption microcalorimetry and TPD.[38] However, supporting HPA reduces the acid strength because of HPA-support interaction[27,28] (Table 1).

Initial testing of supported HPA catalysts modified with platinum group metals showed that Pt catalysts were more active than Pd ones in the alkylation of benzene with propane, in agreement with previous studies.[3] Among Keggin HPAs tested, $H_4SiW_{12}O_{40}$ (HSiW) gave the best performance, followed by $H_3PW_{12}O_{40}$ (HPW). Bulk Cs salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, which is widely used as a strong solid acid catalyst[25,26] showed very low activity. Predictably, the best catalyst support was found to be SiO_2; other oxide supports such as TiO_2, Nb_2O_5, and ZrO_2 gave lower benzene conversions (see below) probably due to decreasing the acid strength of HPA.[27] Best performance in benzene alkylation with propane gave the catalysts comprising 0.5–1% Pt metal and 25%HSiW/SiO_2. These were mesoporous materials with S_{BET} = 181–191 m^2 g^{-1} and pore diameters of 177–194 Å (Table 1). For 1%Pt/25%HSiW/SiO_2, the N_2 adsorption isotherm and pore size distribution are shown in Figures S4 and S5. Benzene conversion increased with temperature from 250 to 300 °C. Further temperature increase to 350 °C did not produce any increase in conversion probably due to catalyst deactivation by coking. Therefore, further catalyst testing was carried out at 300 °C. Representative results are shown in Table 3.

The reaction with either Pt or HSiW as monofunctional catalysts gave a very low benzene conversion of 0.1–0.2% (Table 3). This clearly demonstrates that the alkylation of benzene with propane occurs through bifunctional metal-acid catalysis (Scheme 1).

The most striking feature of the alkylation over Pt/HPA catalysts is its high selectivity to iPrPh, which is the preferred alkylation product from the classical carbenium ion mechanism. For the Pt/HSiW/SiO_2 catalysts, the iPrPh selectivity was in the range of 83–93% (cf. 13–16% with Pt/HZSM-5, Table 3). The main byproducts were unidentified C_{9+} alkylarenes, with only small amounts of EtPh (0.5–1.6%) and nPrPh (2.1–3.0%) formed. MePh was not observed at all among the products. This is in agreement with the results on the alkylation of benzene by propene over supported HPA, which gives high selectivity to iPrPh with only negligible amount of nPrPh formed.[31] The difference in reaction selectivity between Pt/HPA/SiO_2 and Pt/HZSM-5 catalysts indicates that with Pt/HZSM-5 the alkylation is controlled by zeolite shape selectivity, whereas with Pt/HPA/SiO_2 the reaction is likely to occur under kinetic control. It is worth noting that Pt-free monofunctional acid catalysts HSiW/SiO_2 and HZSM-5 exhibited the same selectivity pattern (Table 3), which further strengthens this point.

1%Pt/25%HSiW/SiO_2 catalyst gave 81.6% iPrPh selectivity, with benzene conversion gradually decreasing from 7.5% to less than 4% over 3 h on stream. This can be explained by catalyst coking; 1.2% of coke was found in the spent catalyst, which could block Pt and/or HPA proton sites in the catalyst. The loss of acidity due to HPA reduction can be ruled out as the cause of catalyst deactivation since the HPA reduced only above 500 °C (see the H_2-TPR in Figures S6 and S7). The structural integrity of the HPA was also maintained during reaction as evidenced by the DRIFT spectra of fresh and spent catalysts, showing that the Keggin structure remained intact (Figure S8). The fact that HPW despite its superior acid strength was a less efficient partner in the Pt/HPA catalyst than HSiW may be the result of relatively more intense coking of HPW.

Physical mixture of 7%Pt/C + 25%HSiW/SiO_2 (1:9 w/w) with 0.7% Pt content exhibited more stable performance with a higher average conversion of 5.5% over 6 h on stream and 85.7% iPrPh selectivity. Figure 3 shows the time course for this reaction, which is typical of Pt/HSiW bifunctional catalysts. It is seen that iPrPh selectivity increases during first 2 h on stream to reach steady-state value at about 90%. At the same time,

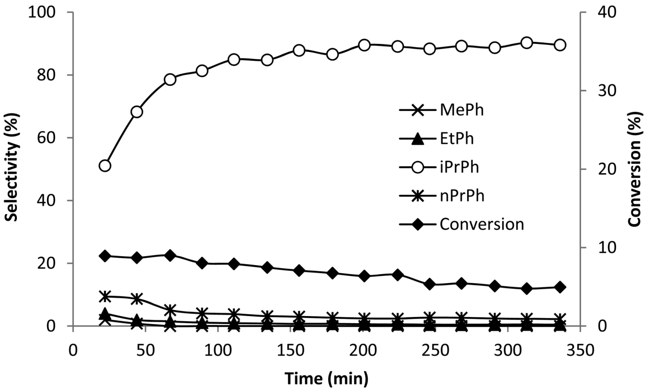

Figure 3. Time course for alkylation of benzene with propane over 7% Pt/C (0.02 g) + 25% HSiW/SiO_2 (0.18 g) physical mixture (0.20 g total catalyst weight, 0.7% Pt; 300 °C, 1 bar pressure, inlet molar ratio C_6H_6/C_3H_8 = 1:9, 10 mL min^{-1} flow rate, W/F = 80 g h mol^{-1}; in situ catalyst pretreatment at 300 °C/1 h in H_2 flow, 10 mL min^{-1}).

benzene conversion gradually decreases to level off at about 5%. This behavior may be explained by catalyst coking.

Even better conversion stability and higher iPrPh yield gave two-bed catalysts comprising 7%Pt/C and 25%HSiW/SiO_2 beds either unseparated or separated with ∼1 mm layer of SiO_2 (Table 3). The unseparated two-bed catalyst gave 7.6% conversion over 9 h on stream (Figure 4) with 90.4% iPrPh selectivity (6.9% yield). This yield is quite close to the equilibrium value (8.2%) and significantly higher than that reported so far (cf. 4.6% yield with hydrogen acceptor and 2.1% without it[16]). The catalyst with silica-separated beds exhibited stable 6.2% benzene conversion for 13 h on stream with iPrPh selectivity of 92.6%, the highest achieved in this work (Figure S9). The high activity of mixed and two-bed catalysts indicates that the reaction is not limited by migration of intermediates between metal and acid sites. The better performance stability of these catalysts in comparison to the supported 1%Pt/25% HSiW/SiO_2 catalyst may be explained by their better resistance to coking.

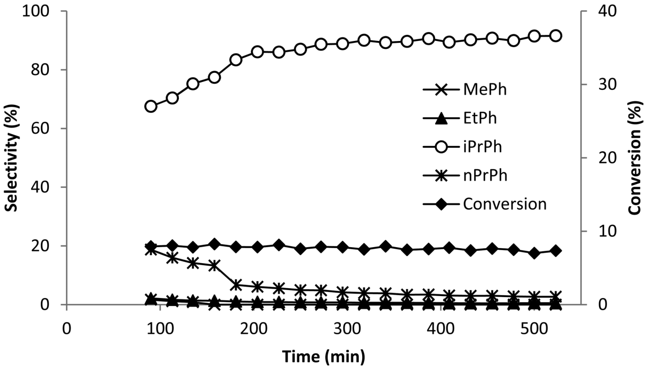

Figure 4. Time course for alkylation of benzene with propane over two-bed catalyst 7%Pt/C (0.02 g, top bed) + 25% HSiW/SiO_2 (0.18 g, bottom bed) (0.20 g total catalyst weight, 0.7% Pt; 300 °C, 1 bar pressure, inlet molar ratio C_6H_6/C_3H_8 = 1:9, 10 mL min^{-1} flow rate, W/F = 80 g h mol^{-1}; in situ catalyst pretreatment at 300 °C/1 h in H_2 flow, 10 mL min^{-1}).

The apparent activation energy for benzene alkylation with 1%Pt/25%HSiW/SiO_2 was roughly estimated to be 50 kJ mol^{-1} (from the results at 250 and 300 °C, Table 3). This value indicates that the reaction was not affected by mass transport limitations, thus supporting the view that the reaction selectivity was not controlled by pore diffusion.

Further mechanistic evidence was obtained from examination of effects of Pt loading and HPA acid strength on the rate of benzene alkylation. Figure 5 shows the effect of Pt loading on benzene conversion and iPrPh selectivity for the reaction over mixed catalyst 7%Pt/C + 25%HSiW/SiO_2. Both parameters increase with Pt loading and reach a plateau at a Pt loading of 0.5%. This indicates that at Pt loading above 0.5% propane dehydrogenation step 1 is at fast quasi-equilibrium. It should be noted that Pt dispersion was not varied here since the same 7% Pt/C catalyst was used in these experiments.

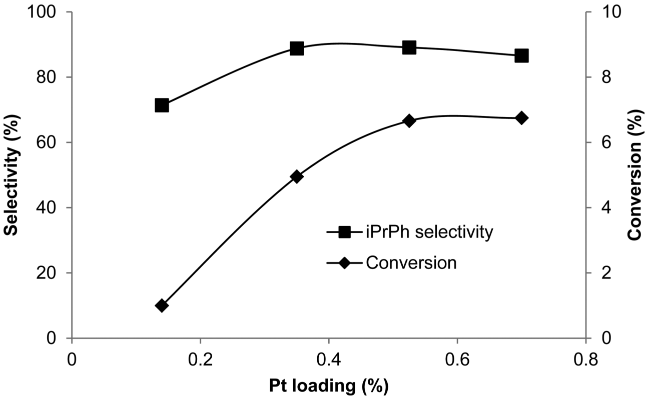

Figure 5. Effect of Pt loading on conversion and iPrPh selectivity of benzene alkylation over 7%Pt/C+25%HSiW/SiO_2 catalyst at 300 °C.

The catalytic activity of HPA in the conventional alkylation of benzene by propene has been found to increase with HPA acid strength.[31] Here the effect of HPA acid strength on catalyst activity in benzene alkylation by propane was assessed using mixed catalysts 7%Pt/C + 15%HPA/Support (1:9 w/w) at 0.7% Pt and 15% HPA loading and SiO_2, TiO_2, Nb_2O_5, and ZrO_2 as the HPA supports (Table 4). We used the mixed rather than two-bed catalysts because the former allowed better reproducible conversions to be obtained. The acid strength of the 15%HPA/Support catalysts has been determined previously by microcalorimetry of ammonia adsorption;[27,28] it decreases in

Table 4. Effect of Support on Alkylation of Benzene with Propane via Bifunctional Catalyzed Pathway[a]

		aromatic selectivity (%)[c]				
catalyst[b]	conversion[c] (%)	MePh	EtPh	iPrPh	nPrPh	C_{9+}
7%Pt/C+15% HSiW/SiO_2	7.3	0	1.0	85.8	3.5	9.7
7%Pt/C+15% HPW/SiO_2	4.0	0.6	1.6	82.5	3.2	12.1
7%Pt/C+15% HPW/TiO_2	2.4	0	1.9	82.9	2.1	13.2
7%Pt/C+15% HPW/Nb_2O_5	3.0	0.8	2.7	82.3	2.8	11.4
7%Pt/C+15% HPW/ZrO_2	2.4	0.5	2.5	83.6	2.2	11.2

[a]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}, 2 h time on stream; in situ catalyst pretreatment at 300 °C/1 h in H_2 flow, 10 mL min^{-1}). [b]Uniform physical mixture 7%Pt/C (0.02 g) + 15%HPA/Support (0.18 g) with 0.7% Pt content. [c]Conversion and selectivity values at 2 h time on stream.

the order of supports SiO_2 > TiO_2 > Nb_2O_5 > ZrO_2 (Table 1) owing to increasing interaction between HPA and support in this series.[27] As seen from Table 4, the conversion of benzene also decreases in this order, although reaction selectivity remains unchanged. The number of surface proton sites in these catalysts can be assumed to be equal to the total number of HPA protons (0.156 mmol g^{-1} for HPW and 0.208 mmol g^{-1} for HSiW).[28] This allows for turnover frequencies (TOF) to be obtained. The TOF values (h^{-1}) were calculated as reaction rate per single proton site. The reaction rate (r) was determined as $r = XF/W$ (mol h^{-1} g^{-1}), where X is the conversion of benzene and W/F = 80 g h mol^{-1} is the contact time. Figure 6 shows the plot of ln(TOF) versus ΔH for benzene alkylation, which demonstrates a fairly good correlation between the turnover reaction rate and the catalyst acid strength. This backs up the reaction mechanism through steps 1 and 2 (Scheme 1) and also supports the conclusion that at Pt loading above 0.5% the reaction is limited by step 2 of benzene alkylation with propene; whereas, step 1 is at fast quasi-equilibrium.

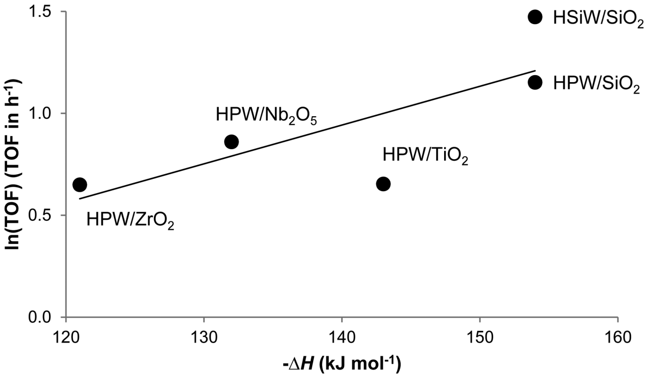

Figure 6. Plot of ln(TOF) vs ΔH for benzene alkylation over 1:9 w/w mixture 7%Pt/C+15%HPA/Support at 300 °C.

Mechanism of formation of alkylated aromatic byproducts in the alkylation of benzene by ethane and propane over Pt/HZSM-5 has been discussed in detail elsewhere.[9−11,16] MePh and EtPh, the main byproducts in the alkylation with propane, are more favorable thermodynamically than the desired iPrPh.[4,16] These have been suggested to arise from acid-catalyzed cracking of propane as well as from cracking and transalkylation of propylbenzenes (iPrPh and nPrPh).[16] In the reaction with Pt/HSiW, only small amounts of EtPh (0.5−3%) and nPrPh (2.1−3%) were formed together with unidentified C_{9+} aromatics (Table 3). As no propane cracking was observed (Table 2) and no MePh found among the products (Table 3), the formation of EtPh may be viewed as the result of iPrPh cracking, which would also produce methane. The latter was indeed found among the alkylation products. As to the nPrPh is concerned, it is likely to come from acid-catalyzed isomerization of iPrPh.

4. CONCLUSIONS

The alkylation of benzene with propane to yield isopropylbenzene proceeds with high selectivity over bifunctional metal-acid catalysts comprising Pt and Keggin heteropoly acid in a fixed-bed reactor at 250−350 °C and 1 bar pressure. Most efficiently the reaction occurs over $Pt/H_4SiW_{12}O_{40}/SiO_2$ catalyst, giving isopropylbenzene with 90−93% selectivity at 6−8% benzene conversion at 300 °C and an inlet C_6H_6/C_3H_8 molar ratio of 1:9. This significantly exceeds the efficiency of previously reported Pt/HZSM-5 catalyst.[16] The alkylation proceeds through the bifunctional reaction pathway (Scheme 1) including dehydrogenation of propane to propene (1) on Pt sites followed by benzene alkylation with propene (2) on acid sites. At Pt loadings above 0.5%, step 1 is at fast quasi-equilibrium and step 2 is the rate-limiting one. There is important difference in performance between $Pt/HPA/SiO_2$ and Pt/HZSM-5 catalysts. With the Pt/HZSM-5, reaction selectivity is controlled by acid-catalyzed transformations within zeolite microporous structure (product shape selectivity), leading to preferential formation of nPrPh together with cracking and transalkylation products such as MePh and EtPh rather that the desired iPrPh. In contrast, the mesoporous $Pt/HPA/SiO_2$ catalyst gives selectively iPrPh, i.e., the alkylation product favored from the carbenium ion mechanism. The preferred reactor design is a two-bed configuration involving Pt/C top (upstream) and $HSiW/SiO_2$ bottom (downstream) catalyst bed, providing better catalyst stability to deactivation as well as higher iPrPh selectivity. Further research is underway to explore other alkane/arene systems and compare the results obtained with the commercial systems for the production of alkylbenzenes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01102.

> Thermodynamic calculations, reactor setup, reaction time courses, DRIFT spectra, and H_2-TPR results (PDF)

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Notes

The authors declare no competing financial interest.

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