Alkylation of 1-dodecene with benzene over $H_3PW_{12}O_{40}$ supported on mesoporous silica SBA-15

Jun Wang* and Hai-Ou Zhu

College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, P.R. China

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The SBA-15 supported 12-phosphotungstic acid catalysts were prepared and measured in the alkylation of benzene with 1-dodecene at the atmospheric batch reactor. It is found that the catalysts exhibit much higher catalytic activity, selectivity and stability than HY zeolite in this reaction at the reaction temperature of 80 °C, with the 1-dodecene conversion of nearly 90%, 2-phenyldodecane selectivity of nearly 40%, and monoalkylbenzene selectivity of 100%.

KEY WORDS: linear alkylbenzene; SBA-15; heteropoly acid; mesoporous molecular sieve; phosphotungstic acid.

1. Introduction

Linear monoalkylbenzene (LAB) is the primary raw material for biodegradable detergent. Nowadays, its production mostly involves HF as the catalyst, which is a source of pollution and equipment corrosion. Thus, many efforts have been concentrated on solid acid catalysts for its environmentally friendly manufacture [1,2]. UOP and CEPSA announced their Detal process in early 1990s based on a fixed bed of solid acid catalyst [1–3]. Recently, zeolites have been the target catalyst, and Y zeolite proved to be one of the most active catalysts [3–5]. However, the unsatisfied catalytic stability and/or selectivity prevent its practical utilization.

Heteropoly acid (HPA) possesses the strong brönsted acidity, and has been widely investigated in numerous acid catalyzed reactions [6,7]. Owing to its very low surface area and high solubility in polar solvent, HPA catalysts supported on various materials, such as active carbon, silica, titania, resin, clay, MCM-41, etc., have been attracting much attention [8,9]. However, only a few and isolated reports have dealt with HPA catalysts for LAB synthesis [10].

Since the newly synthesized mesoporous silica SBA-15 [11] has a high surface area, large pore volume and high stability, it would be a qualified support for HPA. In this work, we initiate our investigation on the SBA-15 supported 12-phosphotungstic acid (PW) catalyst, observing that it is a highly efficient catalyst for the alkylation of benzene with 1-dodecene.

2. Experimental

SBA-15 was synthesized according to the previous literature [11]. According to the X-ray powder diffraction (XRD) and N_2 adsorption results for SBA-15, its *d*(100) is 6.6 nm, BJH pore size is 3.8 nm, and thus its wall thickness is 3.8 nm. PW catalysts supported on SBA-15 were prepared by impregnation as follows. SBA-15 was impregnated in the aqueous solution of $H_3PW_{12}O_{40} \cdot xH_2O$ (Shanghai Chem. Reagent Co., AR) with stirring at room temperature for 12 h, followed by evaporation at 60 °C and drying at 100 °C for 8 h. The obtained sample was denoted as m%PW/SBA-15, where m stands for the percentage of PW in the catalyst by weight. HY was prepared by the repeated ion-exchange of NaY with the aqueous solution of NH_4NO_3 (Shanghai Chem. Reagent Co., AR) at 80 °C for 2 h, followed by filtration, washing with water and drying at 120 °C for 8 h.

Alkylation of benzene with 1-dodecene was carried out at atmospheric pressure in a three-necked glass flask equipped with a magnetic stirrer and a reflux condenser. Before introducing into the reactor, PW/SBA-15 and HY were activated in air for 5 h at 300 and 500 °C, respectively. The reaction temperature was 80 °C, with typically a 5 ml/ml ratio of benzene (Nanjing Chem. Reagent Co., AR) to 1-dodecene (Fluka, 95%) and a 20 ml/g ratio of 1-dodecene to catalyst. The catalyst powder size was less than 200 mesh. The reaction mixture was sampled periodically and filtered to remove catalyst particles, followed by GC analysis using a 30 m SE30 capillary column with FID as the detector. Only 2- to 6-P (2- to 6-phenyldodecanes) were detected in the reaction. 2- to 6-dodecenes were also found, which are considered as the unconverted reactant when calculating the reaction conversion.

BET surface area of catalyst was achieved by N_2 adsorption on the Coulter Omnisorp 100CX equipment. XRD was obtained on the Bruker D8 Advance diffractometer to measure the dispersion of PW on the surface of SBA-15 using Ni-filtered Cu Ka radiation at 40 kV and 20 mA.

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* To whom correspondence should be addressed.
E-mail: junw0212@yahoo.com

Table 1
Conversion of 1-dodecene and product distribution over PW/SBA-15 and HY catalysts (reaction temperature = 80 °C; reaction time = 3 h; benzene/1-dodecene = 5 ml/ml; 1-dodecene/catalyst = 20 ml/g)

Catalyst	Conversion/%	Product distribution /%				
		2-P	3-P	4-P	5-P	6-P
SBA-15	0	–	–	–	–	–
10%PW/SBA-15	3.0	68.3	16.9	6.4	5.7	2.7
20%PW/SBA-15	45.8	44.1	21.7	12.9	12.0	9.3
30%PW/SBA-15	78.5	38.8	21.6	13.9	14.6	11.2
40%PW/SBA-15	84.5	38.3	21.5	14.1	13.8	12.4
50%PW/SBA-15	85.2	37.7	21.7	14.3	14.4	11.9
60%PW/SBA-15	89.7	37.3	22.0	14.3	13.8	12.6
70%PW/SBA-15	77.6	37.8	22.1	14.3	13.6	12.2
90%PW/SBA-15	32.3	49.3	21.3	11.6	10.4	7.4
PW	20.9	56.7	22.0	9.4	7.4	4.5
HY	61.7	30.7	13.7	16.6	17.1	21.9
HF[a]	?	16.7	16.4	17.5	24.1	25.3
HF[b]	92	20	17	16	23	24

[a] From reference [3]. C_{12}-alkylbenzene fraction from commercial LAB: liquid phase reaction; reaction temperature and conversion not indicated.
[b] From reference [13], reaction temperature = 16 ± 3 °C.

3. Results and discussion

The stabilized conversion of 1-dodecene and product distribution over PW/SBA-15 and HY catalysts are shown in table 1. No products were detected over pure SBA-15, while all PW/SBA-15 catalysts are active in the reaction. The conversion of 1-dodecene increases with the increase of PW loading up to 60%, and the further increase of PW loading results in a decrease of conversion. 60%PW/SBA-15 is observed to exhibit the highest conversion of 89.7%, which is four times more active than the pure PW. HY is also very active with the conversion being 61.7%, however, it is still much lower than those over 40–60%PW/SBA-15 catalysts.

The alkylation of benzene with dodecene goes through a carbonium ion mechanism [3,12]. The relative stability of the six possible carbonium ions increases as the C-number increases, the least stable one being the primary ion (1-position). In fact, due to its very low stability, 1-P isomer is not detected in the product. Among the five obtained phenyldodecane isomers, 2-P is the mostly desired one due to its better biodegradability and emulsibility. It is noteworthy in table 1 that 40–60%PW/SBA-15 catalysts show the selectivity for 2-P of nearly 40%, which is much higher than that over HF (⩽20%), where thermodynamic equilibrium is probably reached [3,13]. On the other hand, HY exhibits the selectivity for 2-P of 30.7%, which is also higher than that over HF. However, it is found in figure 1 that for both 40%PW/SBA-15 and HY catalysts, the selectivity for 2-P decreases gradually with the increase of the conversion, and furthermore, whatever the conversion, 40%PW/SBA-15 always gives much higher 2-P selectivity than HY by ca. 15%.

Figure 2 shows the conversion of 1-dodecene as the function of reaction time over HY and the selected PW/SBA-15 catalysts. It is obviously that not only 40%PW/SBA-15 and 60%PW/SBA-15 are more active than HY but also the PW-containing catalysts exhibit higher

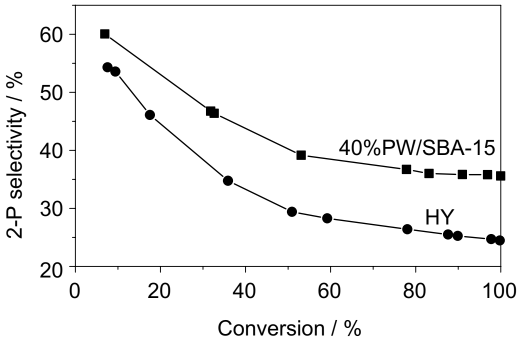

Figure 1. Comparison of the selectivity for 2-P between PW/SBA-15 and HY catalysts at various conversions (reaction temperature = 80 °C; benzene/1-dodecene = 5 ml/ml; 1-dodecene/catalyst = 5 ml/g).

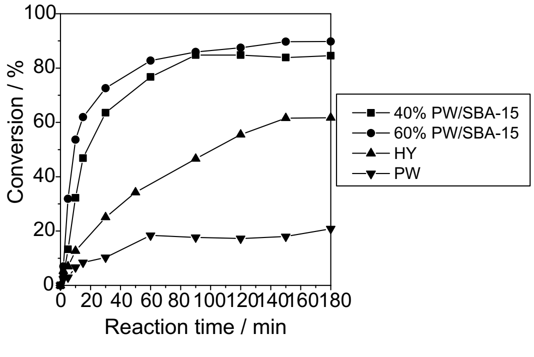

Figure 2. Conversion of 1-dodecene as a function of reaction time in alkylation of benzene with 1-dodecene over various catalysts (reaction temperature = 80 °C; benzene/1-dodecene = 5 ml/ml; 1-dodecene/catalyst = 20 ml/g).

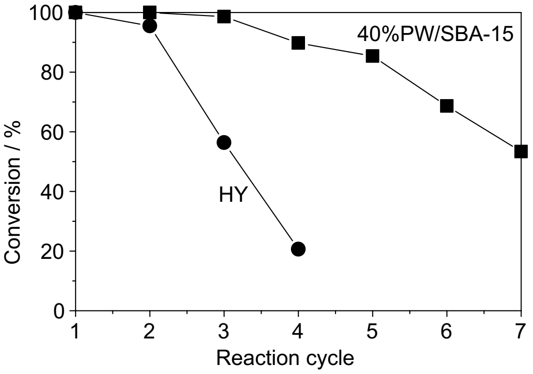

Figure 3. Comparison of the catalytic stability between PW/SBA-15 and HY catalysts (reaction temperature = 80 °C; benzene/1-dodecene = 5 ml/ml; 1-dodecene/catalyst = 5 ml/g).

reaction rate than HY, with the former reaching the steady reaction state within ca. 90 min of reaction time and the later ca. 150 min.

Figure 3 compares the catalytic stability between PW/SBA-15 and HY catalysts. After simply separating the used catalyst from the reaction medium by centrifuge, it was charged into the reaction medium for a new reaction cycle without regeneration. A much slower deactivation rate for PW/SBA-15 than that for HY catalyst is revealed in figure 3. At the fourth reaction cycle, the conversion over HY decreases sharply to 20%, while 40%PW/SBA-15 still shows a high value of 90%.

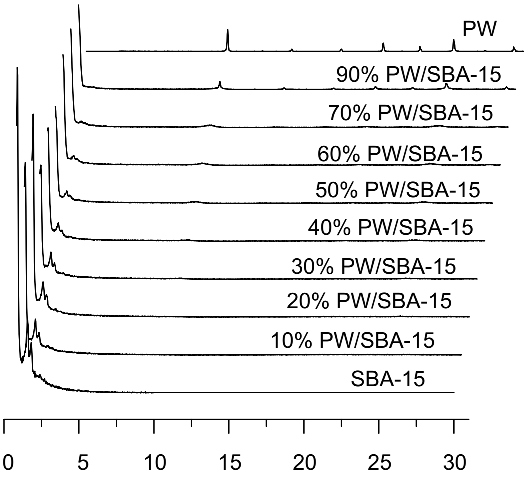

Figure 4. XRD patterns of PW/SBA-15 with various PW loadings.

Table 2

Specific BET surface area and pore volume of PW/SBA-15 samples

Catalyst	S_{BET}/m^2/g	V_p/ml/g
SBA-15	540	0.94
30% PW/SBA-15	433	0.69
40% PW/SBA-15	331	0.49
50% PW/SBA-15	315	0.47
60% PW/SBA-15	225	0.32
70% PW/SBA-15	195	0.22

Figure 4 illustrates the XRD patterns of various PW/SBA-15 samples. It is shown that the peaks at small angles assigned to SBA-15 appear for PW/SBA-15 samples with PW loadings up to 60%, indicating that they keep the mesopore structure well, and the peaks related to PW crystal cannot be detected when the PW loading is below 50%, presumably because PW is well dispersed on the surface of SBA-15 and the range of PW structure orders is then too short for X-ray diffraction. Moreover, the BET surface area and pore volume of PW/SBA-15, as displayed in table 2, are found to decrease gradually with the increase of PW loading, however, 60%PW/SBA-15 still possesses a large surface area of 225 m^2/g.

A surface-type reaction is expected in this nonpolar reaction medium, i.e., only the superficial PW anions may be active. Therefore, the high dispersion of PW onto SBA-15 and the large surface area might account for the high catalytic activity of PW/SBA-15. This may explain the rapid increase of conversion with the increase of the PW loading for 10–40%PW/SBA-15 catalysts. It is interesting to observe the very slow increase of conversion when PW loading excesses 40%, and moreover the decrease of conversion when PW loading is higher than 60% (table 1). This probably ascribes to the occurrence of PW crystal on SBA-15, which lowers down the available acid number of catalyst and finally decreases catalytic activity at very high PW loadings. On the other hand, the microporosity of HY zeolite implies that the produced coke precursor on acid sites inside the pore channel tends to deposit and block the intracrystalline pores of HY, resulting in a rapid deactivation, as shown in figure 3. This observation is in agreement with the previous report [14]. In contrast, the well-preserved mesoporosity of PW/SBA-15 catalyst could be responsible for its comparatively stable catalytic performance.

4. Conclusions

We have prepared the SBA-15 supported PW catalysts, which are very active, stable and selective for 2-P in benzene alkylation with 1-dodecene. The result found herein is believed to be potentially important for industrial production of LAB over solid acid catalysts.

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