



# Characterization and kinetic investigation of tungstophosphoric acid supported on SiO<sub>2</sub> for alkylation of benzene with 1-dodecene to synthesize linear alkylbenzene

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## Abstract

The typical catalyst of tungstophosphoric acid supported on SiO<sub>2</sub> was characterized by using XRD, IR, NMR, BET and TPD apparatus. Its activity and selectivity to synthesize linear alkylbenzene (LAB) and 2-LAB have been investigated in a fixed-bed reactor. This kind of catalyst showed high activity, good selectivity for linear LAB and 2-LAB and stability. Kinetics of benzene alkylation with 1-dodecene over the supported catalyst was also investigated in a fixed-bed reactor with eliminating the influence of internal and external diffusion. Rate models of the reactions forming different products of LAB were obtained and kinetic parameters were determined at the experimental conditions.

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## 1. Introduction

As an important intermediate of the synthetic detergents, linear alkylbenzene (LAB) is traditionally manufactured by benzene alkylation with 1-olefins, mainly 1-dodecene, over the catalysts such as aluminum trichloride or hydrofluoric acid. In recent years, taking account of pernicious effects of those catalysts, the great efforts for development of environmentally benign processes and related catalysts have been made. Solid acid catalysts such as zeolite-based catalysts [1–14], clays [15–18], heteropoly acids [19–22], ionic liquids [23] and fluorided silica-alumina [24–26]

have been widely investigated. A new process based on fixed-bed reactors and an aluminum–magnesium silicate catalyst, developed by UOP/Petresa [27,28], has been industrialized. This system consists of two fixed-bed reactors and each one of them was alternatively operated between the alkylation and the regeneration process. So the alkylation was continuously carried out and an adequate yield and selectivity in the alkylation for the desired product of LAB were obtained. Catalytic distillation (CD) technology coupling the benzene alkylation with 1-olefins with the distillation separation of the products, using a fluorine-containing mordenite as catalyst, has been developed by Hunstman [29,30]. This technology not only can effectively decrease mole ratio of benzene to 1-olefins but also saving energy consumption. A liquid/solid catalytic alkylation technology integrating

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the benzene alkylation and the regeneration of the catalyst adopted in a circulating fluidized bed (CFB) reactor system was also investigated in laboratory [31]. The technology of benzene alkylation with long chain 1-olefins based on the solid acid catalyst has been established commercially. At present time, more research concentrates on the developments of new catalysts and catalytic materials. Recently, a supported tungstophosphoric acid catalyst was investigated by some authors [32], which exhibits high activity and the selectivities for LAB and 2-LAB. It has been used to develop a new catalytic distillation technology for benzene alkylation with 1-olefins, suspension catalytic distillation (SCD) [32–35], in which the small particles of the catalyst is suspended in liquid phases and the influence of internal diffusion is effectively eliminated.

The objective of this work is to investigate the characterization of the preparation catalysts, in which the tungstophosphoric acid was supported on SiO<sub>2</sub>. And the reaction kinetics of benzene alkylation with 1-dodecene, which is lack at the present time, was also investigated over this catalyst, which was important to simulate the process for this supported catalyst to be used in the new developed SCD technology.

## 2. Experimental

### 2.1. Experimental set-up

The investigation was performed in the fixed-bed reactor. This system consisted of three parts, a feed blending station to simulate the reaction mixtures with different compositions, an assembly of fixed-bed reactor electric oven with a multi-channel temperature controller, and an off-line gas chromatograph (GC) and gas chromatograph–mass spectrometer (GC–MS). The feed blending station had two metering pumps for driving benzene and dodecene, respectively, a nitrogen tube for sweeping the reaction system. The metering pumps were calibrated in advance. Feed composition was calculated based on the readings of the metering pumps and checked by gas chromatograph. The main parts of reactor electric oven assembly were a fixed-bed reactor of 8 mm i.d., 300 mm long, and an electric oven of 800 W. The temperature of reaction section was controlled with a temperature programmable controller and measured with a

micro-thermal couple inserted in its center through a small jacket tube. A back-pressure regulator was equipped downstream of the reactor. An off-line gas chromatograph–mass spectrometer, GC–MS–QP5000, was used to analyze qualitatively the composition of alkylation reaction product. Experimental results obtained at the experimental conditions showed that main products were 2-LAB, 3-LAB, 4-LAB, 5-LAB and 6-LAB, and only trace amounts of other compounds were found.

An off-line GC equipped with a FID detector and an OV-101 capillary column was used to quantitatively analyzed compositions of reactant mixtures and products. The volume flow rates of nitrogen used as carrier of GC, hydrogen and air used for FID detector were 30, 30 and 300 ml min<sup>-1</sup>, respectively. The temperature of FID detector and the room of injecting sample were kept at 60 and 250 °C, respectively. Sample was separated in programmed temperature mode from 140 to 240 °C.

### 2.2. Catalyst preparation

A series of catalysts of tungstophosphoric acid supported on SiO<sub>2</sub> with different textual properties were prepared by saturately impregnated method. The support of SiO<sub>2</sub> was impregnated with tungstophosphoric acid under continuous stirring at room temperature. Then, it was filtered and dried at 120 °C for 2–3 h. The catalyst was then calcined in air in a muffle furnace at 150–350 °C for about 3 h. Typically, the textual properties of prepared catalysts are summarized in Table 1. The HPW denotes the used tungstophosphoric acid, and the last number of the catalyst mark is referred to as the content weight percentage of HPW in the catalyst. It showed that BET surface area of the catalysts was decreased with increasing the content

Table 1  
Textual properties of prepared catalysts

Catalyst number	Catalysts mark	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (ml g <sup>-1</sup> )	Pore diameter (nm)
I	HPW-SiO <sub>2</sub> -10	264	0.424	5.0
II	HPW-SiO <sub>2</sub> -17	213	0.532	9.1
III	HPW-SiO <sub>2</sub> -28	200	0.542	9.0
IV	HPW-SiO <sub>2</sub> -37	171	0.837	18.6
V	HPW-SiO <sub>2</sub> -50	111	0.928	32.1

of tungstophosphoric acid, and the pore volume and pore diameter increased with the increasing content of tungstophosphoric acid in the catalyst, which was resulted by pre-treating the support.

### 2.3. Catalyst characterization

Textural properties of the catalyst were determined from the  $N_2$  adsorption–desorption experiments on a Micromeritics ASAP2400 unit. The acidity of the typical sample was determined by infrared spectroscopy with adsorption of pyridine and desorption at 150 °C in a BrukerIFS113V FT-IR apparatus. D/MAX-11/A X-ray powder diffractometer using  $Cu K\alpha$  radiation, AM-300 nuclear magnetic resonance spectrometer and Dupont 2100 TG/DTA unit were respectively adopted to characterize the active phase, the strength of interaction between active species and support and thermal stability of the catalyst. The typical characterization results were provided in this paper and some results of the other details relative to the characterization of the catalysts can be found elsewhere [32].

### 2.4. Other materials

Benzene and 1-dodecene, used in this investigation as reactants, were 99.5 and 95% pure, respectively. Nitrogen, used as sweeping gas and for GC, was 99.5% pure. Helium used for GC–MS system was 99.995% pure. Hydrogen and air, used for FID detector, were supplied by a generator of high pure hydrogen and a generator of air, respectively.

### 2.5. Experimental procedure

The content of water in benzene must be controlled under  $20 \mu g g^{-1}$  because the activity of the catalyst is very sensitive to it. An adsorption column packed with 5A zeolite was used to remove the water in benzene. The content of water in the feed was analyzed with the type of SC-6 water analyzer. Before the alkylation reaction was started, the catalyst was activated at 120 °C at atmospheric pressure in nitrogen flow for 2 h at  $2400 h^{-1}$  space velocity. Then the catalyst bed was cooled to about 60 °C. Shutting the adjusting valve of nitrogen, benzene was introduced into the reactor and the back-pressure regulation valve

Table 2  
Kinetic experimental conditions

Temperature (°C)	85–125
Pressure (MPa)	2.4
Catalyst mass (g)	0.2
Particle size of the catalyst (mm)	0.25
WHSV (benzene) ( $h^{-1}$ )	20
Molar ratio of benzene/dodecene ( $mol mol^{-1}$ )	4–20

was adjusted to the desired pressure (2.4 MPa). After the flow rate of benzene was adjusted to the desired value for each particular experiment, dodecene was introduced into the system and its flow rate was regulated to match with that of benzene. When the stable values of flow rates of the reactants were reached, the temperature of the reaction section was controlled to the desired value for each particular experiment. The samples were periodically drawn out from the liquid effluent to analyze with the off-line GC. During the dynamic experiments, the reactor was charged with amounts of catalyst and some quartz chips were loaded in both sides of the reaction section. Suitable particle size of the catalyst and feed of benzene was determined by a preliminary experiment so as to eliminate the influence of internal and external diffusion. Through series of experiment, it showed that when the average catalyst size was small than 0.375 mm, the amounts of catalyst was loaded between 0.1 and 0.25 g and benzene feed was over  $4.0 mol h^{-1}$ , the influence of internal and external diffusion was eliminated. During the dynamic investigation, the average catalyst size was 0.25 mm, catalyst was loaded 0.2 g and the benzene feed was  $4.55 mol h^{-1}$ . Some of the kinetic experimental conditions are listed in Table 2.

## 3. Results and discussion

### 3.1. Typical characterization of catalysts

To the supported solid acid catalyst, its acid property is important for which to be used in the alkylation reaction. Table 3 was the typical characterization results for the pure HPW and HPW-SiO<sub>2</sub>-28 catalyst by using Hammett reagent methods and NH<sub>3</sub>-TPD as shown in Figs. 1 and 2, respectively. It showed that the acid strength for the HPW-SiO<sub>2</sub>-28 catalyst was less than

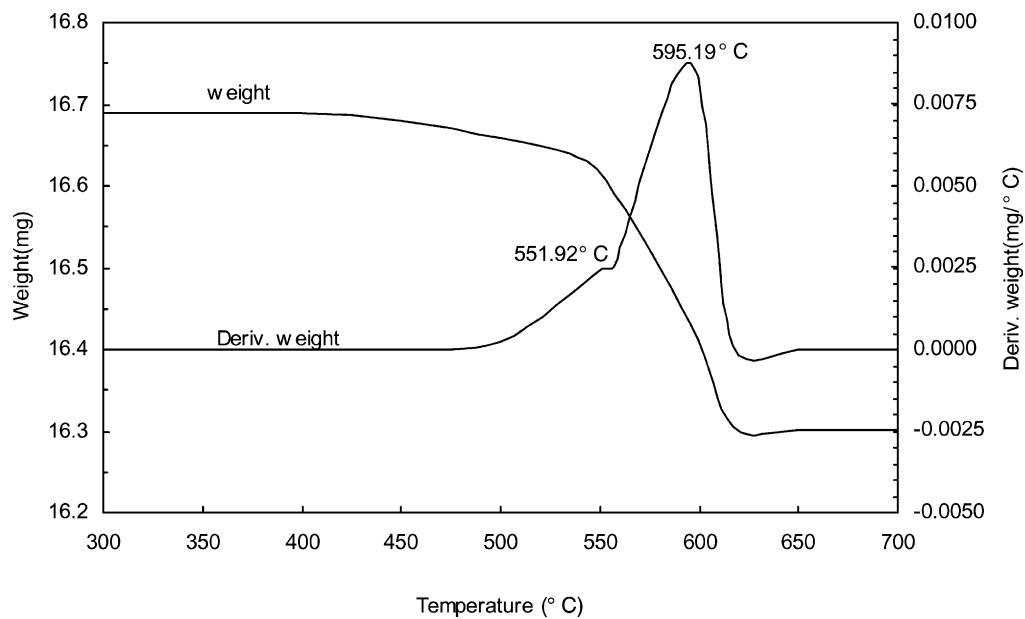
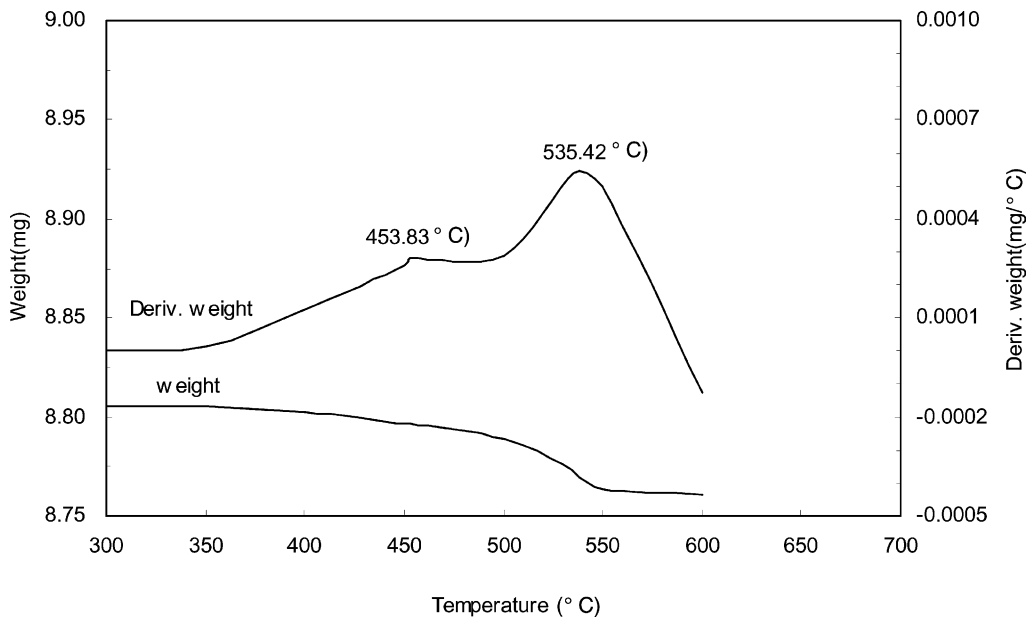
Fig. 1. NH<sub>3</sub>-TPD characterization of HPW.Fig. 2. NH<sub>3</sub>-TPD characterization of HPW-SiO<sub>2</sub>-28 catalyst.

Table 3

The comparison of acidity for the pure HPW and HPW-SiO<sub>2</sub>-28

Acidity	Methods	HPW	HPW-SiO <sub>2</sub> -28
Acid strength	Hammett reagent	$H_0 < -13.0$	$H_0 < -8.0$
	NH <sub>3</sub> -TPD (°C)	$T_{m1} = 551, T_{m2} = 595$	$T_{m1} = 453, T_{m2} = 535$
Amounts of acidity	NH <sub>3</sub> -TPD (mmol NH <sub>3</sub> g <sup>-1</sup> )	1.05	0.3

that of pure HPW. However, the acid distribution for the HPW-SiO<sub>2</sub>-28 catalyst was wide than that of pure HPW according to NH<sub>3</sub>-TPD results. Figs. 3 and 4 were IR patterns of HPW and HPW-SiO<sub>2</sub>-28 catalyst adsorbed by pyridine, respectively. From the IR results, it showed that acid centers are almost Bronsted acid centers ( $\lambda = 1539 \text{ cm}^{-1}$ ) for pure HPW and HPW-SiO<sub>2</sub>-28 catalyst. Fig. 5(a) and (b) were <sup>31</sup>P MAS NMR characterization results of HPW and HPW-SiO<sub>2</sub>-28 catalyst, respectively. It appeared two characteristic peaks to the pure HPW at  $\delta = -12.1$  and  $-16.7$ , however, it appeared only one characteristic peak at  $\delta = -16.5$  for the HPW-SiO<sub>2</sub>-28 catalyst. These phenomena showed that the surrounding environment for the supported tungstophosphoric acid was different from the pure tungstophosphoric acid. Fig. 6 indicated the XRD patterns of the freshly

prepared catalysts. It showed that the characterization peaks of tungstophosphoric acid were obvious with the increasing content of tungstophosphoric acid supported on SiO<sub>2</sub> support. Those results combined with SEM and TEM [32] showed that tungstophosphoric acid was comparatively well dispersed on the SiO<sub>2</sub> support. However, when the content of tungstophosphoric acid supported on SiO<sub>2</sub> was over 28 wt.%, it had little effect on the supported catalyst activity according to the preprimary experiment [32–34]. It can be concluded that the suitable content of tungstophosphoric acid on the prepared support is not over than 28 wt.% in order to effectively make use of it. The following further investigation for the preparation catalyst of tungstophosphoric acid supported on SiO<sub>2</sub> was mainly carried out at the catalyst of HPW-SiO<sub>2</sub>-28.

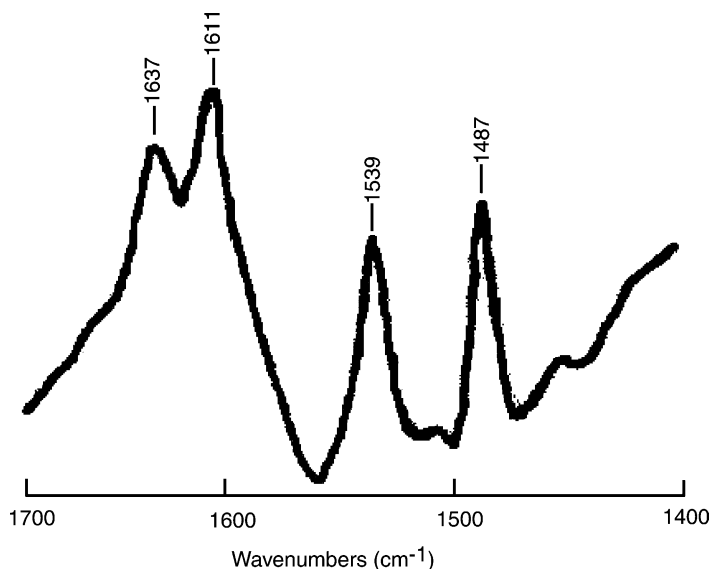


Fig. 3. IR patterns of HPW adsorbed by pyridine.

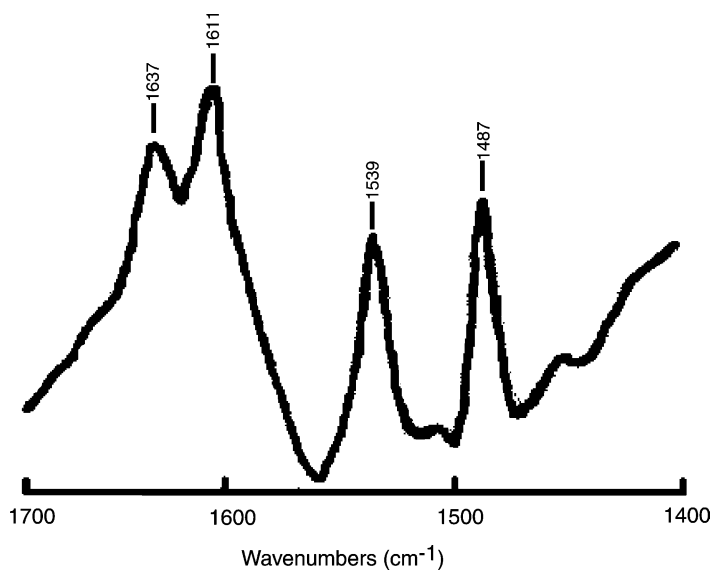


Fig. 4. IR patterns of HPW-SiO<sub>2</sub>-28 catalyst adsorbed by pyridine: (a) HPW and (b) HPW-SiO<sub>2</sub>-28 catalyst.

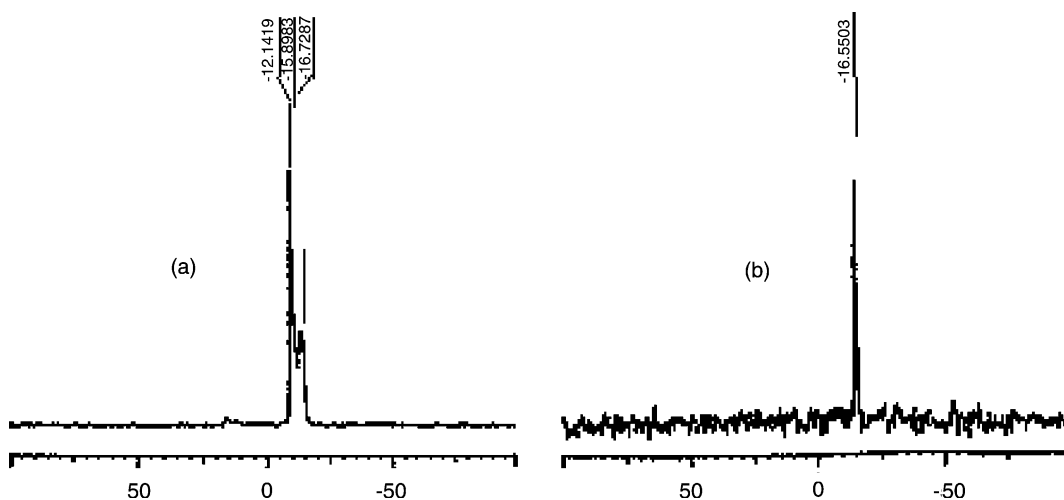


Fig. 5. <sup>31</sup>P MAS-NMR patterns of HPW and HPW-SiO<sub>2</sub>-28 catalyst.

### 3.2. Investigation of HPW-SiO<sub>2</sub>-28 on alkylation

The reaction property of HPW-SiO<sub>2</sub>-28 catalyst had been investigated at the fixed-bed reactor during the following conditions. The reaction temperature, pressure, weight space velocity (WHSV) and mole ratio of benzene to 1-dodecene was 120 °C, 1.0 MPa, 2.5 and 20 h<sup>-1</sup>, respectively. The conversion ratio of

1-dodecene, linear alkylbenzene selectivity and 2-LAB selectivity were shown in Figs. 7–9, respectively. From the Fig. 7 result, it showed that the conversion ratio of 1-dodecene remained 100% during 400 h running and the selectivity of production LAB remained almost 100%, as shown in Fig. 8. Further analysis results showed that the products of LAB are mainly consisted of 2-LAB to 6-LAB. The selectivity

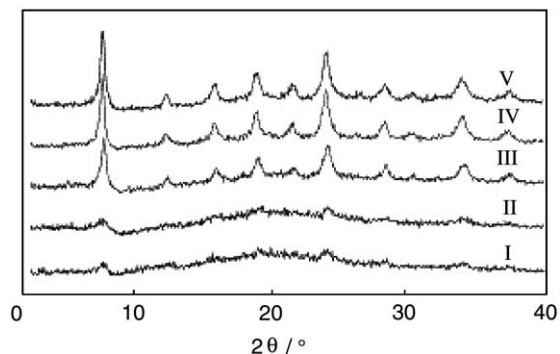


Fig. 6. XRD patterns of prepared fresh catalysts. WHSV =  $2.5 \text{ h}^{-1}$ ,  $T = 120^\circ\text{C}$ ,  $P = 1.0 \text{ MPa}$ , mole ratio of benzene to dodecene = 20.

of production of 2-LAB could be reached to about 35% during the entire running time, as shown in Fig. 9. It indicates that the catalyst of HPW-SiO<sub>2</sub>-28 has high activity, good selectivity and stability at the experimental conditions.

### 3.3. Dynamic investigation over HPW-SiO<sub>2</sub>-28 catalyst

#### 3.3.1. Reaction rate models

Alkylation of aromatics with olefins is commonly considered as proceeding via a carbenium ion mechanism [36]. Firstly, alkene is protonated by a Bronsted acid site to form an alkylcarbenium ion. The second step is involved in that alkylcarbenium ion is attached by benzene to form alkylbenzene. Alkylbenzene can also be isomerized to produce other isomers. In the

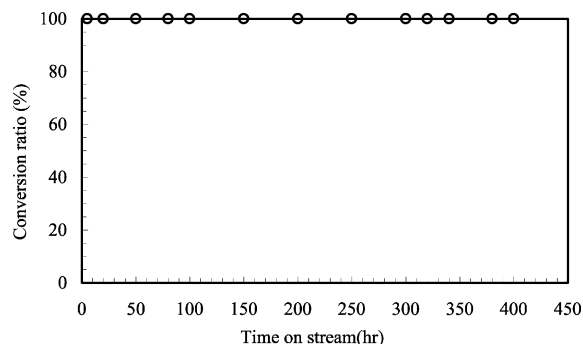


Fig. 7. The effect of time on stream on conversion ratio over HPW-SiO<sub>2</sub>-28 catalyst. WHSV =  $2.5 \text{ h}^{-1}$ ,  $T = 120^\circ\text{C}$ ,  $P = 1.0 \text{ MPa}$ , mole ratio of benzene to dodecene = 20.

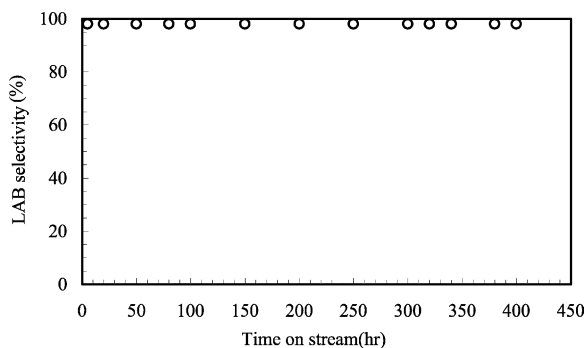


Fig. 8. The effect of time on stream on LAB selectivity of HPW-SiO<sub>2</sub>-28 catalyst. WHSV =  $2.5 \text{ h}^{-1}$ ,  $T = 120^\circ\text{C}$ ,  $P = 1.0 \text{ MPa}$ , mole ratio of benzene to dodecene = 20.

case studied here, it was possible to form five stable isomers of linear alkylbenzene from 2-LAB to 6-LAB, as observed in the above experiments. Besides these reactions, some other side reactions as consecutive alkylation to yield multialkylbenzene, polymerization of 1-dodecene and benzene alkylation with trace amount of diolefin in feed probably proceed. However, besides the isomers of alkylbenzene from 2-LAB to 6-LAB, only trace amounts of the products formed by other side reactions were detected at the experimental conditions. Very high selectivity of linear alkylbenzene suggests that the kinetics of benzene alkylation with 1-dodecene can be described by a set of parallel reactions yielding different isomers of the alkylbenzene from 2-LAB to 6-LAB, for the sake of simplification.

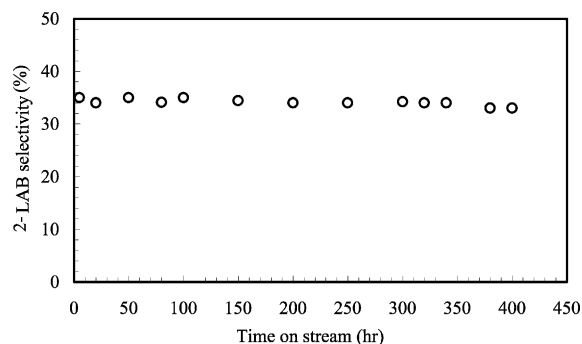
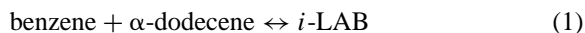
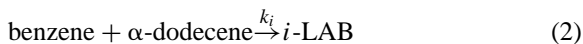


Fig. 9. The effect of time on stream on 2-LAB selectivity of HPW-SiO<sub>2</sub>-28 catalyst.

Thermodynamic calculation with respect of equilibrium constant for alkylation reaction showed that this reaction could factually be considered as irreversible as one and so the stoichiometric relation (1) should be rewritten in the following schema:



In which  $k_i$  was rate constant of the reaction forming  $i$ -LAB. Different types of rate models, including Langmuir–Hinshwood type and Ehrlich–Redhead type, should be experimental identified. From viewpoint of simplification, we preferred a power law type to others. So, the rate of every reaction could be expressed as follows:

$$R_i = k_{0,i} \exp\left(-\frac{E_i}{RT}\right) C_B^{n_{B,i}} C_D^{n_{D,i}} \quad (3)$$

where  $i$  denoted the reaction of forming  $i$ -LAB, and  $C_B$  and  $C_D$  presented the concentrations of benzene and dodecene, respectively.

As lower conversion of 1-dodecene than 20% was observed for all of experimental conditions during the dynamic investigation, the average rates of forming  $i$ -LAB in the reaction section of the laboratory fixed-bed reactor should be considered to be equal to the reaction rates of producing  $i$ -LAB at the average concentration of benzene and 1-dodecene in the reaction section.

### 3.3.2. Reaction rate equations

In order to determine the reaction rate parameters in the Eq. (3) by filling the predicted values of rate models with experimental data, an objective function in terms of square sum of relative difference was defined as follows:

$$F_i(\vec{k}_0, \vec{E}\vec{n}) = \sum_j \left( \frac{R_{i,j}^m - R_{i,j}^e}{R_{i,j}^e} \right)^2 \quad (4)$$

where superscripts m and e indicated model predicted and experimental, respectively. Subscript  $j$  stands for the ordinal numbers of kinetic experiments, and subscript  $i$  has been mentioned earlier.

Nonlinear regression algorithm was used to minimize the objective function (4) and rate parameters involved in Eq. (3). The results of parameter estimation showed that the reaction order of every reaction with respect to benzene and 1-dodecene is all equal

Table 4

The values of rate constants for different reactions

Ordinal number of reaction	$k_{0,i}$ ( $\text{m}^6 (\text{kg h kmol})^{-1}$ )	$E_i$ ( $\text{kJ mol}^{-1}$ )
2-LAB	402.8	45.7
3-LAB	743.9	46.6
4-LAB	792.1	48.0
5-LAB	892.2	48.3
6-LAB	217.8	48.2

to 1.0 according to the experimental results. Apparent activation energies and pre-exponential factors of every reaction were summarized in Table 4. It showed that the apparent activation energy for the reaction of forming 2-LAB was little lower than those of other reactions, which suggests that the selectivity for 2-LAB would be increased with the decreasing reaction temperature. Statistical measures for these models have been done and its relevant parameters were computed to identify their significance. The  $\rho^2$  measurements for from 2-LAB to 6-LAB were 0.98, 0.96, 0.98, 0.99 and 0.99, respectively, and were all greater than 0.9 which indicated statistically significant. Besides,  $F$  measurements for every rate model were all greater than  $10F\alpha$  ( $\alpha = 0.01$ ). All these results of statistical measure showed that the models proposed were acceptable from the viewpoint of application. The comparisons between the model predictions to the reaction rates and experimental data were also investigated. For the 2-LAB, its result was shown in Fig. 10. It was seen that the rates predicted by the model were all in good agreement with the data obtained in a wide range of experimental conditions. The similar results

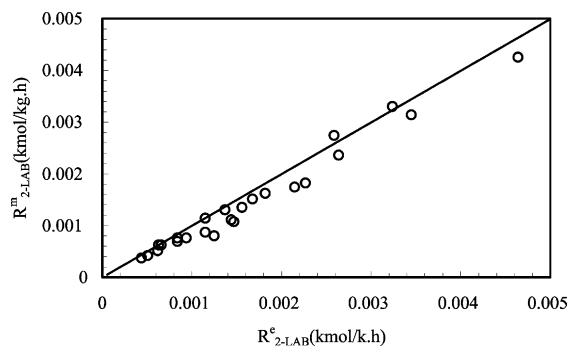


Fig. 10. Comparison between simulated rates of producing 2-LAB and experimental data.



were also obtained for the others established dynamic equations.

#### 4. Conclusions

The characterization results showed that the acid strength for the HPW-SiO<sub>2</sub>-28 catalyst was less than that of pure HPW. However, the acid distribution for the HPW-SiO<sub>2</sub>-28 catalyst was wide than that of pure HPW. The reaction property for HPW-SiO<sub>2</sub>-28 catalyst was investigated in the fixed-bed reactor. It showed that the conversion ratio of 1-dodecene remained 100% during 400 h running. The selectivity of production LAB remained almost 100%. Further analysis showed that the products of LAB were mainly consisted of 2-LAB to 6-LAB. The selectivity of production of 2-LAB could be reached to about 35% during the entire running time. It indicated that HPW-SiO<sub>2</sub>-28 catalyst had high activity, good selectivity and stability at the experimental conditions. Reaction kinetics of benzene alkylation with 1-dodecene to produce linear alkylbenzene over HPW-SiO<sub>2</sub>-28 catalyst was investigated, which was carried out in a fixed-bed reactor with eliminating the influences of internal and external transport. A set of rate equations in power law type of forming different isomers of LAB was proposed, and kinetic parameters were estimated by fitting the experimental data. The data of apparent activation energies suggested that lower reaction temperature could be beneficial for increasing the selectivity of forming 2-LAB.

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