Study of the catalytic behaviors of concentrated heteropolyacid solution. I. A novel catalyst for isobutane alkylation with butenes

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A novel liquid acid catalyst, composed of heteropolyacid and acetic acid for the alkylation of isobutane with butenes is reported. The conditions for the formation of catalytic active phase as well as its catalytic behaviors in alkylation of isobutane with butenes have been studied. It was found that acetic acid, as a solvent, exerts a synergistic effect on the acid strength of heteropolyacid, and the contents of crystal water in HPAs have influence over the formation of active phase and the catalytic activity. This novel catalyst is comparable to the sulfuric acid in catalytic activity.

Keywords: concentrated heteropolyacid–acetic acid solution, catalytic active phase, isobutane/butene alkylation, crystal water contents of HPAs

1. Introduction

Heteropolyacids (HPAs) and related compounds have attracted increasing interest in catalysis, owing to their ability to catalyse both acidic and redox reactions. HPAs as acidic catalysts, at present, are those with Keggin structure, having the general formula $X^{n+}M_{12}O_{40}^{(8-n)-}$, where X is the central atom (Si, P, etc.) and M is the coordinate atoms (W, Mo, etc.). The Keggin anion is composed of a central tetrahedron XO_4 surrounded by 12 edge- and corner-sharing metal–oxygen octahedron MO_6 (figure 1). Solid HPAs possess a discrete ionic structure, comprising fairly mobile basic structural units-heteropolyanion and countercations (proton, metal ion or their mixture). A series of reviews discussing the structure, characterization and catalytic performance of HPAs have been published [1].

The most important reason for HPAs as acidic catalysts results from their lower electron density on the surface of the spherical heteropolyanion. HPAs have a very strong Brønsted acidity, due to that the electron is nonlocalized, and the proton exhibits an extremely high mobility. On the one hand, their acidity is 100 times that of sulfuric acid when they are used in solid as well as in solution, and on the other hand, they have their advantages, such as lower volatility and being corrosiveless, higher selectivity over some other mineral acids in many reactions. These properties render HPAs potentially promising catalysts for replacing ordinary acids, e.g., H_2SO_4, etc. in the synthesis of many fine chemicals. But, in practice, if HPAs are used in reaction directly, there is still a difficulty of separating product from catalytic system. Due to their complex physicochemical properties, in addition to their relatively expensive price, they cannot be discarded rashly, therefore, there has been a worldwide seeking for supporting HPAs on suitable carriers [2] and for developing concentrated solutions which can be used repeatedly. For the practical purpose several new industrial processes based on HPAs concentrated solutions have been developed and commercialized by Japanese research groups [3].

We have drawn the conclusion from the literature that the selected solvent must meet the demands: (a) higher solubility to HPAs, (b) inert to catalyst and reactant, (c) easy separation from product. Based on these ideas, and considering that the isobutane alkylation with butenes must be carried out under the conditions of higher acid strength ($H_0 \leqslant -12$) and lower temperature ($<50\,^{\circ}C$) [4], we investigated systematically the liquid catalytic system which is composed of HPAs (phosphorus and silicon as central atom tungsten heteropolyacids) with Keggin structure and various solvents [5]. We find that the catalytic system composed of acetic acid as solvent shows best catalytic behaviors for alkylation of isobutane with butene; its higher activity is comparable with that of H_2SO_4.

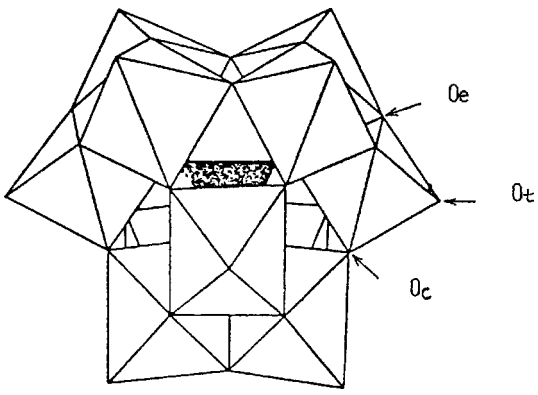

Figure 1. Primary structure of HPAs with Keggin structure. O_e – edge-bridging oxygen, O_t – terminal oxygen, O_c – corner-bridging oxygen.

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Table 1
Composition of hydrocarbon feed.[a]

	Component					
	Propane	Isobutane	Butane	(n,i)-butene	*cis*-butene-2	*trans*-butene-2
Content (%)	1.44	84.92	4.48	9.61	0.64	0.05

[a] Ratio of paraffin/olefin = 8.7 (isobutane/butene = 8.2).

2. Experimental

2.1. Material

Phosphatotungstic acid ($H_3PW_{12}O_{40}\cdot xH_2O$, abbreviated as PW_{12}), silicotungstic acid ($H_4SiW_{12}O_{40}\cdot xH_2O$, abbreviated as SiW_{12}), and glacial acetic acid were purchased from Beijing Xinhua chemical reagent plant; they are analytically pure. Hydrocarbon feed was obtained directly from industrial raw material of alkylation; its composition is given in table 1.

2.2. Preparation of catalytic active phase (CAP) and alkylation experiments

The preparation of CAP and alkylation reactions were carried out in a stainless-steel (Cr18Ni9Ti) autoclave (500 ml). The temperature was monitored by a PID controller. A four-blade downward-thrust impeller provides positive agitation with speeds ranging from 0 to 2000 r.p.m. In a typical experiment, heteropolyacid (PW_{12} or SiW_{12}) with certain amounts of crystal water (the quantity of crystal water was measured by the method of thermal gravimetric analysis) together with corresponding weight of AcOH, and mixed hydrocarbon were introduced into the reactor at dry ice–ethanol temperature, and then heated to the desired temperature. The reaction was continued under the pressure of about 5 atm (emerge of mixed hydrocarbon themselves) for proper hours. After reaction, the reactor was depressurized and excess isobutane was vented at room temperature. The upper layer was separated from the acid mixture, washed several times with distilled water, and collected as product (alkylate); the lower layer was the catalyst (CAP).

2.3. Analysis of alkylate

The analysis of alkylate was carried out by use of a gas chromatograph (Shanghai Analysis Instrument Group Company, GC112, equipped with a 50 m × 0.25 mm fused silica capillary column coated with SE-54), detected by a hydrogen flame ionization detector. The products were qualitatively identified by GC-MS (HP5890 combined with VG-Quattro), and classified into three groups: C_5–C_7 alkanes, C_8 alkanes and C_{9+} alkanes.

2.4. Characterization of liquid acid catalyst

The acid strength of the HPA–AcOH mixed solution was determined using both ^{13}C NMR spectra ($\Delta\delta^0$ method [6]) and UV-Vis spectra [7]. The ^{13}C NMR of mesityl oxide in solution was recorded at 100 MHz on a Bruker MSL 400 instrument at 20 °C, using α,β-unsaturated ketones, mesityl oxide as indicator. The UV-Vis spectra were recorded at room temperature (15 °C) with Specord UV-Vis (Carl Zeiss, Jena) spectrophotometer, and 2,4-dinitrofluorobenzene ($pK_a = -14.52$) and nitrobenzene ($pK_a = -12.44$) were used as indicators.

3. Results and discussion

3.1. Effect of acetic acid on acid strength of HPAs and catalytic activity

We discovered that crystal water contents in HPAs remarkably influenced the acid strength and catalytic activity of our catalytic system. For solutions composed of HPAs with different crystal water contents and equal weight of acetic acid, the acid strengths are inversely proportional to the crystal water contents of HPAs, namely, the larger the crystal water content, the smaller the acid strength (the larger the H_0). The results are shown in table 2 and figure 2.

In our previous work, we observed when the molar contents of crystal water in HPAs are ten or so, the acid strength of HPAs is $H_0 < -8.6$ [8], while in acetic acid, the acid strength is $H_0 \leqslant -12.8$. Thus, on the one hand, acetic acid could exert an effect of promoting HPAs acidic strength, and manifested a higher acid strength than H_2SO_4 and $HClO_4$, too (cf. figure 2). It was thought this is because the hydrons of HPAs in acetic acid could dissociate independently, rather than consecutively as in other polybasic acids [6]. Moreover, it can be seen that acetic acid as solvent has a stabilizing effect on acid strength. Differing from that of supported HPAs, in this case, when the contents of crystal water change in a certain range, the acid strength of the solution varied fairly small, and a sudden change of acid strength was not observed [9].

The catalytic activity (expressed in the yield of alkylate, theoretical value: 204%, or butenes conversion, theoretical value: 100%) of different samples prepared from HPAs with various contents of crystal water are given in figure 3. We can find that the catalytic activity is proportional to the acid strength of the catalytic system, that is, the bigger the acidic strength is, the better the activity is.

3.2. Discovery and formation of catalytic active phase (CAP)

It can be seen from figure 3 that the catalytic activity of the simple catalytic system composed of HPAs with dif-

Table 2
Values of H_0 and ionization ratios of the HPA–AcOH systems.

Sample[a]	H_2O	2,4-dinitrofluorobenzene[b]		Nitrobenzene[c]	
	(mol%)	log I	H_0	log I	H_0
$PW_{12}\cdot 19H_2O$	10.6	−2.39	−12.13	−0.13	−12.31
$PW_{12}\cdot 17.25H_2O$	9.73	−2.24	−12.28	−0.09	−12.35
$PW_{12}\cdot 15.16H_2O$	8.65	−2.18	−12.34	−0.05	−12.39
$PW_{12}\cdot 10.17H_2O$	5.98	−2.13	−12.39	0.02	−12.46
$PW_{12}\cdot 8.2H_2O$	4.88	−2.05	−12.47	0.17	−12.61
$PW_{12}\cdot 6.83H_2O$	4.09	−1.99	−12.53	0.22	−12.66
$PW_{12}\cdot 0.73H_2O$	0.45	−1.83	−12.69	0.28	−12.72
$SiW_{12}\cdot 23.0H_2O$	12.6	−2.01	−12.51	−0.02	−12.42
$SiW_{12}\cdot 18.15H_2O$	10.2	−1.92	−12.60	−0.05	−12.39
$SiW_{12}\cdot 16.97H_2O$	9.59	−1.95	−12.57	0.09	−12.53
$SiW_{12}\cdot 12.71H_2O$	7.36	−1.88	−12.64	0.06	−12.50
$SiW_{12}\cdot 10.52H_2O$	6.17	−1.82	−12.70	0.27	−12.71
$SiW_{12}\cdot 7.32H_2O$	4.38	−1.77	−12.75	0.34	−12.78

[a] The concentration of HPA is 6.94×10^{-4} mol/l.
[b] The concentration of 2,4-dinitrofluorobenzene is 5×10^{-3} mol/l.
[c] The concentration of nitrobenzene is 9.76×10^{-4} mol/l.

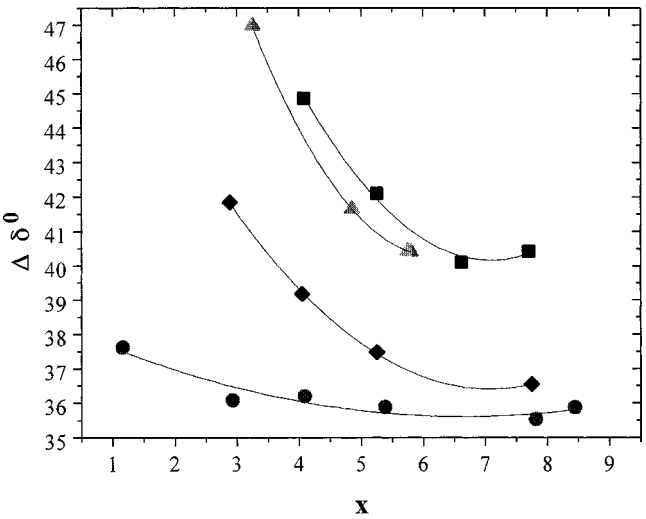

Figure 2. Acid strength ($\Delta\delta^0$) of different acids ($AH\cdot xH_2O$) toward mesityl oxide in glacial acetic acid. AH = $(1/3)H_3PW_{12}O_{40}$ (■), $(1/4)H_4SiW_{12}O_{40}$ (▲), $HClO_4$ (♦) and $(1/2)H_2SO_4$ (●). Temperature 20 °C, HPA : AcOH = 1 : 42.7 (molar ratio).

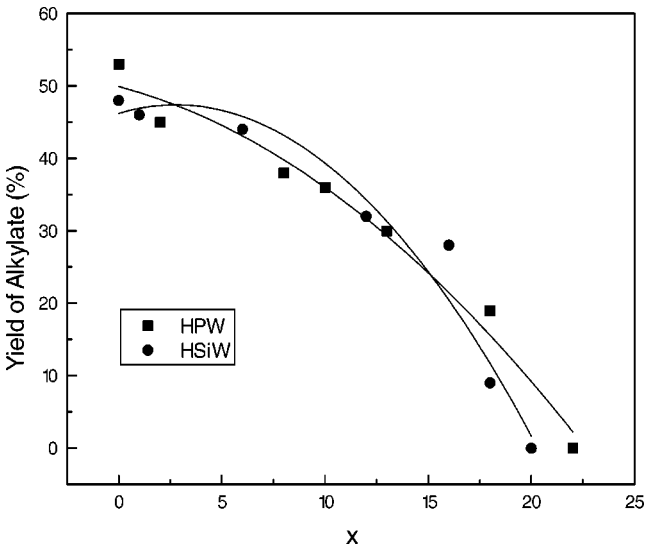

Figure 3. Effect of crystal water contents in HPAs on catalytic activity. Temperature 50 °C, time 6 h, catalytic system used: HPA 10 g, AcOH 10 ml, mixed hydrocarbon 10 ml.

ferent contents of crystal water directly dissolving in acetic acid, is not fairly good (the yield of alkylate is lower than 50%). But we found that in the catalytic system an oily viscous fluid formed similar to that formed when H_2SO_4 is used as catalyst. Separating the oily viscous fluid from the catalytic system and using it as catalyst, a better activity and alkylate quality could be obtained. We called thus the oily viscous fluid as "catalytic active phase" and concluded that in the reaction of isobutane alkylation with butene catalyzed by HPA–AcOH, the HPAs act just as a precursor; only after the HPAs combined (or reacted) with acetic acid and reactant (or product) resulting in the formation of an active phase possessing catalytic properties, can the alkylation take place.

3.2.1. Effect of crystal water contents of HPAs on the formation of CAP

Our primarily examination showed that the solubility of HPAs in acetic acid can change with the contents of crystal water of HPAs, and generally, increases with increasing contents of crystal water of HPAs, forming three different states: solid–liquid phase, two liquid phase and a uniform liquid phase. Namely, HPAs with higher contents of crystal water can completely dissolve in acetic acid forming a uniform liquid phase; HPAs with lower contents of crystal water can dissolve only a little or even not in acetic acid; a solution composed of HPAs with proper contents of crystal water in acetic acid could form two liquid phase, the upper layer consisting of acetic acid and a small amount

Table 3
Effect of crystal water contents on the formation of CAP-mother liquid.

Sample	H_2O : HPW (mol)	HPW (g)	HAc (g)	HPW : H_2O : HAc (mol)	Amount of CAP-mother liquid[a] (g)
$HPWD_1$	24.58	13.5	11.0	1 : 24.58 : 44.68	17.7
$HPWD_2$	14.80	13.5	11.0	1 : 14.80 : 42.33	16.0
$HPWD_3$	8.38	13.5	11.0	1 : 8.38 : 40.67	7.0
$HPWD_4$	1.83	13.5	11.0	1 : 1.88 : 39.17	0.0

[a] Temperature 50 °C, time 4 h, hydrocarbon feed 30.0 g.

Table 4
Effect of amount of solvent on the conversion of olefins.[a]

Amount of solvent (ml)	Reaction runs														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	Conversion of olefins (%)														
20	–	–	–	–	–	–	40	46	56	60	68	54	50		
40	–	–	–	94	(106)	80	82	100	92	76	88	80	82	(104)	80
60	–	–	–	–	44	40	42	100	88	80	(102)	92			

[a] Reaction conditions: time 5 h, temperature 50 °C, agitation level 800 r.p.m., PW_{12} used 50 g. (−) Induction period, no alkylate was obtained.

Table 5
Effect of water added on the catalytic behavior of CAP.[a]

Experiment No.	Precursor of CAP[b] (ml)	Added H_2O (g)	Hydrocarbon feed (g)	Yield of alkylate (%)	CAP recovery (g)
$D_{4\text{-}1}$	10	0.0	36.5	107.0	7.5
$D_{4\text{-}2}$	10	0.2	36.1	158.3	9.2
$D_{4\text{-}3}$	10	0.3	38.1	152.9	7.5
$D_{4\text{-}4}$	10	0.4	33.9	144.5	9.4

[a] Reaction temperature 50 °C, reaction time 14 h.
[b] Prepared CAP molar ratio HPW : H_2O : HAc = 1 : 6.83 : 77.88, reaction temperature 50 °C, reaction time 44 h.

of HPAs, the lower layer consisting of HPAs and a small amount of acetic acid. Therefore, when HPAs are used as the precursor of catalyst to prepare the CAP, the contents of crystal water of HPAs should exert an obvious effect on the formation of CAP.

In this work, in order to investigate the effect of the contents of crystal water in HPAs on the formation of CAP, four samples of each PW_{12} and SiW_{12} with different contents of crystal water namely, 1.83, 8.38, 14.80 and 24.58 were first prepared [10], and examined under the same conditions by adding the same amounts of solvent and reactant (isobutane/olefins = 8.2, mass ratio). The results obtained using PW_{12} as an example of catalyst are given in table 3. It could be seen from the results that the amount of CAP-mother liquid being obtained is directly proportional to the content of crystal water in HPAs. Further examination indicated that the homogeneous CAP-mother liquid obtained from HPAs with larger contents of crystal water ($HPWD_1$, $HPWD_2$) required a longer induction period, owing to the relatively lower concentration of HPAs, while HPAs with small amount of crystal water ($HPWD_4$) can hardly form even the CAP-mother liquid. An active CAP can be obtained only when the HPAs have proper contents of crystal water.

3.2.2. Effect of amount of solvent on the formation of CAP

Solvent is a key component of this catalytic system, so it is very important to determine the optimum amounts of solvent in the catalytic system. The effect of amounts of solvent on the conversion of olefins is given in table 4 for PW_{12}. When PW_{12} with ten or so crystal water by varying the amount of acetic acid added is used as the catalyst precursor, it is shown from the results that the reaction in each case has a certain induction period (denoted by −) and the conversion of olefins is closely related to the amounts of solvent. For example, when the quantity of solvent is 40 ml together with 50 g PW_{12} (mass ratio HPA/AcOH $\approx$ 1), a relatively short induction period is required, as well as a rather higher conversion can be obtained.

3.2.3. Effect of water added on the catalytic behavior of CAP

The effect of the amounts of adding water on the catalytic behavior of CAP by using a prepared CAP with adequate composition as shown below table 5 was investigated; the results are given in table 5.

From table 5, we found that there must be an adequate amount of water in the reaction system, which can obviously improve the catalytic activity of CAP.

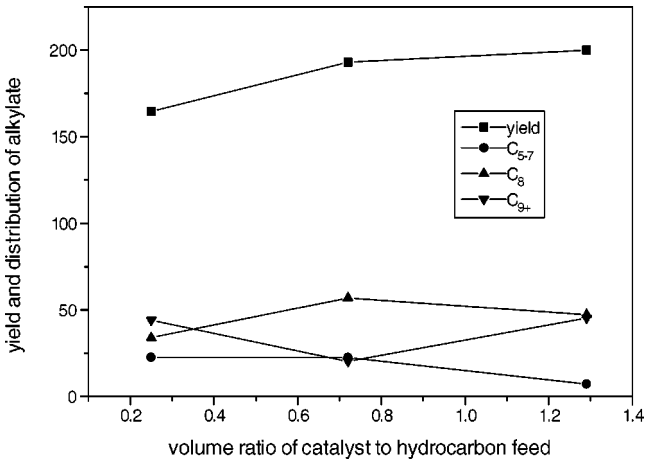

Figure 4. Effect of volume ratio of CAP to feed. Temperature 50 °C, time 6 h, catalyst used: SiW_{12}–AcOH catalyst precursor, 250 g $HSiW{\cdot}17H_2O$, agitation speed 1200 r.p.m.

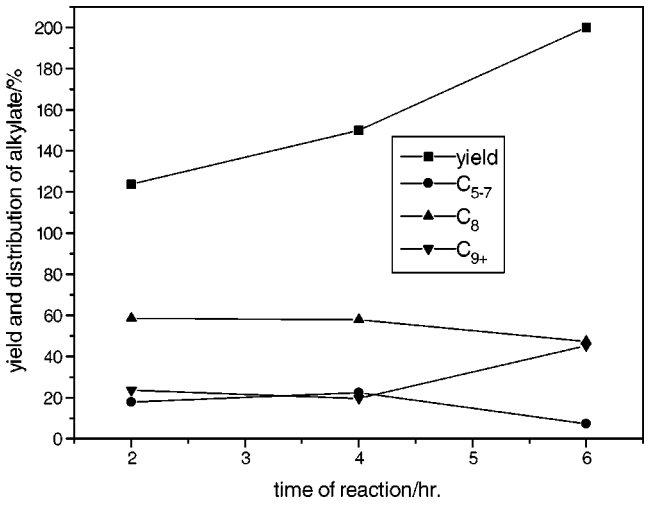

Figure 5. Effect of reaction time on catalytic behavior. Temperature 50 °C, catalyst used: SiW_{12}–AcOH catalyst precursor, 250 g $HSiW{\cdot}17H_2O$, agitation speed 1200 r.p.m.

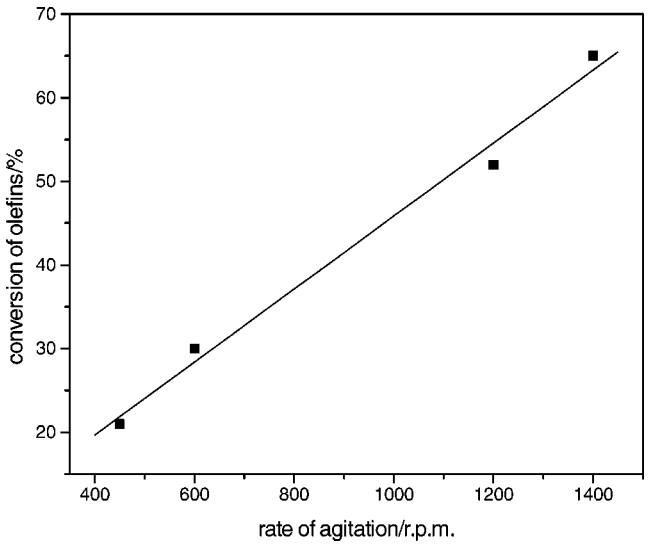

Figure 6. Effect of agitation speed. Temperature 50 °C, time 5 h, catalytic system used: PW_{12} 50 g, AcOH 40 ml.

It is almost a general rule that such oily compound could be formed in the reaction of hydrocarbons catalyzed by acids [11]. The nature of this compound to date is not quite clear [12,13], therefore further investigation should be in progress about the nature of the compound formed in the HPA–AcOH system.

3.3. Catalytic performance of CAP

3.3.1. Effect of volume ratio of catalyst to feed

The effect of volume ratio of CAP to mixed hydrocarbon is given in figure 4. The results show that when the volume ratio of catalyst to feed is in the range of 0.75–1.25, the alkylation proceeding at the temperature of 50 °C for 6 h, could give the yield of alkylate about 200%. This revealed that the catalyst (CAP) has a larger productive capacity.

3.3.2. Effect of reaction time

The effect of reaction time on catalytic activity and product distribution is given in figure 5. The results show that higher catalytic activity can be obtained while C_8 fraction decreases and C_{9+} fraction increases with the prolonged reaction time.

3.3.3. Effect of stirring speed

The results obtained under above conditions, show that the catalytic activity is proportional to the number of agitation level in the range of 500–1500 r.p.m.

3.3.4. Stability of CAP

Higher catalytic activity can be kept in a considerable number of reaction cycles but, when CAP was continuously used in a number of reaction cycles, its physical properties and chemical composition as well as the catalytic activity in further cycles would be changed to a certain extent. As seen from the results given in figure 7, the loss of solvent as well as H_2O in the treatment of alkylate results in the increase of catalyst density. Further experiments have supplied proof that its higher activity can be renewed by adding adequate amounts of solvent and H_2O.

3.4. Products distribution and basic properties of alkylate

3.4.1. Distribution of alkylate

The gas chromatogram of alkylate is given in figure 8. It can be seen that when isobutane/butene alkylation is catalyzed by one of the catalysts, e.g., SiW_{12}–AcOH, the alkylate can be divided into four categories: cracking product C_5–C_7, alkylate C_8, trimer C_{12} and tetramer C_{16}.

3.4.2. Comparison of products distribution

A comparison of products distribution of alkylation catalyzed by PW_{12}–AcOH, SiW_{12}–AcOH and H_2SO_4 is given in figure 9. The results show that C_8 fraction as well

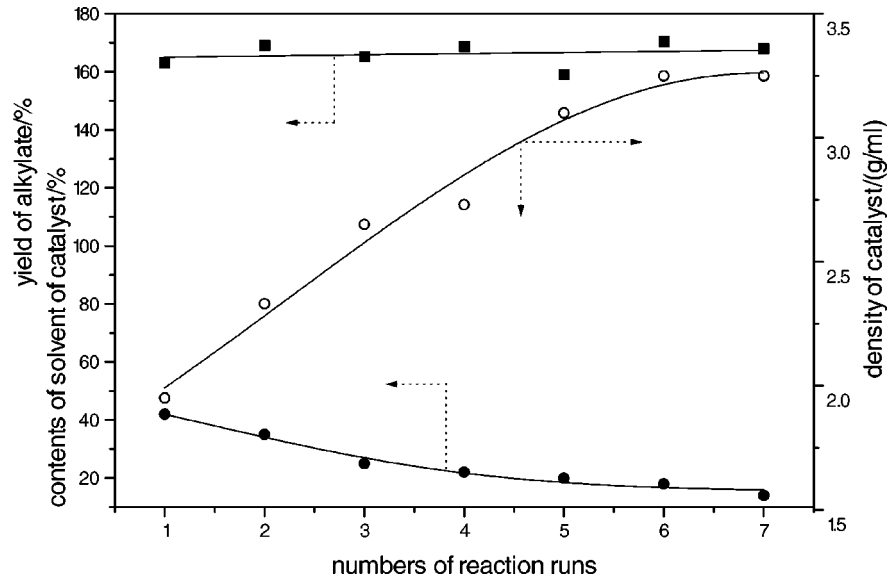

Figure 7. Variation of physicochemical properties vs. reaction runs: (■) yield of alkylate, (○) density of CAP and (●) amounts of solvent in CAP. Temperature 50 °C, time 4 h, catalyst used: SiW_{12}–AcOH.

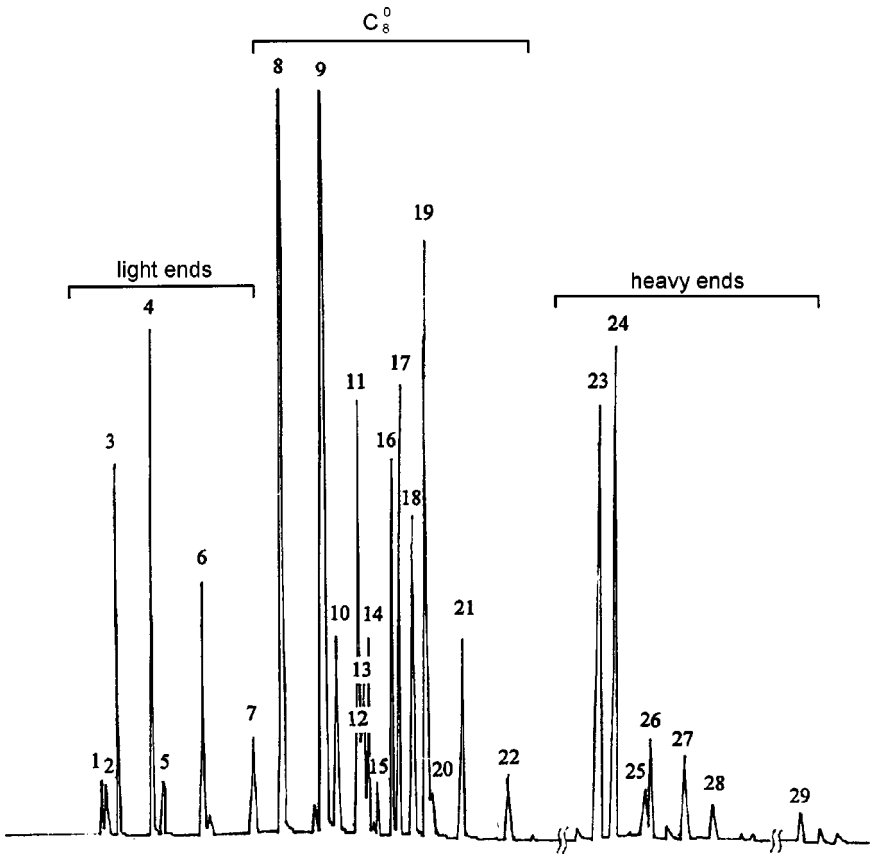

Figure 8. Products distribution of alkylation of isobutane/butene in SiW_{12}–AcOH system (temperature 50 °C, time 4 h). (1) Isobutane, (2) butane, (3) pentane, (4) 3-methylpentane, (5) 2-methylpentane, (6) 2,2-dimethylpentane, (7) 2-methylhexane, (8) 2,2,4-trimethylpentane, (9) unidentified, (10) 2,2,4-trimethylpentene-1, (11) 2,2,3-trimethylpentane, (12) 2,3,4-trimethylpentane, (13) 2,3,3-trimethylpentane, (14) and (15) 5,5-dimethylpentene-1, (16) unidentified, (17) 2,2,4-trimethylpentene-1, (18) 2,3,3-trimethylpentene-1, (19) 1,1-dimethylcyclohexane, (20) isobutyl acetate, (21) 2,3,4-trimethylpentene-2, (22) 2,3-dimethylhexene-2, (23)–(28) trimers, (29) tetramer.

as polymerization products (C_{12} and C_{16}) of this catalytic system are more than that of the H_2SO_4 system, but the cracking product is less, which is probably due to that the reaction time is too long and the acid properties of this system in this reaction state is not so benefit as that of H_2SO_4.

Table 6
ASTM fraction of alkylate.

	SiW_{12}		PW_{12}		H_2SO_4 (literature value [14])	
	ASTM distillation	°C	ASTM distillation	°C	ASTM distillation	°C
Initial b.p.	–	42	–	37	–	31.3–38
	15%	90	25%	98	10%	87.0–92.0
	33%	106	51%	116	20%	97.0–100.5
	51%	108	75%	140	30%	102.0–103.5
	88%	108	92%	184	40%	105.5–106.0
	96%	180	96%	194	50%	108.0–109.5
					60%	110.0–103.5
					70%	112.5–119.0
					80%	117.0–130.0
					90%	133.0–178.0
Residues	3.7%	200	3.8%	200		
Final b.p.		200		200		203.0–242.0
Specific gravity	0.730		0.730		0.706–0.707	

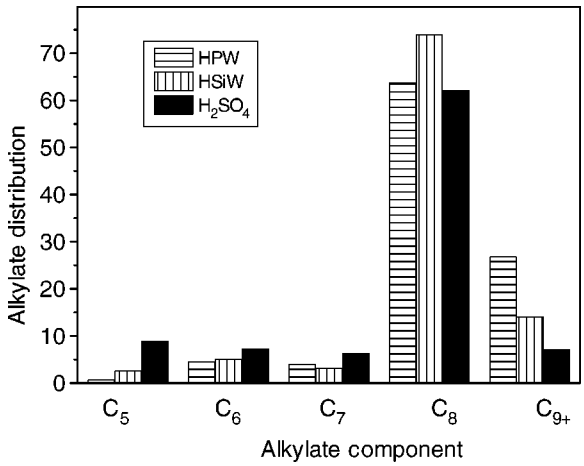

Figure 9. Comparison of product of alkylation catalyzed by HPAs–AcOH and H_2SO_4. Experimental conditions: reaction time 6 h, temperature 50 °C, yield of alkylate 194.4% for SiW_{12} and 185.8% for PW_{12}.

3.4.3. Comparison of basic properties of product

The distilled fraction and specific weight of products of alkylation catalyzed by PW_{12}–AcOH, SiW_{12}–AcOH and H_2SO_4 are given in table 6.

Comparing this catalytic system with H_2SO_4 system, obviously, the higher primary distillation point light ends results from the less cracking product and the remaining residue heavy ends and greater specific weight, could be attributed to the side reaction polymerization.

4. Conclusion

(1) Acetic acid could enhance the acid strength of HPAs and raise the stability of HPAs.

(2) Concentrated solution of HPAs in acetic acid possesses a comparatively higher activity with respect to H_2SO_4 for alkylation of isobutane with butene.

(3) The amounts of solvent and the contents of crystal water in HPAs influence the formation of CAP and its catalytic performance.

(4) Properties and activity of CAP change with reaction cycles, but its higher activity can be maintained by adding adequate amounts of solvent and water.

(5) CAP possesses a higher productive capacity.

Acknowledgement

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