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Isobutane/butene alkylation over supported heteropoly acid catalysts: I. Influence of the structure of silica

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Catalysts consisting of heteropoly acids (HPAs) supported on different silica and mesoporous molecular sieves have been prepared by impregnation and the sol–gel method, respectively, and their catalytic behavior in fixed-bed alkylation of isobutane with butene has been investigated. The activity, selectivity and stability of the supported-HPA catalysts could be correlated with the surface acidity of the catalysts, the structure of supports as well as the time on stream (TOS). In the fixed-bed reactor, the acidity of the heteropoly acid is favorable to the formation of dimerization products ($C_8^=$); especially, the pore size of supports was seen to have an important effect on activity and product distribution of the catalysts. Contrary to the traditional solid-acid catalysts, the supported-HPA catalysts own an excellent stability for alkylation, which makes it possible for these supported catalysts to replace the liquid-acid catalysts used in industry.

Keywords: alkylation, heteropoly acid, supported catalyst

1. Introduction

The alkylation of isobutane with n-butene allows the preparation of a gasoline cut with a high octane number. Commercially, only concentrated sulphuric acid and anhydrous hydrofluoric acid are used as catalysts [1–4]. Unfortunately, the expected increase in alkylation capacity in the coming years is relatively low due to limitations imposed on the use of highly corrosive and contaminating acids as commercial catalysts. Therefore, the increased alkylation would dramatically change if the liquid acids could be replaced by new solid non-contaminant catalysts. Much effort has been made in the last decades along this line, for example, zeolites [5], ion-exchange resins [6] and solid superacids [7] have been studied as potential alkylation catalysts. But, the alkylation itself has a special nature:

- The alkylation requires an acidity as much as or higher than 100% H_2SO_4, i.e., a $H_0 < -12$.
- Temperature must be low (<50 °C) in order to optimize the yield and product quality because the alkylation is exothermal.

So, based on these requirements of the alkylation, despite the potential benefit presented by solid catalysts, zeolites, ion-exchange resins as well as solid superacids have still not achieved commercial use as alkylation catalysts due to the fast catalyst decay [8].

Heteropoly acids (HPAs) have attracted increased interest in catalysis owing to their molecular structure and properties, especially, heteropoly acids own high acid strength which can be comparable with H_2SO_4 [9]. Recently, two papers about the reactivities of cesium salts of SiW_{12} and PW_{12} in the alkylation of isobutane with 2-butene have been published [10,11]. In our previous work, we have systematically investigated the catalytic behavior of HPAs (PW_{12} and SiW_{12}) and their salts in liquid phase on the alkylation of isobutane with n-butene [12]. In this work, we report the results of the alkylation catalyzed by HPA catalysts supported on various SiO_2 supports, and study the effect of structure of supports on the activity, selectivity and stability of the catalysts in the alkylation reaction.

2. Experimental

2.1. Preparation of supported catalyst

2.1.1. Impregnation

Supported-HPA catalysts were prepared by impregnation of commercial SiO_2 (designed S_0), modified SiO_2 (carried out by steam-treatment of commercial SiO_2 at 40 and 50 atm pressure, and designed S_{40} and S_{50}, respectively) and mesoporous molecular sieves (MCM-41 and HMS) with an aqueous solution of PW_{12} or SiW_{12}, followed by vigorous stirring at approximately 100 °C. The precipitates obtained together with the solution were subsequently evaporated until dried samples were obtained. In this case, the HPA content for all supported catalysts was about 50 wt%.

2.1.2. Sol–gel method

Silica-included $H_3PW_{12}O_{40}$ (or $H_4SiW_{12}O_{40}$) was prepared by the sol–gel method according to the literature [13]. After extraction with hot water at 80 °C for 3 h, filtering and then washing with water, no $H_3W_{12}O_{40}$ was detected in the washed liquid.

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2.2. Reaction

The alkylation experiments were carried out in a fixed-bed stainless steel reactor heated by an electric furnace at 80 °C reaction temperature (see figure 1), 0.8 MPa total pressure, a space velocity (LHSV) of 2 h^{-1} referred to isobutane–butene mixture with molar ratio of 10. Under these conditions, both reactants and products are in liquid phase. A preliminary experiment was carried out treating the catalyst at 150 °C *in situ* for 2 h in a nitrogen flow prior to the reaction. Once cooled to 80 °C, the feed mixture enters the reactor which is maintained at the reaction pressure

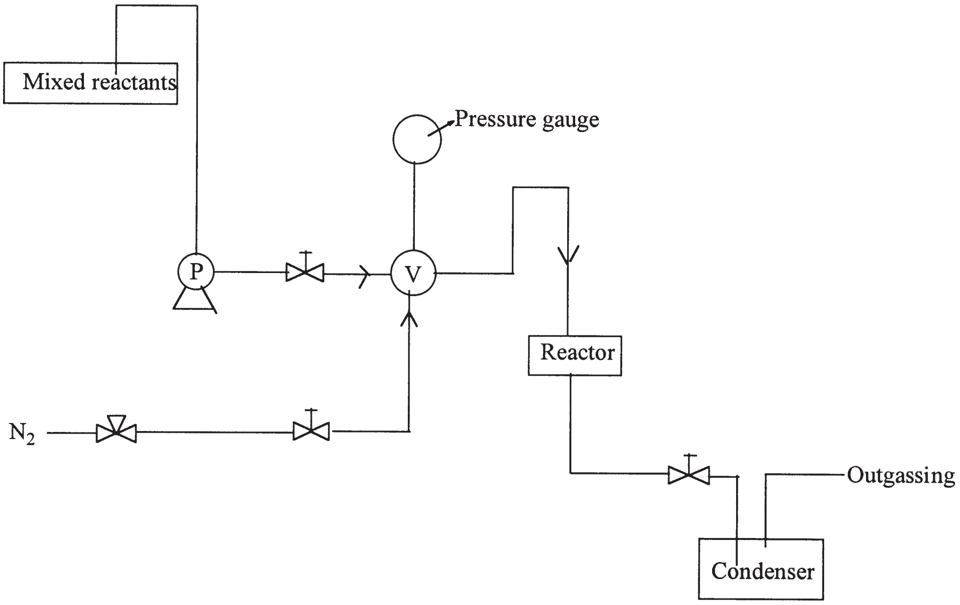

Figure 1. Schematic representation of the isobutane–butene alkylation system.

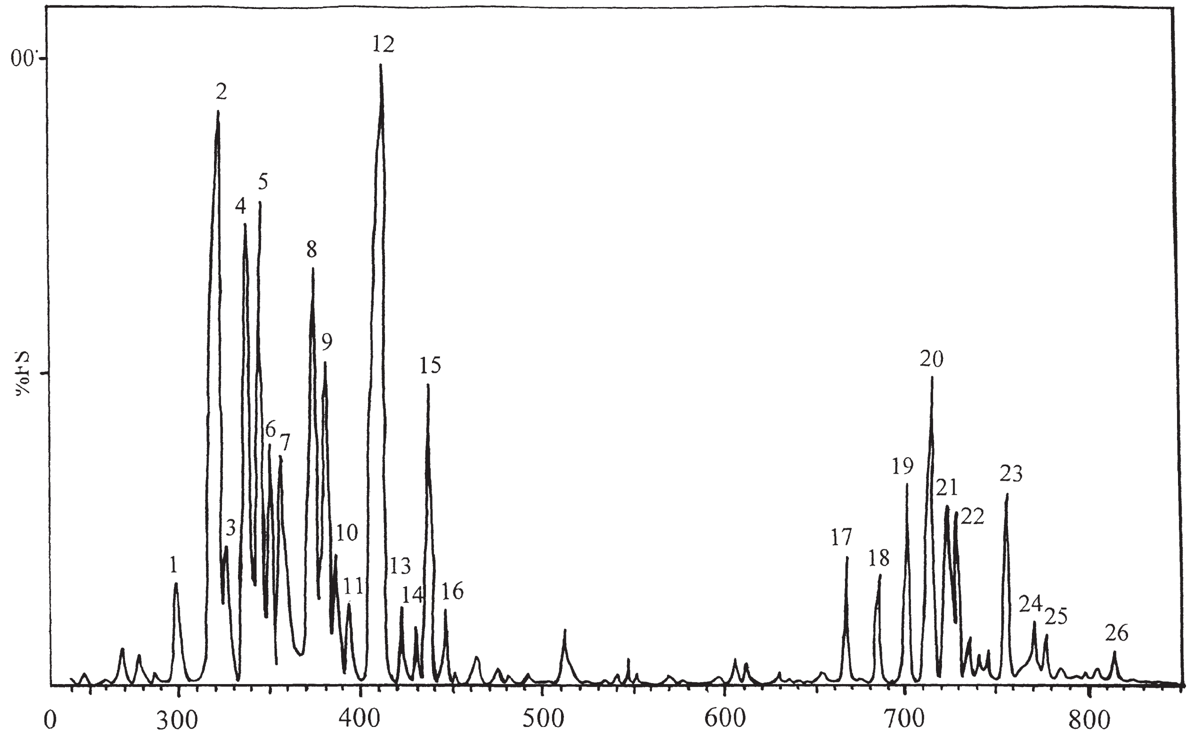

Figure 2. Products distribution of the alkylate over the supported heteropoly acid catalysts: (1) 2,2,3,3-tetramethylbutane, (2) 2,4,4-trimethylpentene-1, (3) 2-methylheptene-3, (4) 2,4,4-trimethylpentene-2, (5) undecene-3, (6) 2,3-dimethylhexene-2, (7) 4-methylheptene-3, (8) 3,4,4-trimethylhexene-2, (9) 2,5-dimethylhexene-2, (10) 2,2-dimethylhexene-3, (11) 2-methyl-3-ethylpentene-1, (12) 2,3,4-trimethylpentene-2, (13) 3,3-dimethyloctene-1, (14) 4-methylheptene-3, (15) octene-4, (16) 2,5,5-trimethylhexene-2, (17)–(22) trimers of 2-methylpropene, (23) decene-1, (24)–(26) tetramers of butenes.

in a nitrogen atmosphere. The reaction stream coming out of the reactor is then condensed with dry ice in order to collect the products totally.

After the experiment was completed, the condensate was first evaporated slowly at about −10 °C to eliminate the reactants while the residue as products was quantitatively analyzed in the GC using a FID detector after seperation of the individual compounds in a 50 m capillary column (XE-60). Individual hydrocarbons were identified by GC-MS. Spectrometric component analyses of alkylates are shown in figure 2.

3. Results and discussion

3.1. The activity and selectivity of the supported catalysts

The product distribution of the alkylates obtained at 4 h TOS on the different supported catalysts is presented in table 1.

It can be observed in table 1 that the parent acids, PW_{12} and SiW_{12}, are less active than the supported HPAs. This is explained by the very low surface area of the parent acids. In the case of all supported catalysts, it can also be seen that, compared to liquid-phase alkylation [12], very little amounts of alkylate oil (butene conversion) are obtained in the fixed-bed reactor, and a product distribution toward the formation of octenes, which are mainly formed by dimerization of the butenes on acid sites of weaker acidity (cf. figure 2). These results indicate that on these samples, with low concentration of strong Brønsted acid sites, the product distribution could be explained in terms of dimerization. There is, however, another important factor which has to be considered in order to explain the majority of $C_8^=$ products: the ability of the HPA/support to catalyze hydrogen transfer reactions. For the alkylation processed in the fixed-bed reactor, the fact that the time of contact of the isobutane–butene mixture with the catalyst is not long enough could decrease the capacities of 2,2,4-TMP$^+$ and hydrogen transfer.

On the other hand, it can also be seen that the acidity of supported catalysts has an effect on the activity. The acidity of heteropoly acids and their salts has been frequently determined by common characterization techniques such as Hammett indicators [14,15], TPD of NH_3 [16,17] or pyridine [18,19] and NMR spectroscopy [20]. Here, Hammett indicators were used to measure the acidity of supported catalysts. The results are listed in table 2.

It can be observed in table 2 that a correlation between the acidity measured by Hammett indicators and the catalytic acitivity for alkylation is found. Generally, to determine the catalytic activity of supported catalysts for alkylation requiring different acidities is probably the best way to study the surface acidic characteristics of these catalysts. In this sense, our results obtained for isobutane/butene alkylation, a reaction requiring strong acid sites, showed that the activity can be correlated with the surface acidity of the supported catalysts, giving a maximum for PW_{12}/S_0, SiW_{12}/S_0, PW_{12}/HMS, and SiW_{12}/HMS ($H_0 \approx -12.77$). In respect to heteropoly acids, it can be found that the activity of supported-SiW_{12} catalysts is higher than that of supported-PW_{12} catalysts. The reason is that $SiW_{12}O_{40}^{4-}$ of the heteropoly anion is much softer than $PW_{12}O_{40}^{3-}$, which makes it easier for $SiW_{12}O_{40}^{4-}$ to form a stable coordination while combining with t-C_4^+ [21]. For this reason, the activation energy for the alkylation is lowered. Moreover, supported-PW_{12} catalysts give higher selectivity to C_8 products as compared to SiW_{12}/support. Since the acid strength required to perform the different reactions occurring during isobutane–butene alkylation decreased in the order: cracking > alkylation > dimerization (oligomerization) [22], these results suggest a higher acid strength of the surface protons in PW_{12}. Furthermore, supported-PW_{12}

Table 1
Alkylate product distribution (TOS=4 h) for supported catalysts.

Catalyst	SiW_{12}	SiW_{12}/S_0	SiW_{12}/S_{40}	SiW_{12}/S_{50}	SiW_{12}/MCM-41	SiW_{12}/HMS	SiO_2-included-SiW_{12}
Weight of alkylate (g/g cat)	0.1	0.42	0.25	0.07	0.22	0.26	0.15
Yield of alkylate[a] (%)	3.96	16.4	8.92	2.92	9.20	10.8	6.25
Product distribution (wt%)							
C_5–C_7	2.43	2.35			1.36	3.88	
$C_8^=$	74.6	72.2	73.3	50.2	61.5	81.6	63.3
Total C_8^0	1.93	1.87	1.32	1.06	2.31	2.89	1.46
C_9^+	21.04	15.9	25.4	48.7	23.7	11.5	34.94

Catalyst	PW_{12}	PW_{12}/S_0	PW_{12}/MCM-41	PW_{12}/HMS	SiO_2-included-PW_{12}
Weight of alkylate (g/g cat)	0.09	0.27	0.16	0.17	0.13
Yield of alkylate[a] (%)	3.20	10.4	8.0	8.70	5.91
Product distribution (wt%)					
C_5–C_7	2.85	2.70	1.45	1.13	1.27
$C_8^=$	76.4	73.5	59.3	60.3	76.6
Total C_8^0	2.01	3.40	2.21	0.93	2.43
C_9^+	19.1	10.4	21.3	37.7	19.7

[a] Based on butene.

Table 2
The acidity of supported catalysts measured by Hammett indicators.[a]

Supported catalyst	H_0 -5.6	-8.22	-11.99	-12.77	-13.75
PW_{12}	+	+	±	−	−
PW_{12}/S_0	+	+	+	+	−
PW_{12}/HMS	+	+	+	+	−
PW_{12}/MCM-41	+	±	−	−	−
SiW_{12}	+	±	−	−	−
SiW_{12}/S_0	+	+	+	+	−
SiW_{12}/S_{40}	+	±	−	−	−
SiW_{12}/S_{50}	+	±	−	−	−
SiW_{12}/HMS	+	+	+	±	−
SiW_{12}/MCM-41	+	+	−	−	−

[a] Symbol "+" shows the color change of indicators; "−" shows no change of indicator color.

Table 3
The textural properties of various supports.

Support	S_0	S_{40}	S_{50}	HMS	MCM-41
Surface area (m^2/g)	473	64	48	>900	972.4
Pore diameter (Å)	36	212	299	44	52

catalysts would give a high selectivity toward the C_8 products with the increase of the acid strength, in accordance with the above hypothesis. These general concepts of the acidic property of heteropoly acids have been summarized in a recent paper of Kozhevnikov [23].

In regard to the distribution of the individual hydrocarbons, it can be seen that the textural properties of supports (including surface area and pore size) play an important role. The textural characteristics of supports are given in table 3.

For three SiO_2 samples, the activity of catalysts increases with the specific surface area. The effect of the structure of supports can also be obviously observed on the selectivity to C_8. The results given in tables 1 and 2 indicate that the yield of alkylate oil and the selectivity to C_8 decrease when increasing the pore diameter of the support. This result is in agreement with that reported in the literature [24]. The researchers have found in the alkylation of benzene with alkene that, in order to design highly active and selective alkylation catalysts, one has to achieve a catalyst with suitable pore diameter which is not too large and too small. And they have assumed that a composition in which the pore size of 70% of the pores is slightly larger than reactants is favorable to the activity and selectivity of the supported catalysts, and the pore size of the other 30% of the pores must be much larger than the reactants so that it can prevent poisoning of catalyst and producing the side products. As said above, it can be concluded that the higher catalytic activity and selectivity of the catalyst supported on commercial SiO_2 (S_0) can be ascribed to its ideal pore size and suitable distribution proportion; on the other hand, as far as modified SiO_2 (S_{40} and S_{50}) is concerned, the higher amount of C_{9+} hydrocarbons which are formed by oligomerization is ascribed to its pore size, all of which may be much larger than that of the reactants. At this point it appears that the alkylation properties of a given supported catalyst are determined by support factors such as surface area, especially pore structure. In addition, for mesoporous molecular sieve supports, such as MCM-41 and HMS, despite of their higher surface area, the critical effect of pore size would make the activity and selectivity of catalysts lie between those of catalysts supported on commercial SiO_2 and modified SiO_2.

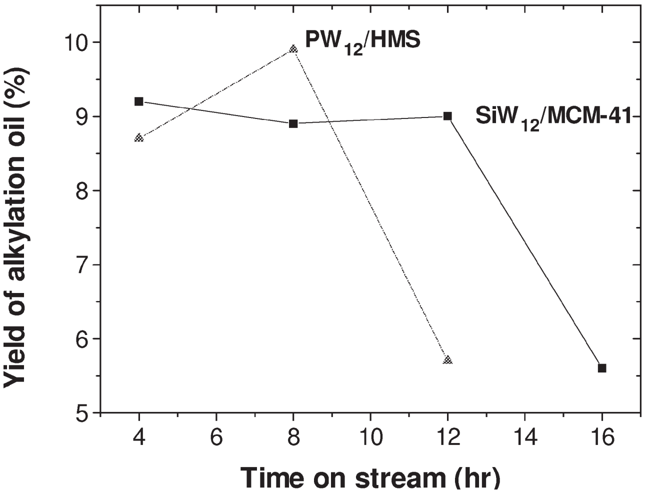

Figure 3. Change in yield of alkylate oil with TOS obtained during isobutane/butene alkylation.

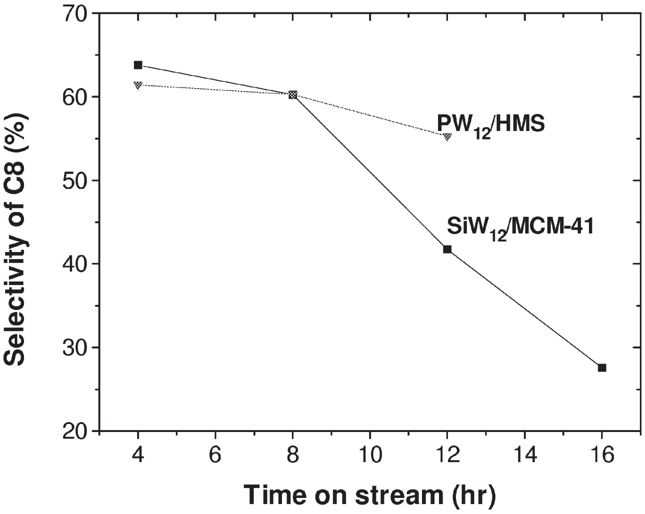

Figure 4. Change in selectivity to C_8 with TOS obtained during isobutane/butene alkylation.

3.2. The stability of supported catalysts

The change in the activity and selectivity with time on stream (TOS) for SiW_{12}/MCM-41 and PW_{12}/HMS is presented in figures 3 and 4. It can be seen that, under our reaction conditions, the supported-HPA catalysts seem to own an excellent stability and the activity of catalysts tends to keep unchangeable even after higher TOS of 8 or 12 h. Their stability is much higher than those of the zeolites [24] and solid superacids [7] reported in literature, whose major drawback as alkylation catalysts is catalyst deactivation which occurs after a few minutes. In order to further discuss the deactivation behavior of the catalysts, it could be interesting to study the change of the different components of the product with catalyst aging. Thus, the change in selectivity to C_8 with TOS for PW_{12}/HMS and SiW_{12}/MCM-41 is given in figure 4. In two cases, the selectivity to C_8 products rapidly decreases with TOS. It has been reported in literature that the strongest Brønsted acid sites were responsible for the alkylation reaction (formation of C_8), while oligomerization (formation of C_{9+}) mainly occurred on the weakest sites. Based on the results, it can be concluded that the stronger Brønsted acid sites deactivate with increase of TOS. This probably occurs as a consequence of acid site poisoning and pore blockage by large molecules formed mainly by oligomerization reaction. The decrease in the stronger acid sites is responsible for an increase of the C_{9+} products, which is accompanied by a decrease in selectivity to C_8.

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