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Silica-supported heteropoly acids promoted by Pt/Al_2O_3 for the isomerization of *n*-hexane

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Silica-supported heteropoly acids promoted by Pt/Al_2O_3 present efficient catalytic activity for the isomerization of *n*-hexane, and among them 50 wt% $HSiW/SiO_2$ promoted by Pt/Al_2O_3 shows the best catalytic performance, which might be closely related to the maintenance of the surface structure of heteropoly acids during reaction.

KEY WORDS: silica-supported heteropoly acids; isomerization of *n*-hexane; surface structure.

1. Introduction

Very recently, renewed interest arose in the selective isomerization of *n*-alkanes to high-octane-number branched isomers [1–4]. As might be expected, Pt-promoted solid acids are among the most studied systems. In the past decade heteropoly compounds promoted by platinum have been paid considerable attention for the isomerization of *n*-alkanes due to their strong intrinsic acidity. It is generally claimed in the literature that the acid strength decreases in the series of heteropoly acids of Keggin structure: $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_5BW_{12}O_{40}$ [5,6], and the catalytic activity for the isomerization is closely related to the acid strength of catalysts [7]. Therefore, $H_3PW_{12}O_{40}$ and its acidic salts have been performed for the isomerization of *n*-alkanes [8,9]. In contrast, little work has been done on the other heteropoly acids such as $H_4SiW_{12}O_{40}$ and $H_5BW_{12}O_{40}$ or their acidic salts. Here we report on various silica-supported heteropoly acids promoted by Pt/Al_2O_3 for the isomerization of *n*-hexane.

2. Experimental

Heteropoly acids (HPAs) were prepared in a classical way as described in the literature [10]. Silica-supported heteropoly acids were prepared by the impregnation method as described in ref. [11]. The surface area of silica, 50 wt% HPW/SiO_2, 50 wt% $HSiW/SiO_2$, and 50 wt% HBW/SiO_2 was 321, 124, 111, and 115 $m^2\,g^{-1}$ respectively, where HPW, HSiW, and HBW denoted, respectively, $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $H_5BW_{12}O_{40}$. Pt/Al_2O_3 (1 wt%) was prepared by impregnating the support γ-Al_2O_3 (100 $m^2\,g^{-1}$) with a solution of hexachloroplatinic acid [12]. The metal dispersion estimated from hydrogen chemisorption measurements was 0.58. The samples placed into a U-type glass fixed-bed microreactor were first reduced at 498 K for 4 h in hydrogen with a flowing rate of 21.8 ml min^{-1} under atmospheric pressure, and then their catalytic properties were evaluated under the same conditions but hydrogen passed through a saturator containing *n*-hexane. The WWH (weight of *n*-hexane per weight of catalyst and per hour) was 0.36 h^{-1}.

3. Results and discussion

The reactivity of various 50 wt% HPA/SiO_2 after 5 min on stream for the isomerization of *n*-hexane is presented in table 1. Apparently, silica-supported heteropoly acids have isomerization activity but are very easy to deactivate by coke deposition. If one considers that the higher the selectivity for the cracking, the stronger the acidity of the samples, then the acidic strength in the series follows the order HPW < HSiW < HBW, which is the reverse order mentioned above. However, the conversion of *n*-hexane in the series follows the order HPW > HSiW > HBW.

It is well known that isomerization reactions should be carried out on a bifunctional catalyst, consisting of a protonating acid function and a hydrogenating/dehydrogenating metal function. In this work, 1 wt% Pt/Al_2O_3 was used as a hydrogenation promoter, although no product is detected under reaction conditions for 1 wt% Pt/Al_2O_3 alone. It is found that for various 50 wt% HPA/SiO_2 promoted by 1 wt% Pt/Al_2O_3, both the conversion of *n*-hexane and the selectivity for the isomerization are improved remarkably, and the best

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Table 1
The reactivity of various 50 wt% HPA/SiO_2 after 5 min on stream

HPA/SiO_2	Selectivity (%)		
	HPW/SiO_2	$HSiW/SiO_2$	HBW/SiO_2
2,2-Dimethylbutane	2.7	1.9	4.1
2,3-Dimethylbutane	2.3	4.6	–
2-Methylpentane	33.5	20.7	13.7
3-Methylpentane	17.4	12.6	–
Isomerization	55.9	39.8	17.8
Cracking	44.1	60.2	82.2
Conversion (%)	28	21	1

Note: Dash indicates trace amount.

Table 2
Catalytic properties of various 50 wt% HPA/SiO_2 promoted by 1 wt% Pt/Al_2O_3

HPA/SiO_2	Selectivity (%)		
	HPW/SiO_2	$HSiW/SiO_2$	HBW/SiO_2
2,2-Dimethylbutane	2.8	3.6	1.3
2,3-Dimethylbutane	11.6	11.2	7.1
2-Methylpentane	52.7	52.5	55.9
3-Methylpentane	32.2	32.0	35.3
Isomerization	99.3	99.3	99.6
Cracking	0.7	0.7	0.4
Conversion (%)	50	61	21

performance appears in the vicinity of 1 : 1 ratio in weight for 50 wt% HPA/SiO_2 and 1 wt% Pt/Al_2O_3.

As shown in figure 1, it is very interesting to find that three silica-supported heteropoly acids promoted by 1 wt% Pt/Al_2O_3 (1 : 1 ratio in weight) show completely different catalytic behaviour before the steady state. For 50 wt% HPW/SiO_2 promoted by 1 wt% Pt/Al_2O_3 the conversion of *n*-hexane decreases slowly with time on stream. In contrast, for 50 wt% $HSiW/SiO_2$ promoted by 1 wt% Pt/Al_2O_3, the conversion of *n*-hexane increases rapidly and for 50 wt% HBW/SiO_2 promoted by 1 wt% Pt/Al_2O_3, the conversion remains constant. This might be due to their different behaviour of surface reactive species during reaction. The activation period for the 50 wt% $HSiW/SiO_2$ promoted by 1 wt% Pt/Al_2O_3 sample might be owing to the exceptional softness of $SiW_{12}O_{40}^{4-}$ [13].

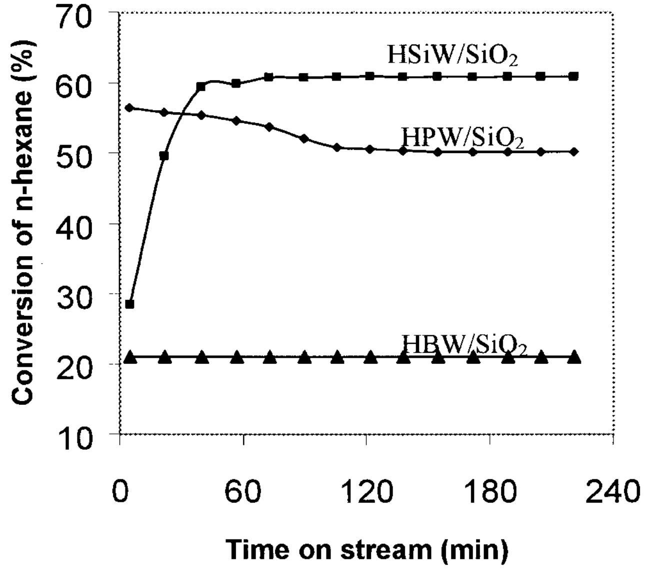

Figure 1. Conversion of *n*-hexane over 50 wt% HPA/SiO_2 promoted by 1 wt% Pt/Al_2O_3.

Catalytic properties of various 50 wt% HPA/SiO_2 promoted by 1 wt% Pt/Al_2O_3 (1 : 1 ratio in weight) after reaching a steady state are presented in table 2. For the three mechanical mixtures, the selectivity for

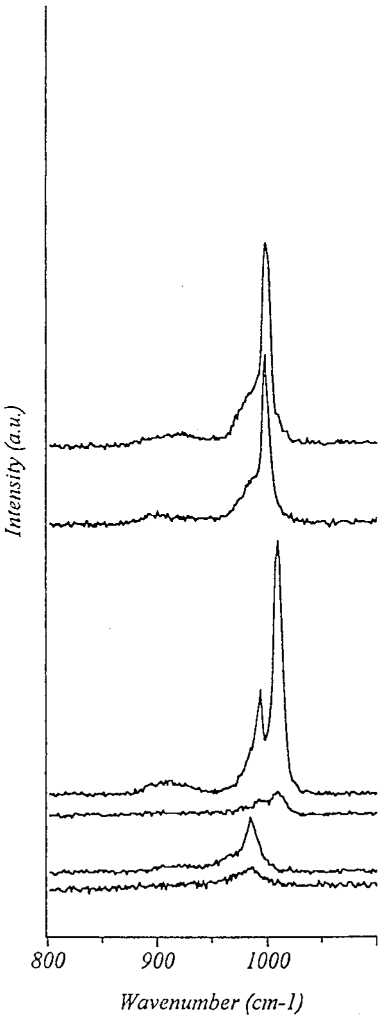

Figure 2. FT-Raman spectra of various samples (the samples from top to bottom are, respectively, 50 wt% $HSiW/SiO_2$, 50 wt% $HSiW/SiO_2$ promoted by 1 wt% Pt/Al_2O_3 after reaction, 50 wt% HPW/SiO_2, 50 wt% HPW/SiO_2 promoted by 1 wt% Pt/Al_2O_3 after reaction, 50 wt% HBW/SiO_2, and 50 wt% HBW/SiO_2 promoted by 1 wt% Pt/Al_2O_3 after reaction).

the isomerization is as high as 99.2–99.6%, while the conversion of *n*-hexane is in the range 21–61%. This indicates that silica-supported heteropoly acids promoted by 1 wt% Pt/Al_2O_3 are promising catalysts for the isomerization of *n*-hexane. Note that the conversion of *n*-hexane follows the order HSiW > HPW > HBW, which is not consistent with the order of their acid strength reported in the literature [5,6] and our results on pure 50 wt% HPA/SiO_2 described above. Moreover, it is very interesting to note that the selectivity for 2-branched isomers (2,2-dimethylbutane and 2,3-dimethylbutane), which is very beneficial for improving the octane number, also follows the order HSiW > HPW > HBW. These results might show the importance of the balance between the hydrogenation function and the acidic function in the bifunctional catalysis and more particularly the synergetic effect obtained in the isomerization of *n*-hexane.

Moreover, the FT-Raman spectra shown in figure 2 clearly indicate that after reaction 50 wt% HSiW/SiO_2 promoted by 1 wt% Pt/Al_2O_3 is among the best samples for keeping the intensities of bands associated with various heteropoly acids. This indicates that 50 wt% HSiW/SiO_2 is among the best samples for keeping the surface structure of heteropoly acids and thus the surface acid strength. As reported previously [14], under hydrogen flow various heteropoly acids may be partially reduced to the heteropoly blues whose acidity is definitely lower than that of the precursor, and HPW is among the easiest to reduce. Other hypotheses found in literature are (1) a strong interaction between HPA and protonated silanol groups on the surface through three proton exchanges, and thus HSiW possesses one supplementary available proton for the reaction [15]; (2) $SiW_{12}O_{40}^{4-}$, as a soft base which complexes with an organic carbocation to form a stable intermediate, is more effective than $PW_{12}O_{40}^{3-}$ [13], and might also be related to the catalytic performances shown in figure 1 and table 2.

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