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REVIEW

RECENT TOPICS IN HETEROGENEOUS CATALYSIS OF HETEROPOLYACIDS

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Abstract – First, the state of the art of the catalyst design based on heteropoly compounds is briefly overviewed. Then, selected topics of solid heteropoly catalysts, that is, the selective oxidation of isobutyric acid and isobutane over molybdovanadophosphoric acids, the methyl t-butyl ether synthesis in pseudoliquid of heteropolyacids, and the shape-selective and bifunctional (combined with noble metals) acid catalysis of cesium and ammonium salts of tungstophosphoric acid are described based on the recent studies from our laboratory.

Key words: *Heteropolyacid, Selective Oxidation, Pseudoliquid Behavior, Alkane Isomerization*

INTRODUCTION --- Design of heteropoly catalysts

Heteropoly acids and their salts (HPA) are interesting catalyst materials due to their controllable acid and redox properties. They can be used as acid and oxidation catalysts either in the solid state or in solution. There are actually several large-scale commercialized processes using heteropoly catalysts. Besides, HPA catalysts are expected to provide efficient routes for the synthesis of fine chemicals [Okuhara et al., 1996].

From the viewpoint of catalyst design, the controllability of the HPA catalysts at atomic/molecular levels is very important and gives us a good opportunity for the design of practical catalysts at this level. The following relationships at the atomic/molecular levels are very useful for this purpose. Needless to say, the reactor as well as process design is necessary for the commercialization, in addition to catalyst design.

$$\boxed{\text{Catalytic performance}} \leftrightarrow \boxed{\text{Physical and chemical properties}} \leftrightarrow \boxed{\text{Structure and composition}} \leftrightarrow \boxed{\text{Method of preparation of catalyst}} \quad (1)$$

The acid strength can be controlled mainly by the polyanion structure and its charge, and the acid amount by the kind and amount of counter cation. It is possible to control the oxidation ability by the counter cation in the case of hydrogen form and alkali salts of heteropolymolybdates. The combination of noble metals and heteropolyacids is another promising technique of the catalyst design. Pd combined with HPA is the commercial catalyst for the production of acetic acid from ethylene in one step Pt-promoted Cs salt of HPA catalyzes isomerization of C4-C6 alkane very selectively.

Physical properties such as surface area and pore structure can also be controlled precisely by choosing the cation species and precipitation conditions. Shape selective adsorption and catalysis were actually demonstrated. Bulk-type catalysis including pseudoliquid behavior as well as soft basicity of polyanion are the other important factors controlling the catalytic function of heteropolyacids. In practical applications, the selection of adequate supports is also useful.

The state of the art of the catalytic chemistry of HPAs related to the design of catalyst are described in detail in reference [Okuhara et al., 1996].

1. Selective Oxidation by Heteropolymolybdovanadates (P-Mo-V)

The fundamental correlations between the redox properties and catalytic activities have successfully been established for the hydrogen form and alkali salts of 12-molybdophosphoric acid [Okuhara et al., 1996]. Good correlations between the oxidizing abilities of catalysts and the rates of several catalytic oxidations are present, respectively for the surface- and bulk-type catalysis, as shown in Fig. 1.

Although in practical applications heteropoly compounds containing Mo and V usually exhibit superior performances for catalytic oxidation, the attempts to find similar relationships for mixed coordinated HPA such as molybdovanadophophates have not been successful, due to their insufficient thermal stability. For example, $H_4PVMo_{11}O_{40}$ tends to decompose at about 200 °C, as in Eq. (2). The VOy, a mixture of monomeric and polymeric species, was shown to improve the selectivity of the catalytic oxidation of isobutane to methacrylic acid by modifying the redox properties [Inumaru et al., to be published], but the thermal instability makes difficult the establishment of the correlations as in Eq. (1) required for the catalyst design.

$$(12/11)PMo_{11}VO_{40} \rightarrow PMo_{12}O_{40} + (1/11)POx + (12/11)VOy \quad (2)$$

We attempted to stabilize the molybdovanadates of Keggin-type by forming their cesium salts. Although the possibility

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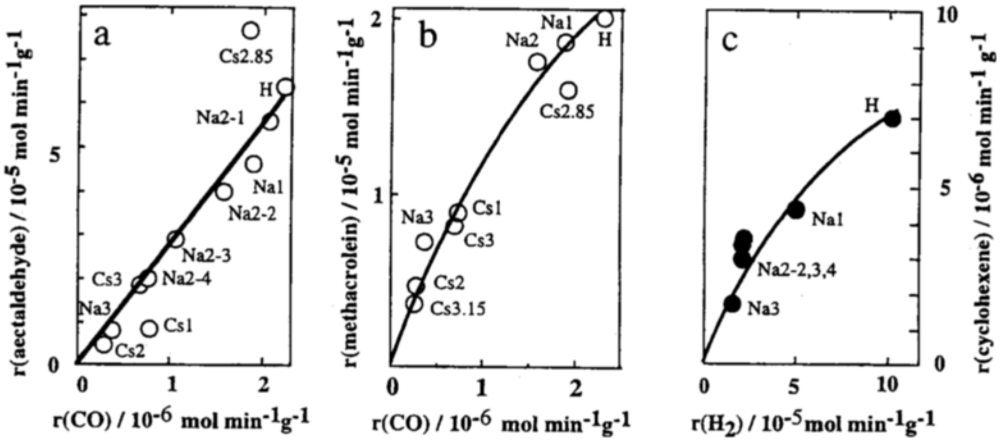

Fig. 1. Correlations between rates of catalytic oxidation and oxidizing abilities of catalysts.
a; oxidation of acetaldehyde (surface-type), b; oxidation of methacrolein (surface-type), and c; oxidative dehydrogenation of cyclohexene (bulk-type). r(CO) and r(H_2); rates of noncatalytic reduction of catalysts by CO (surface) and H_2 (bulk), respectively.

of slight decomposition could not be excluded, thermal stability was much improved and high yields of methacrylic acid were obtained for the oxidative dehydrogenation of isobutyric acid, as shown in Fig. 2 [Lee et al., 1997]. In this case, it was also shown that the surface acid-base properties were widely and interestingly varied by the content of Cs in $Cs_xH_{4-x}PMo_{11}VO_{40}$ (x=0-4).

A crystalline vanadium phosphorous oxide may be regarded to be a heteropoly compound in a broad sense. By applying ex situ and in situ spectroscopies, we found that the surface of $(VO)_2P_2O_7$ was reversibly oxidized to X1 (or δ) phase of $VOPO_4$ under the reaction conditions of the oxidation of *n*-butane to maleic anhydride [Koyano et al., 1996, 1997]. It was indicated that this redox cycle is essential for the selective oxidation.

Various molybdovanadophosphates have been applied to the selective oxidation of alkanes [Centi et al., 1990; Mizuno et al., 1996]. Patent literature describes a fair yield of the reduced and non-reduced $H_3PMo_{12}O_{40}$ for isobutane to methacrolein and methacrylic acid [JP 1988-145249, 1991-106839]. Some of the results of Mizuno et al. [1996] are given in Table 1 in comparison with the best data in the literature under the similar reaction conditions. Ueda et al. obtained a high yield for isobutane oxidation by using a reduced heteropolymolybdate-pyridine composite catalyst [Li and Ueda, 1991].

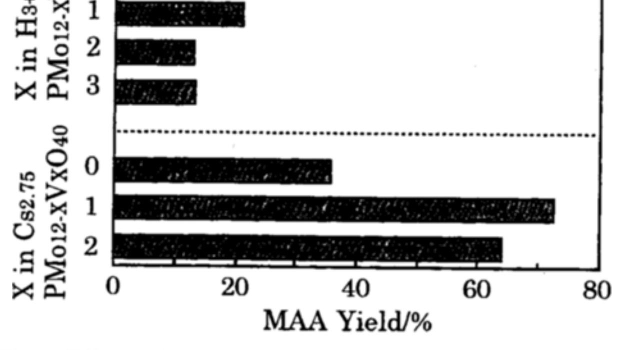

Fig. 2. Effects of V and Cs contents on the yield of methacrylic acid (MAA) at 350 °C over $H_{3+x}PMo_{12-x}V_xO_{40}$ and $Cs_{2.75}H_{0.25+x}PMo_{12-x}V_xO_{40}$.

Table 1. Selective oxidation of lower alkanes by molybdovanadophosphates combined with transition metal cations [JP 1988-145249, 1991-106839]

Alkane	Product	Catalyst	Yield/%	Yield and catalyst in the literature/%
Isobutane	Methacrylic acid	Ni/$Cs_{2.5}H_{1.5}$-$PVMo_{11}O_{40}$	9	6(Mo-P-As-Cs-Cu-O)
Propane	Acrylic acid	Fe/$Cs_{2.5}H_{1.5}$-$PVMo_{11}O_{40}$	13	11(V-P-Te-O)
Ethane	Ethane	Mn/$Cs_{2.5}H_{1.5}$-$PVMo_{11}O_{40}$	5	4(Mo-Nb-O)

2. MTBE Synthesis in Pseudoliquid Phase of $H_3PW_{12}O_{40}$ and $H_6P_2W_{18}O_{62}$

Fig. 3 shows the methyl t-butyl ether (MTBE) yields at the steady states, which were attained within one hour, as a function of reaction temperature for various unsupported HPA [Shikata et al., 1995]. The yields were reproducibly obtained when the reaction temperature was changed up and down. The selectivities (based on both methanol and isobutylene) were close to 100 % below 343 K. It is remarkable that $H_6P_2W_{18}O_{62}$ (Dawson-type) showed a much higher activity than the other Keggin-type HPA's in the lower temperature range that is favored from the equilibrium of MTBE formation. The decreases of the yield in the high temperature region are mainly due to the equilibrium limitation.

The very high catalytic activity of $H_6P_2W_{18}O_{62}$ as compared with $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, etc. at about 340 K can not be explained by the acid strength measured by Hammett indicators and by calorimetric measurement of NH_3 absorption. On the other hand, the rates of absorption of methanol and MTBE at 313-323 K were faster for $H_6P_2W_{18}O_{62}$, corresponding to its high catalytic activity.

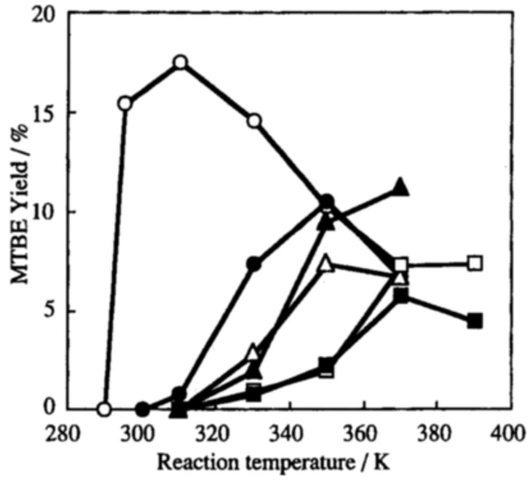

Fig. 3. Dependence of MTBE yield and selectivity on reaction temperature of MTBE.
○; $H_6P_2W_{18}O_{62}$, ●; $H_3PW_{12}O_{40}$, △; $H_4SiW_{12}O_{40}$, ▲; $H_4GeW_{12}O_{40}$, □; $H_5BW_{12}O_{40}$, ■; $H_6CoW_{12}O_{40}$. Methanol : isobutylene : N_2=1 : 1 : 3

The dependencies of the rate on methanol pressure are shown in Fig. 4. Unusual reaction orders with respect to the methanol pressure which are somehow similar to those observed for ethanol dehydration [Lee et al., 1992] are noted. This dependency is similar to that for an ion-exchange resin (Amberlyst 15), but in striking contrast with those observed for H-ZSM-5, SO_4-ZrO_2 and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. These results demonstrate that the MTBE synthesis proceeds in the pseudoliquid phase in the case of hydrogen forms of HPA.

It was found for isopropanol dehydration that there were two pseudoliquid phases; one had a much higher activity and a smaller amount of absorbed alcohol than the other [Takahashi et al., 1985]. Hence, the fact that the $H_6P_2W_{18}O_{62}$ was much more active at low temperatures is understandable, since the rate of absorption was high and the amount of absorption at the steady state of the reaction was moderate for $H_6P_2W_{18}O_{62}$.

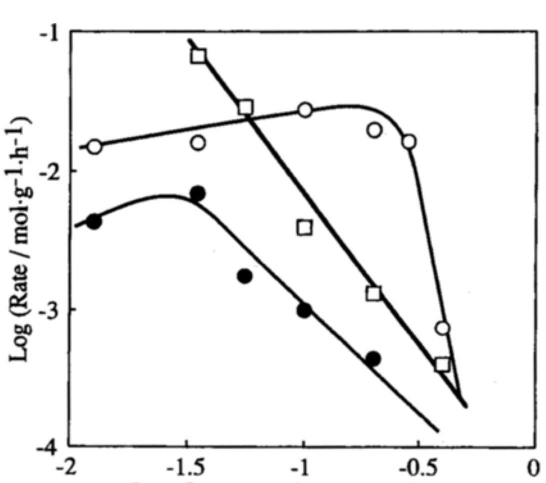

Fig. 4. Pressure dependency of MTBE formation on methanol at 323 K.
○; $H_6P_2W_{18}O_{62}$, ●; $H_3PW_{12}O_{40}$, □; $Cs_{2.5}H_{0.5}PW_{12}O_{40}$

A remarkable correspondence between the secondary structures determined by powder XRD (carefully avoiding the exposure to the humidity) and the reaction rates were observed. It is likely that the secondary structure is more flexible when it is amorphous and hence the absorption and desorption are easier. It is also probable that the oval shape of the Dawson anion favors the formation of an amorphous structure, while the spherical Keggin anion favors stable crystalline structure. It is here assumed that non-polar isobutylene is absorbed into HPA bulk, being assisted by co-existing methanol.

The catalytic activities of $H_6P_2W_{18}O_{62}$ (Dawson) and $H_3PW_{12}O_{40}$ (Keggin) increased remarkably (particularly for the Keggin) when they were supported on silica gel [Shikata et al., 1997]. The activities of both HPA's were about the same as that of Amberlyst 15 and the selectivities were comparable or better than Amberlyst 15 under the same reaction conditions. Unusual pressure dependencies of the rate similar to that in Fig. 4 indicate that the reaction over supported HPA also proceeds in the pseudoliquid (or in the solid bulk of HPA particle).

3. Shape-selective Catalysis and Epitaxial Self-assembly. Microstructure of Cs_x and $(NH_4)_xH_{3-x}PW_{12}O_{40}$

When protons of $H_3PW_{12}O_{40}$ are gradually substituted by Cs or NH_4 to form $Cs_xH_{3-x}PW_{12}O_{40}$ (CsX) or $(NH_4)_xH_{3-x}PW_{12}O_{40}$, the catalytic activity initially decreases, but sharply increases for x > 2. The activity of Cs2.5 is often much higher than the hydrogen form and other solid acids, and hence a promising candidate of solid "superacid" [Tatematsu et al., 1984; Okuhara et al., 1992]. This is due to the very high surface acidity, that is, the number of protons on the surface, brought about by the increase in the surface area. The catalytic activity is usually in parallel with the surface acidity (Fig. 5). It has recently been found that this parallelism does not hold for certain reactions, which indicates the presence of shape selectivity. The shape selective catalysis and adsorption have been demonstrated [Okuhara et al., 1996].

Furthermore, it was found recently that under certain pre-

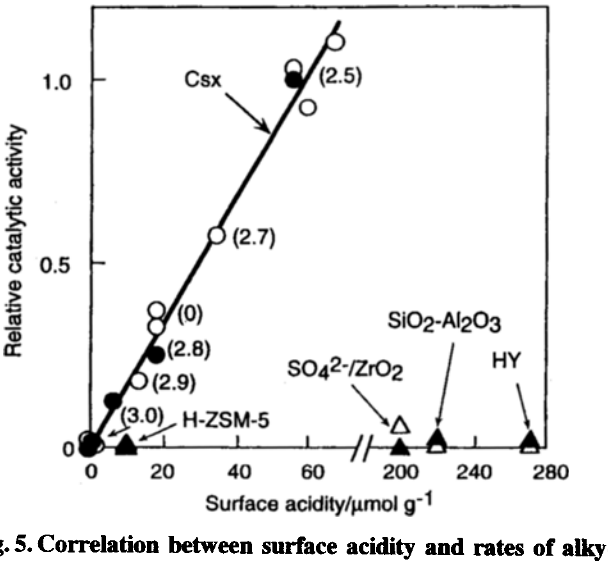

Fig. 5. Correlation between surface acidity and rates of alkylation of 1,3,5-trimethylbenzene (●) and decomposition of cyclohexyl acetate (○).

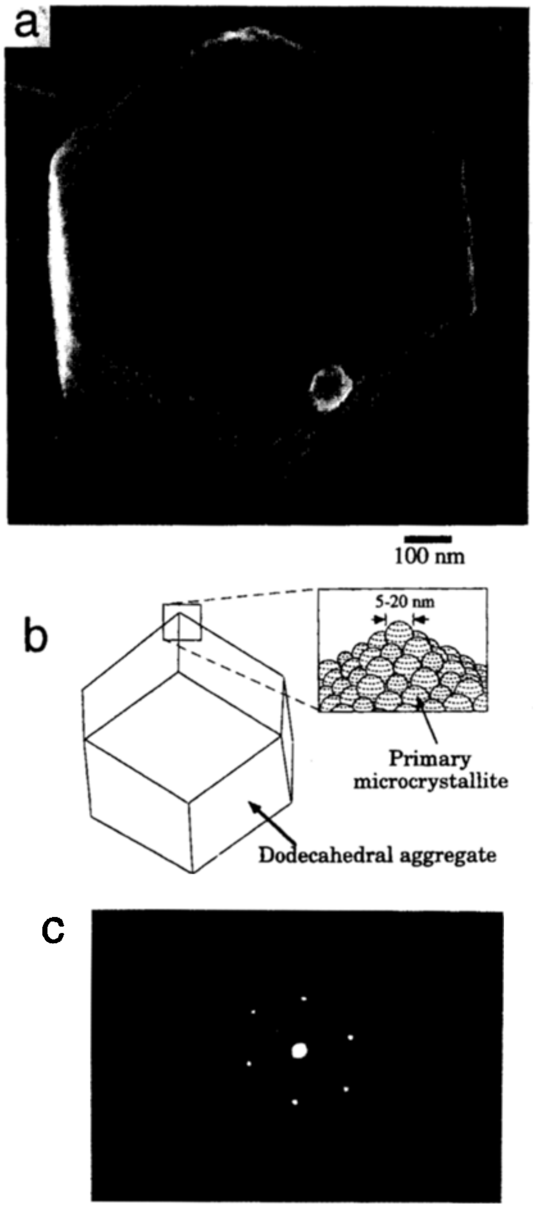

Fig. 6. (a) SEM image, (b) schematic model, and (c) ED pattern of epitaxially self-assembled $(NH_4)_3PW_{12}O_{40}$.

paration conditions epitaxially self-assembled microcrystallites were formed [Inumaru et al., 1996]. They have micro- and/or mesopores that are present in the space between the microcrystallites. The microcrystallites in one aggregate have the same crystal orientation and are connected with each other epitaxially, so that each aggregate looks like a porous "single crystal". This was demonstrated by the measurements of SEM, electron diffraction (ED), XRD line width, and N_2 adsorption isotherm. An ED pattern and a schematic model of a $(NH_4)_3$-$Pw_{12}O_{40}$ aggregate having a dodecahedral shape are shown in Fig. 6.

4. Isomerization of Alkanes Catalyzed by Composite Catalysts: Noble Metals+Heteropolyacids

Isomerization of light *n*-alkanes which leads to branched alkanes is important for the production of a high octane-number gasoline with low contents of aromatics and lead. It is believed that this reaction proceeds through a carbenium ion intermediate which requires the presence of strong acid sites, as low temperatures favor the production of branched isomers with respect to the equilibrium product distribution. Catalysts consisting of noble metals and solid acids, such as Pt/SO_4-ZrO_2, Pt-zeolites, Pt modified clay minerals and Pd_xH_{3-2x}-$PW_{12}O_{40}/SiO_2$, have been reported for the skeletal isomerizations of *n*-pentane and *n*-hexane at medium temperatures (473-573 K).

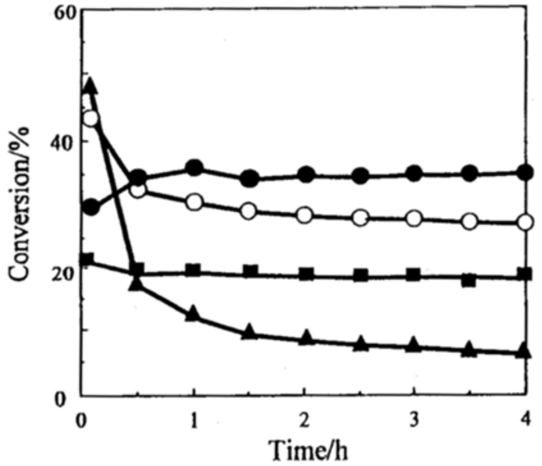

Fig. 7. Time courses of *n*-pentane isomerization at 453 K.
●; Pt/Al_2O_3+Cs2.5, ○; Pt/Cs2.5 (Pt impregnated on Cs 2.5), ▲; $Pt/Al_2O_3+SO_4^{2-}/ZrO_2$ (mechanical mixture), and ■; Pt/Al_2O_3+H-ZSM-5 (mechanical mixture). *n*-pentane: $H_2:N_2=0.05:0.05:0.90$.

Recently, we have found that an acidic Cs salt of H_3PW_{12}-O_{40}, that is, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Cs2.5), is very active for the skeletal isomerization of *n*-butane [Na et al., 1993] and the stationary activity was greatly enhanced by the addition of platinum at low H_2 pressure [Na et al., 1997].

Here, the isomerization of *n*-pentane and *n*-hexane with Pt-promoted Cs2.5 catalysts are described and the results are compared with Pt-promoted SO_4/ZrO_2 (SZ) and H-ZSM-5 (HZ) [Liu et al., in press]. Fig. 7 shows the time courses of pentane isomerization catalyzed by Pt+Cs2.5, Pt+HZ, and Pt+SZ [all mechanical mixtures of Pt/Al_2O_3 (Pt 1 wt%) and solid acids]. Results of Pt/Cs2.5 (impregnated) are also shown in Fig. 7. Pt+Cs2.5 exhibited a high constant conversion of 34.8 % after a slight initial increase. Pt+SZ showed the highest initial conversion (47 %), but the conversion decreased rapidly to the stationary level of 9.4 %. For Pt+HZ, the deactivation was small, giving a modest conversion at the stationary state. After a certain deactivation, Pt/Cs2.5 showed a high stationary conversion, but it was lower than Pt+Cs2.5. As for the selectivity to isopentane, Pt+Cs2.5 and Pt+HZ showed higher selectivities (96.9 and 93.3 %, respectively) than 79.4 % of Pt+SZ. Pt/SZ and Pt+HZ used in this study are very similar to those reported in the literature, since they reproduced the yields and selectivities in the literature.

Stationary conversions and selectivities of *n*-hexane isomerization catalyzed by Pt+Cs2.5, Pt+HZ, and Pt+SZ are summarized in Table 2. Time courses were similar to those of *n*-pentane isomerization. Pt+Cs2.5 showed the highest station-

Table 2. Product distribution in hexane isomerization over Pt/Al_2O_3+Cs2.5, Pt/Al_2O_3+SO_4^{2-}/ZrO_2, and Pt/Al_2O_3+H-ZSM-5 at 453 K

Catalyst	Pt/Al_2O_3+ Cs2.5	Pt/Al_2O_3+ H-ZSM-5	Pt/Al_2O_3+ SO_4^{2-}/ZrO_2
Conversion/%	58.6	31.3	24.1
Selectivity/%	98.4	95.8	89.2
Product distribution/%			
Propane	0.0	0.2	1.4
Butane	0.9	2.2	3.6
Pentane	0.5	1.5	4.4
2,2-Dimethylbutane	3.6	5.3	4.1
2,3-Dimethylbutane	13.7	11.6	9.3
3-Methylpentane	33.9	35.2	36.7
2-Methylpentane	47.2	43.7	39.1
Methylcyclopentane	0.0	0.0	0.3
Cyclohexane	0.0	0.0	0.2
Heptanes	0.2	0.3	0.9

n-Hexane : H_2 : N_2=0.05 : 0.20 : 0.75, W/F=40 ghmol^{-1}, catalyst=1 g.

ary conversion (58.6 %) and the highest selectivity to branched hexanes (98.4 %) with little deactivation. Pt+HZ showed lower conversion and selectivity.

High temperature (>473 K) and excessive H_2 (e.g., $H_2 >$ 90 %) are usually required for the isomerization reaction of light alkanes. Although the reaction becomes faster at high temperatures, side reactions such as cracking and disproportionation become significant. In this study, high activity and selectivity were achieved by Pt+Cs2.5. The order of the acid strength is reported to be SZ > Cs2.5 > HZ [Okuhara et al., 1996]. SZ may be too strongly acidic and causes great deactivation, and the weak acidity of Pt+HZ results in a low activity. Pt+Cs2.5 showed the highest activity and selectivity in both reactions possibly because of moderate and uniform strength of acid sites.

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