

GAS-PHASE ISOMERIZATION OF ETHYLBENZENE OVER PT-HETEROPOLY ACID/ZEOLITE CATALYSTS

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(Received 16 September 1985, accepted 27 January 1986)

Abstract—The catalytic performance and availability of heteropoly compounds in vapor phase isomerization of ethylbenzene to xylene have been studied. 12-molybdophosphoric acid and its salts of four first row transition metals (Cr, Fe, Co and Ni) were chosen as heteropoly compounds, and they were supported together with platinum over Y-zeolite. The experiments were carried out at 400°C, 18 kg/cm² of H₂ pressure, 4.6 of H₂/ethylbenzene mole ratio and 1.5 gr-feed/hr·gr-cat of LWHSV (Liquid Weight Hourly Space Velocity). As the results of experiments, heteropoly acid enhances the activity and selectivity of isomerization and the activity of isomerization is strongly affected by the method of catalyst preparation. In case of 12-molybdophosphates, their acidities vary with the kind of counteranions and it seems that the acidity is closely related to the electronegativity of the corresponding counteranion. The pretreatment with hydrogen shows an enhanced activity and selectivity.

INTRODUCTION

The importance of xylene has been increased continuously in the field of chemical industries. In earlier times, the most of xylene was originally used for a solvent and as a component of high-octane quality fuels. The use of individual pure xylene isomers has come to be begun with the development of petroleum industry since 1940. Especially, in recent years, as the demands of polyester fiber increase and BTX chemical industry develops, the demand of xylene also tends to increase [1, 2].

In earlier times, xylene was recovered as one of by-product chemicals from coal carbonization. However, as petroleum industry developed, the production of xylene from petroleum was begun. Recently, typical industrial production of xylene is carried out by separation of o-, m- and p-xylene from mixed xylene obtained from reforming of naphtha. But this kind of mixed xylene contains ethylbenzene in a fairly large amount, and thus the separation of ethylbenzene from the mixed xylene or the isomerization of ethylbenzene to xylene is needed.

In addition, more beneficial use of ethylbenzene, which is primarily employed as a solvent or a raw material for the manufacture of styrene, is required. Recently, because of an economical sense about the separation of ethylbenzene from mixed xylene, the research for the

isomerization of ethylbenzene to xylene has been increased. Up to now, however, only a few patents concerning isomerization of ethylbenzene to xylene have been reported [3, 4, 5], and the systematic investigations on it have been recently carried out [6, 7].

In this study, heteropoly acid, which has strong Brönsted acidity and has attracted much interest as a solid acid catalyst recently, is used as a promoter. The roles of 12-molybdophosphoric acid in ethylbenzene isomerization, effects of the methods of catalyst preparation and pretreatment, and acidity effect of 12-molybdophosphates are investigated.

THEORY

The reaction mechanism of isomerization of ethylbenzene to xylene is complex, that is, this isomerization proceeds through hydrogenation-skeletal isomerization-dehydrogenation. Pitts et al. [8] reported that isomerization of ethylbenzene proceeds via hydrogenated intermediates over bifunctional catalysts. Gnep and Guisnet [9] postulated the reaction mechanism of ethylbenzene isomerization to be ethylcyclohexene-1, 2-methylethyl cyclopentene-1, 2-dimethyl cyclohexene-O-xylene, which further isomerizes to m- and p-xylene. Röbschläger and Christoffel [10] also reported that over Pt/Al₂O₃ catalyst, where the carrier displays only weak acidity, xylene is formed from ethylbenzene mainly via the route of ethylbenzene → ethylcyclohexene-1,2-methy-

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ethylcyclopentene-1, 2-dimethylcyclohexene-*o*-xylene, in which skeletal rearrangement of tertiary carbocation are only considered to be rate-determining steps, while over Pt/zeolite catalyst with higher acidity, skeletal isomerization in which secondary carbocation is involved contributes, in addition to the route mentioned above, to the measured product distribution.

From the facts mentioned above, the catalyst used in this isomerization must be bifunctional catalyst, that is, dual function catalyst and acid catalyst. The former displays hydrogenation and dehydrogenation activities and the latter offers acid site at which skeletal isomerization occurs. And it is recognized that the acidity of catalyst contributes to the skeletal isomerization.

Acid type catalysis of heteropoly acid has attracted our attention because heteropoly acid has strong Brönsted acidity to be applicable to acid-catalyzed reactions [11, 12, 13].

Heteropoly acid with Keggin structure has large void volume in their structure and it also contains large amount of water. From recent NMR study of heteropoly acid, it is identified that the protons of heteropoly acid are present as H_3O^+ . And from the FT-IR analysis of pyridine adsorption by heteropoly acid, Yoneda et al. [14] reported that the Brönsted acidity of heteropoly acid is very strong. In this study, therefore, heteropoly compounds are expected to play an important role in skeletal isomerization.

EXPERIMENTAL

(1) Apparatus and Procedure

Ethylbenzene isomerization was carried out at 400°C, 18 kg/cm² of H_2 pressure, 4.6 of H_2 /ethylbenzene mole ratio and 1.5 gr-feed/hr-gr-cat of LWHSV using a microcatalytic reactor. Catalyst (1.5g, 1/16" pellet) was packed in a short section of 1/4" stainless steel tubing. H_2 gas stream which was adjusted by a regulator and passed through a check valve and ethylbenzene which was evaporated in the preheating zone were joined together and led to the reactor. The reaction temperature was measured by means of chromel-alumel thermocouple attached to the outer wall of reactor. Prior to the start of reaction, all the catalysts were heated at reaction temperature in flow of 1 atm H_2 (25 cc/min-gr-cat) for 10 hrs. Reaction products were sampled at the intervals of an hour and analyzed by gas chromatography (Packard, Model 438) equipped with Bentone 34 + DNP column (ϕ 3mm \times 4m) kept at 80°C.

(2) Catalysts

The supported heteropoly compounds were used as catalysts. 12-molybdophosphoric acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$, abbreviated hereafter as H_3PMo) was prepared according to the method reported by Tsigdinos [15]. The

preparations are briefly described below. H_3PMo was prepared from MoO_3 and H_3PO_4 . Its salts were also prepared from H_3PMo and metal carbonate or nitrate by neutralization [16]. Each supported catalyst was prepared by impregnating a support with aqueous solution of H_3PMo or its salts and chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and then by drying at 120°C and calcined at 400°C for 3 hours, respectively. The support used in this experiment was HY-zeolite which was obtained by treating NaY (1/16" pellet, Strem Chemicals, Inc.) with aqueous NH_4Cl solution, and then by washing and calcining. All the catalysts contained 0.5 wt% Pt and 0.5% heteropoly acid or its salts. According to the order of impregnation, three kinds of catalysts were prepared. One was impregnated beforehand with Pt and then with H_3PMo (denoted hereafter as Pt + $\text{H}_3\text{PMo}/\text{HY}$), the other was impregnated beforehand with H_3PMo and then with Pt (denoted hereafter as $\text{H}_3\text{PMo} + \text{Pt}/\text{HY}$), and one another was impregnated with Pt and H_3PMo simultaneously (denoted hereafter as (Pt + $\text{H}_3\text{PMo})/\text{HY}$).

(3) Characterization of Catalysts

IR spectra were recorded after pressed into a KBr disk with an aid of IR spectrometer (Jasco, DS-701G). In the case of 12-molybdophosphoric acid, a central PO_4 tetrahedron is surrounded by 12 MoO_6 octahedra having common edges and vertices [17]. So IR spectra of heteropoly acid prepared in this experiment showed various peaks and each peak was assigned according to the literature [18] as follows: 1060 cm^{-1} to P-O stretching, 970 cm^{-1} to Mo=O stretching, 880, 790 cm^{-1} to Mo-O-Mo stretching, and 598 cm^{-1} to O-P-O bending vibrations. In the cases of heteropoly acid salts, these peaks were not changed and so heteropoly acid salts were identified to have also keggin structures.

The results of DTA using a thermogravimetric analyzer (Rigaku, PTC-10A) revealed that 12-molybdophosphoric acid and its salts begin to decompose at the temperatures above 400°C.

The surface shapes of the catalysts were roughly observed by means of SEM (JEOL, JSM-35). $\text{H}_3\text{PMo} + \text{Pt}/\text{HY}$ showed similar character to that of Pt/HY, and Pt + $\text{H}_3\text{PMo}/\text{HY}$ showed similar character to that of $\text{H}_3\text{PMo}/\text{HY}$. (Pt + $\text{H}_3\text{PMo})/\text{HY}$ revealed the characters of both Pt/HY and $\text{H}_3\text{PMo}/\text{HY}$. These suggest that in the case of $\text{H}_3\text{PMo} + \text{Pt}/\text{HY}$, Pt exists predominantly at the outer surface of catalyst and in the case of Pt + $\text{H}_3\text{PMo}/\text{HY}$, H_3PMo exists predominantly at the outer surface of catalyst, while in the case of (Pt + $\text{H}_3\text{PMo})/\text{HY}$, Pt and H_3PMo may exist evenly at the outer surface of catalyst.

The surface area was determined conventionally using BET method after drying at 300°C for 1 hr in flowing dry nitrogen. This measurement was carried out by Quantasorb surface area analyzer (Quantachrome)

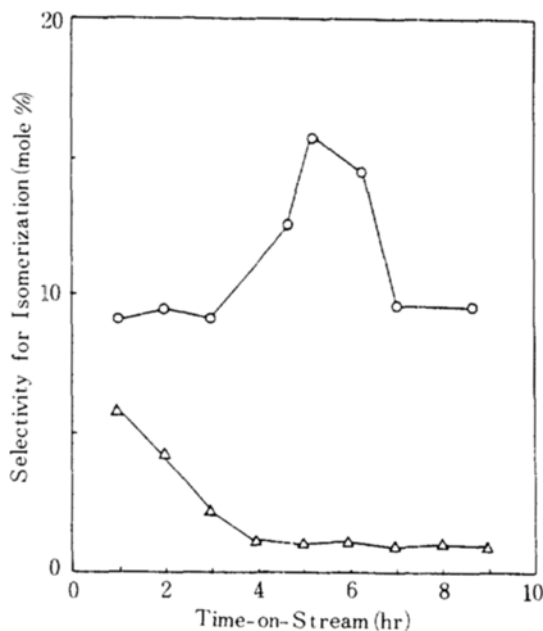


Fig. 1. Selectivity for isomerization vs. time-on-stream on Pt/HY & (Pt+H₃PMo)/HY.

○ (Pt+H₃PMo)/HY △ Pt/HY

where carrier gas and adsorption material were He and N₂, respectively. All catalysts have relatively large surface areas, that is, 600m²/g(HY-zeolite), 493m²/g (Pt/HY-zeolite), 361-483m²/g (Pt and H₃PMo or its salt/HY-zeolite). From the above results, it seems that heteropoly compounds exist mainly in macropores of zeolite, and that supported heteropoly compound blocks only a part of micropores of zeolite. This assumption is reasonable because the molecular size of heteropoly compound is larger than the size of micropore in zeolite.

RESULTS AND DISCUSSION

(1) The Roles of Heteropoly Acid in the Isomerization of Ethylbenzene

The comparison of selectivity of (Pt+H₃PMo)/HY catalyst with that of Pt/HY catalyst in the isomerization of ethylbenzene is shown in Fig. 1. (Pt+H₃PMo)/HY has higher selectivity than Pt/HY. It seems that the higher isomerization selectivity of (Pt+H₃PMo)/HY is due to the strong Brönsted acidity of H₃PMo. The strong Brönsted acidity of H₃PMo accelerates the formation of carbocations which are intermediates of skeletal rearrangement in the isomerization of ethylbenzene. So isomerization selectivity increases. Röbschläger and Christoffel [10] reported that strong acidity of catalyst suppresses the cracking caused by ring opening and accelerates isomerization. Similar results were reported by Piens

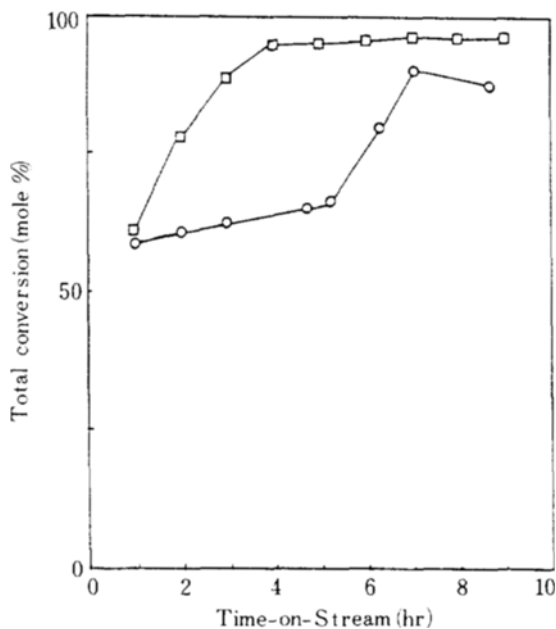


Fig. 2. Total conversion vs. time-on-stream on Pt/HY & (Pt+H₃PMo)/HY.

□ Pt/HY ○ (Pt+H₃PMo)/HY

and Csicsery [19]. So it seems that the strong Brönsted acidity of H₃PMo suppresses cracking of ethylbenzene. In the case of (Pt+H₃PMo)/HY, the selectivity tends to increase at the initial stage of time-on-stream and then decrease with time-on-stream. Lien [20] reported that ethylbenzene readily isomerizes in moderate acidity rather than excessively strong acidity, and Gnep and Guisnet [9] revealed that excessively strong acidity of catalyst can bring about the disproportionation of ethylbenzene and so moderate acidity is appropriate for the isomerization of ethylbenzene. So at the initial stage of reaction the acidity of H₃PMo is so excessively strong that isomerization does not take place well, but as reaction goes on, the acidity decreases and finally it reaches the appropriate value for isomerization and so the selectivity tends to increase. After that time, acidity decreases continuously and so cracking rather than isomerization takes place. As is shown in Fig. 2, in the case of (Pt+H₃PMo)/HY, excessively strong Brönsted acidity suppresses cracking, so at the initial stage of reaction, the extent of total conversion is relatively low, but finally it reaches the same extent of total conversion as that of Pt/HY. At this time, the acidity of H₃PMo already decreased to be appropriate for cracking.

(2) The Effects of Impregnation Methods

According to the order of impregnation of HY-zeolite with Pt and H₃PMo, catalytic activity varies greatly. These results are given in Figs. 3 and 4. The catalyst im-

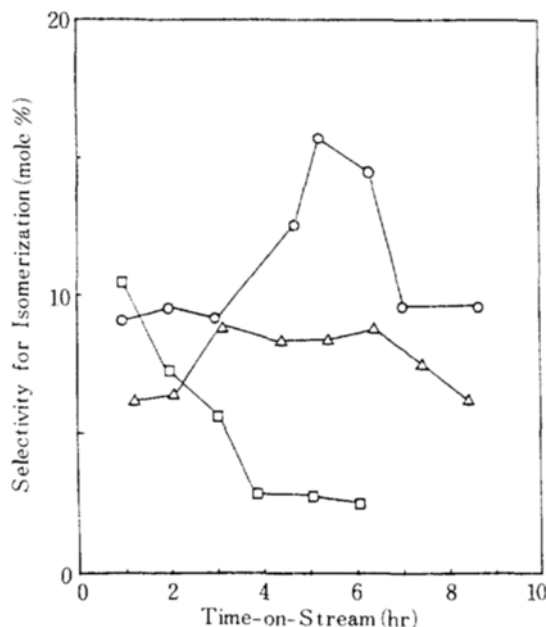


Fig. 3. Selectivity for isomerization vs. time-on-stream on (Pt+H₃PMo)/HY, Pt+H₃PMo/HY and H₃PMo+Pt/HY.

○ (Pt+H₃PMo)/HY △ Pt+H₃PMo/HY
 □ H₃PMo+Pt/HY

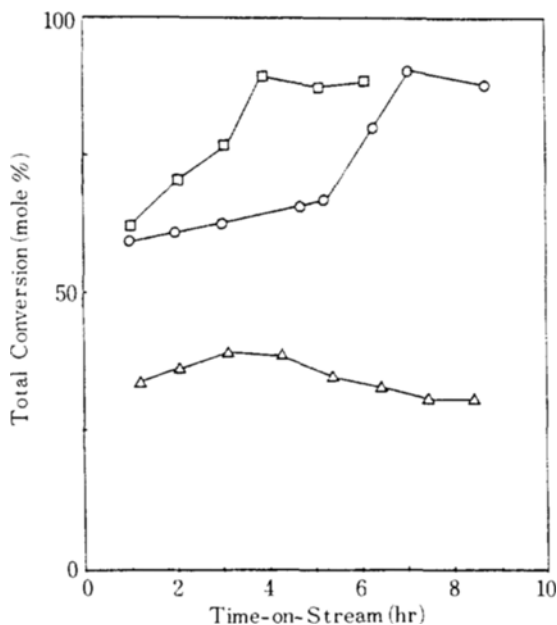


Fig. 4. Total conversion vs. time-on-stream on (Pt+H₃PMo)/HY, Pt+H₃PMo/HY and H₃PMo+Pt/HY.

○ (Pt+H₃PMo)/HY △ Pt+H₃PMo/HY
 □ H₃PMo+Pt/HY

pregnated afterward with H₃PMo, Pt+H₃PMo/HY, shows similar tendencies to the case of (Pt+H₃PMo)/HY discussed in the previous section. That is, Pt+H₃PMo/HY shows low conversion and its selectivity for isomerization increases and then decreases forming a maximum or a plateau. From such results, it seems to Pt+H₃PMo/HY that H₃PMo exists predominantly at the outer surface of the catalyst and so the behavior of H₃PMo can be directed. The selectivity of Pt+H₃PMo/HY keeps almost constant for a fairly long duration, showing rather a lower value than that of (Pt+H₃PMo)/HY which is simultaneously impregnated. It seems that the proper distribution of two different active sites plays an important role to isomerization of ethylbenzene due to bifunctional reaction mechanism. Pt+H₃PMo/HY also shows lower total conversion. This result can be explained by the fact that most part of Pt is covered with H₃PMo and so the function of Pt which contributes the first step of isomerization, i.e., hydrogenation, is suppressed.

In the case of the catalyst impregnated afterward with Pt, H₃PMo+Pt/HY, isomerization selectivity decreases continuously and total conversion increases at almost the same rate as the case of Pt/HY catalyst. This suggests that Pt exists predominantly at the outer surface of catalyst covering H₃PMo component and so

resulting in disappearance of the behavior of H₃PMo. Simultaneously impregnated (Pt+H₃PMo)/HY catalyst shows the best results. Therefore, it is recognized that catalytic activity depends on the proper distribution of the two active sites which play important roles in two typical steps of ethylbenzene isomerization, that is, carbonium type reaction and hydrogenation-dehydrogenation reaction.

(3) The Effects of Counteraction

12-molybdophosphates were prepared by substitution of protons in H₃PMo for transition metals in aqueous solution. Among them, Cr-, Fe-, Co-, and Ni-molybdophosphates (abbreviated hereafter as CrPMo, FePMo, Co₃(PMo)₂, and Ni₃(PMo)₂, respectively) were chosen as catalysts because of their relatively high thermal stability. The selectivity and total conversion of these catalysts are shown in Figs. 5 and 6, respectively. In the cases of 12-molybdophosphates, their catalytic activities differ obviously from that of the corresponding acid depending on the kind of counteraction. These results agree well with those of Niiyama et al. [21], which reveal that in acid type catalysis, the active sites of heteropoly acid salts are metal cations.

CrPMo shows no enhanced activity. In the cases of the other salts, the initial activity and selectivity are in the order of Ni > Co > Fe and deactivation rate is also

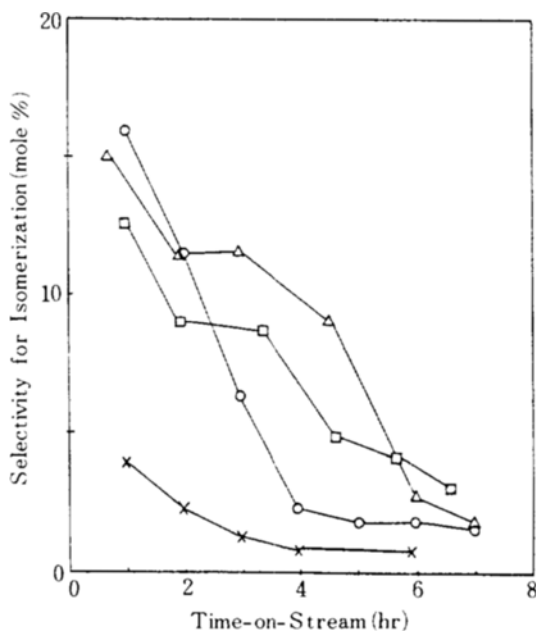
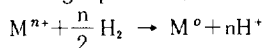


Fig. 5. Selectivity for isomerization vs. time-on-stream on various (Pt+12-molybdophosphate)/HY.

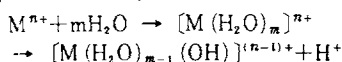
× CrPMo □ FePMo
 △ Co₃(PMo)₂ ○ Ni₃(PMo)₂

in the same order. The catalytic activity and selectivity in solid acid catalysis may depend on the type and number of acid site, and on acid strength. Acid strength of heteropoly acid changes when the protons of heteropoly acid are substituted for metal cations [22]. As was shown in the results of this work, both activity and selectivity decrease continuously with reaction time in all cases of these heteropoly acid salts. It seems that the initial acid strength of these heteropoly acid salts may be low enough to be appropriate for the isomerization of ethylbenzene.

At the counteraction which is active site in heteropoly acid salts, the Brönsted acidity may be formed by the following equation. [23].



On the other hand, Niyama et al. [21] proposed that water coordinated to metal cation (M^{n+}) yields protons by the following reaction.



According to this work, the former is more plausible because of the experimental observation that the pretreatment with H_2 enhances the catalytic activity markedly as shown in Fig. 7.

The acid strength of these compounds depends on

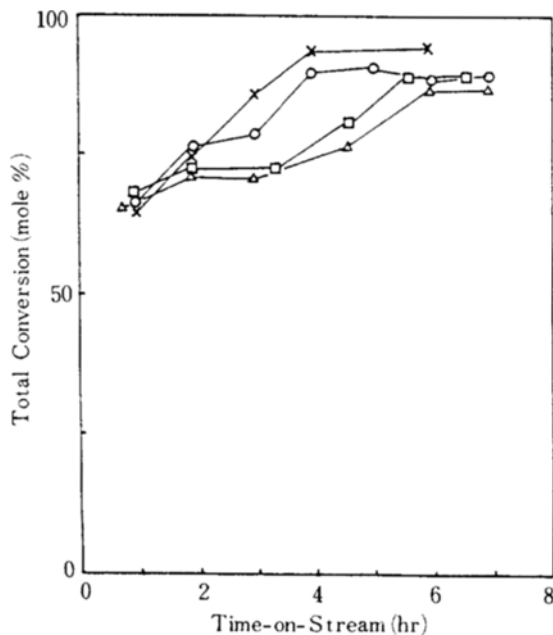


Fig. 6. Total conversion vs. time-on-stream on various (Pt+12-molybdophosphate)/HY.

× CrPMo □ FePMo
 △ Co₃(PMo)₂ ○ Ni₃(PMo)₂

the electronegativity of the corresponding counteranions as usual. In group VIII elements, the electronegativity decreases in the order of Ni > Co > Fe (Allred-Rochow's scale) and it is in accord with the order of initial activity and selectivity of the catalysts, that is, Ni₃(PMo)₂ > Co₃(PMo)₂ > FePMo. In addition, electronegativity of counteranion may affect the reducibility of anion. Misono [24] suggested that reducibility of anion increases with increasing electronegativity of metal cation, and Akimoto et al. [12] also reported that the increase in the reducibility of anion with increasing electronegativity of cation indicates that Keggin anions electrically interact with these cations. In the case of heteropolymolybdates, deactivation is significant due to the reduction of the catalyst [24]. With the above reasons, the deactivation rate is to be in the order of Ni₃(PMo)₂ > Co₃(PMo)₂ > FePMo.

In the case of CrPMo, this salt is reduced and decomposed to the component oxides by the present pretreatment and so it shows no enhanced activity.

After pretreatment, Ni₃(PMo)₂, Co₃(PMo)₂, and FePMo were soluble in water and revealed dark-blue solution. This suggests that these samples are not decomposed to the corresponding component oxides completely and the large portion of them remains in a reversible reduced form. On the other hand, for reduced CrPMo, only a small portion of it was soluble in water suggesting

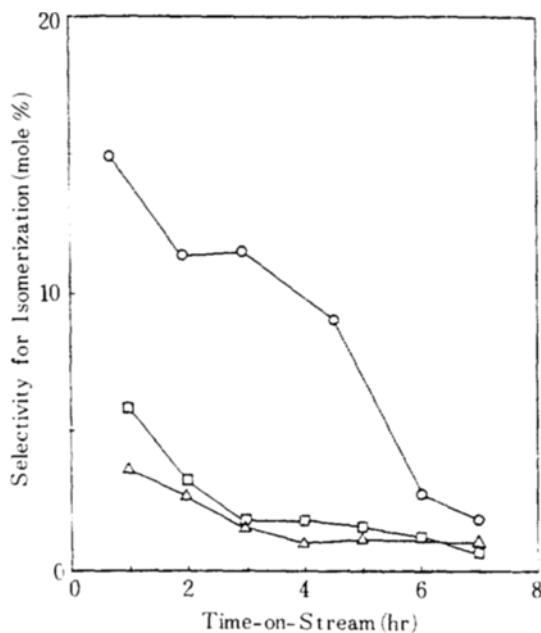


Fig. 7. Selectivity for isomerization vs. time-on-stream on pretreatment effect of (Pt + Co₃(PMo)₂)/HY.

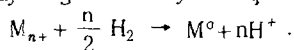
○ H₂-pretreatment □ N₂-pretreatment
△ No pretreatment

that most of this compound was decomposed to the form of insoluble black particles which reveal light-blue solution. Therefore, it is recognized that most of CrPMo is decomposed to the corresponding component oxides when reduced by the pretreatment used in this study.

(4) The Effects of Pretreatment

The effects of pretreatment were studied on (Pt + Co₃(PMo)₂)/HY, which shows comparatively high activity and low deactivation rate. The pretreatments were carried out by heating at reaction temperature in stream of H₂(1 atm) or N₂(1 atm) (25cc/min·gr-cat) for 10 hrs. The results are shown in Figs. 7 and 8.

On the whole, the pretreatment with H₂ showed higher activity and selectivity than that with N₂ or no pretreatment. The pretreatment with N₂ revealed a similar result to that of no pretreatment. The low activity and selectivity of (Pt + Co₃(PMo)₂)/HY without pretreatment indicates that there exists only a small acidity in this catalyst, but during pretreatment with H₂, acid sites may be generated by the equation,



In addition to the above fact, dissociative adsorption of N₂ on active sites also affects the results of experiment. It seems that dissociative adsorption of N₂ on the active sites decays the role of these active sites, namely,

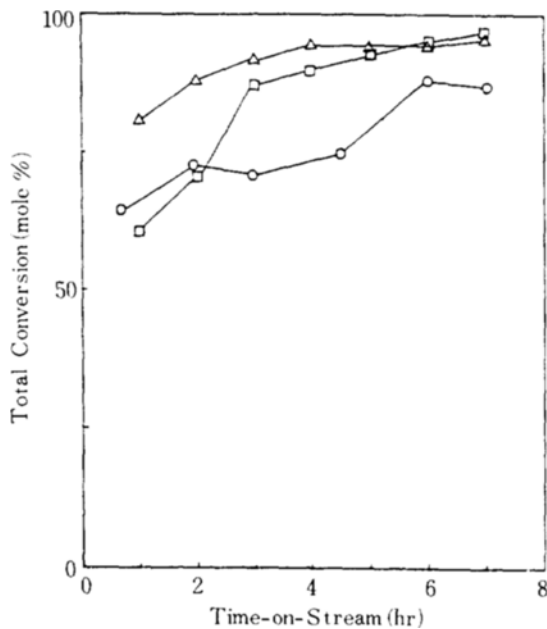


Fig. 8. Total conversion vs. time-on-stream on pretreatment effect of (Pt + Co₃(PMo)₂)/HY.

○ H₂-pretreatment □ N₂-pretreatment
△ No pretreatment

formation of acid sites and adsorption of reactant on active sites are suppressed. The above suggests that dissociative adsorption of N₂ on Pt has a high activation energy and so the adsorption of N₂ on Pt may be difficult, while in case of Co, where dissociative adsorption of N₂ on it has relatively low activation energy [25], adsorbed nitrogen prohibits the reaction on active sites to some extent.

It is, in conclusion, suggested that pretreatment with H₂ creates relatively strong acidity, which enhances isomerization activity and suppresses cracking, and so it gives high selectivity for isomerization and comparatively low total conversion, while in the cases of pretreatment with N₂ and no pretreatment, there exists only a small acidity and so cracking is not suppressed, therefore, low selectivity and high total conversion are revealed.

CONCLUSIONS

1. The optimum strength of Brönsted acidity in the isomerization of ethylbenzene is between the strong acid strength of H₃PMo and the weak acid strength suitable for cracking.
2. Isomerization activity and selectivity of a catalyst vary with impregnation method during preparation.

The simultaneously impregnated catalyst shows relatively high activity and selectivity in isomerization.

3. The acidity of 12-molybdophosphates of transition metals varies with the kind of counteraction and it is closely related to the electronegativity of counteraction.
4. The pretreatment affects counteraction mainly. The pretreatment with H₂ shows higher activity and selectivity than that with N₂ or no pretreatment.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of Korea Science and Engineering Foundation for this work.

APPENDIX

1. Total conversion (%)

$$= \frac{\text{moles of ethylbenzene converted to all products}}{\text{moles of ethylbenzene passed through the reactor}} \times 100$$

2. Activity for isomerization (%)

$$= \frac{\text{moles of ethylbenzene isomerized to xylene}}{\text{moles of ethylbenzene passed through the reactor}} \times 100$$

3. Selectivity for isomerization (%)

$$= \frac{\text{moles of ethylbenzene isomerized to xylene}}{\text{moles of ethylbenzene converted to all products}} \times 100$$

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