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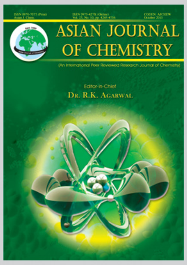

Heteropolyanions Catalysts for *n*-Heptane Conversion: Effect of the Counter Cation and the Addenda Atoms

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Different heteropoly compounds (HPC) $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_4PMo_{11}VO_{40}$ and $Cu_{1.5}PMo_{12}O_{40}$ were prepared and characterized by means of FTIR and thermogravimetry. Their catalytic properties for the *n*-heptane reaction were evaluated at 300 ºC. In this study the effect of the addenda atoms (W, Mo and V) and the counter cations (H^+ and Cu^{2+}) was investigated. The substitution of W atoms with Mo ones increased the conversion and favoured the cracking selectivity to the detriment of that of cyclization while isomerization selectivity remained unchanged. When the protons were replaced with copper ions, cracking and cyclization reactions were favoured to the detriment of that of isomerization. Heteropolyacids have been found more active than the copper heteropolymolybdate salt. Increasing hydrogen pressure favoured cyclization and cracking reactions to the detriment of isomerization one.

Key Words: *n*-Heptane, Isomerization, Heteropoly compounds, Solid acid, Bifunctional catalyst.

INTRODUCTION

Reactions of *n*-alkanes conversion are highly important for potential applications in petroleum chemistry, refining and fine chemical. Among these reactions *n*-heptane conversion into branched, cyclic and aromatic hydrocarbons is widely investigated[1-9]. It has been found that the both Bronsted and Lewis type and character redox are useful to active the C-H bond[10-13]. The branched alkanes, which are obtained by the skeletal isomerization, are the preferred gasoline components. However, their obtention is affected by that of cracking, cyclization and aromatization. Generlly the reaction is catalyzed by bifunctional catalysts in the presence of excess hydrogen in order to prevent the deactivation of catalysts caused by the carbon deposits on the catalysts or by the oligomerization of by products with the formation of condensation products on the surface of catalysts[14,15]. Some catalysts are composed of a metal (redox sites) loaded on a support (acidic sites). Others are zeolites (acidic sites) in which ions of one or more metals are within the frame of the zeolites. Heteropolyacids (HPA) demonstrate a unique coupling of acid and redox properties that enable them to catalyze various reactions[16-18]. The redox and acidic properties of these bifunctional catalysts can be controlled systematically by proper choice of constituent elements of polyanions and counter cations. The counter cation controls not only the acidic property but also the bulk-type behaviour; pseudoliquid and surface-type. Heteropoly compounds have been proven to be useful catalytic materials in fundamental studies as well as in practical synthetic processes. In the present study, we performed the conversion of *n*-heptane over a series of heteropoly compounds as bifunctional catalysts. The effect of the counter cation, the addenda atoms and the hydrogen was investigated.

EXPERIMENTAL

Preparation of the catalysts: The catalysts $H_3PW_{12}O_{40}$, H_3PMoO_{40} heteropolyacids were prepared according to the methods of Deltcheff *et al.*[19]. The H_4PMoVO_{40} heteropolyacid was prepared to the method of Tsigdinos *et al.*[20]. The $Cu_{1.5}PMoO_{40}$ salt was obtained as precipitate by adding slowly a required amount of $Ba(OH)_2.8H_2O$ (to neutralize the three protons) to the aqueous solution of H_3PMoO_{40} and then the required amount of $CuSO_4.5H_2O$ was added. After eliminating the formed $BaSO_4$ precipitate, the $Cu_{1.5}PMoO_{40}$ salt was extracted from the solution by evaporation by bubbling nitrogen in the resulting solution.

Physico-chemical techniques: The purity, the Keggin structure and the thermal stability of the sample was checked by IR, thermogravimetry, differential scanning calorimetry and XR-diffraction. IR spectra were recorded with an infrared spectrometer GENESIS II- FTIR (4000-400 cm^{-1}) as KBr pellets. TGA and DSC were carried out in flow of argon in a thermo gravimeter (PERKIN-ELMER, TGA/DSC). Samples around 5-10 mg of heteropolyacids were heated at 5 K per minute up to 793 K for TGA and up to 763 K for DSC. The XRD powder patterns were recorded on a PHILIPS X PERT, PRO diffractometer using CuK$_\alpha$ radiation.

Catalytic measurements: Catalytic tests were carried out at atmospheric pressure using a fixed-bed continuous-flow reactor made of a Pyrex tube. The catalysts (500 mg) packed in the reactor, was preconditioned under H_2 flow for 2 h with a rate of 80 mL/min at 300 ºC. After the pretreatment, the reagent mixture (H_2/*n*-heptane) was admitted in the reactor (admission of *n*-heptane was carried out automatically and continuously by micro-injection through a syringe). The reaction was conducted at 300 ºC. Reaction products were analyzed by gas-phase chromatography with FID type PYE UNICAM PU 4500 connected to an integrator-recorder PERKIN ELMER LCI-100. The hydrocarbons were separated by SE-30 packed column of 1.5 m of length.

RESULTS AND DISCUSSION

Infrared spectra: The spectra of the samples are shown in Fig. 1. The IR spectra have been assigned according to previous reports[19,21]. For $PW_{12}O^{3-}_{40}$, $PMo_{12}O^{3-}_{40}$ and $PMo_{11}VO^{4-}_{40}$ the main characteristic features of the Keggin structure are observed at 1080-1060 cm^{-1} (ν_{as} P-O$_a$), at 990-960 cm^{-1} (ν_{as} Mo-O$_d$), at 900-870 cm^{-1} (ν_a Mo-O$_d$-Mo) and at 810-760 cm^{-1} (ν_{as} Mo-O$_c$-Mo). For all the samples, the features of the IR spectra (Table-1) agree with the general behaviour of substituted Keggin compounds[22].

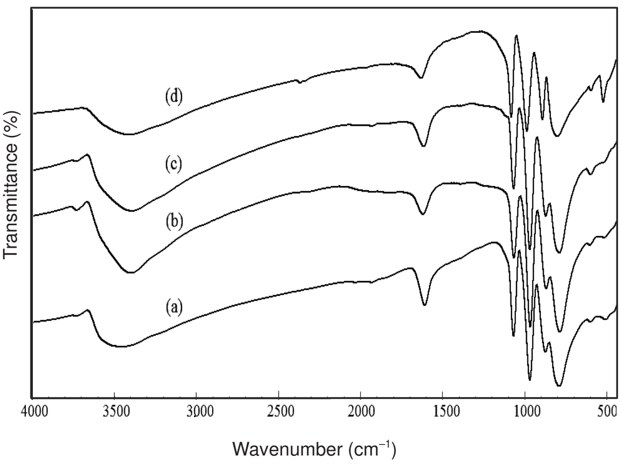
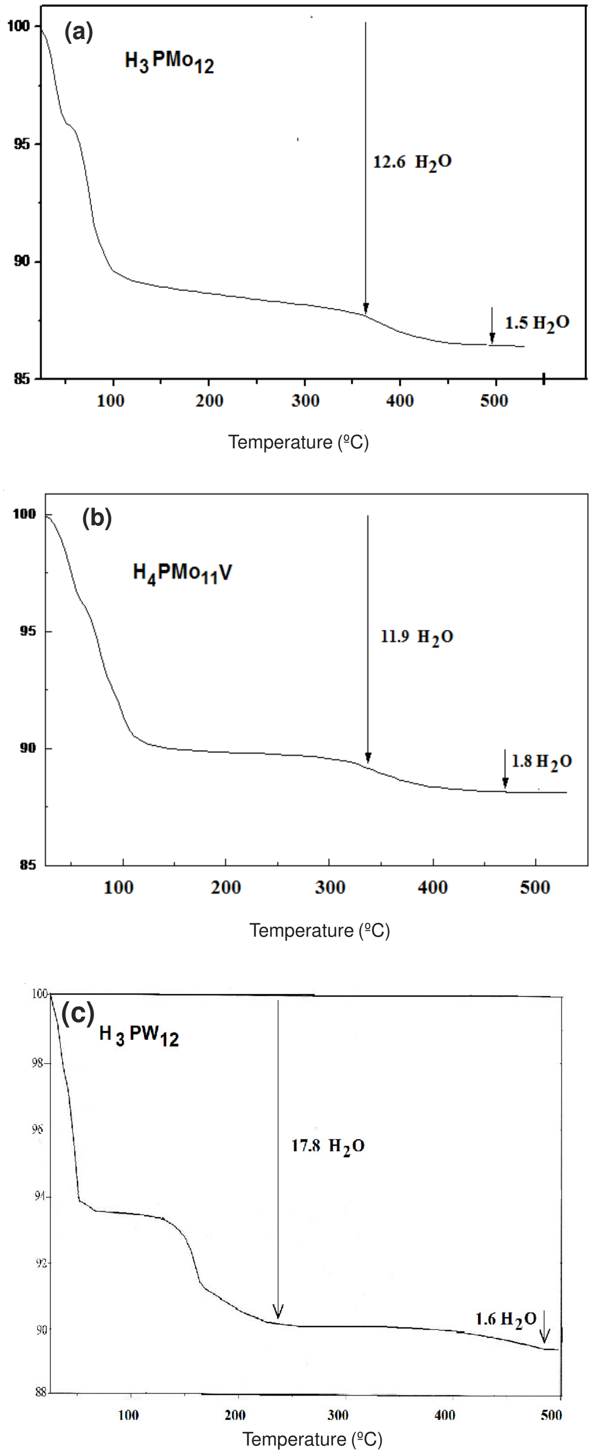


Fig. 1. Infrared spectra of a) $H_3PMo_{12}O_{40}$; b) $H_4PMo_{11}VO_{40}$; c) $H_3PW_{12}O_{40}$; d) $Cu_{1.5}PMo_{12}O_{40}$

TABLE-1
RELEVANT FREQUENCY (cm^{-1}) AND ASSIGNMENTS OF THE PREPARED KEGGIN HETEROPOLY COMPOUNDS

Catalyst	ν_{as}(P-O$_a$)	ν_{as}(Mo-O$_d$)	ν_a(Mo-O$_d$-Mo)	ν_a(Mo-O$_c$-Mo)
$H_3PW_{12}O_{40}$	1077 vs	998 sh	920 sh	808 vs
$H_3PMo_{12}O_{40}$	1059 vs	979 sh	895 m	798 vs
$H_4PMo_{11}VO_{40}$	1072 sh	980 sh	885 m	790 vs
$Cu_{1.5}PMo_{12}O_{40}$	1080 s	955 sh	870 m	785 vs

Thermogravimetric analysis: Thermogravimetric analysis shows a loss of weight as soon as the temperature is increased. Some modifications in the thermogravimetric curves can be correlated with the existence of intermediary hydrates (8-hydrates for $H_3PMo_{12}O_{40}$ and $H_4PMo_{11}VO_{40}$, 6-hydrate for $H_3PW_{12}O_{40}$). A plateau corresponding to the anhydrous acid is observed between 140 and 270 ºC for $H_3PMo_{12}O_{40}$, 200 and 360 ºC for $H_3PW_{12}O_{40}$. With a further increase of the temperature, protons come off with oxygen from the polyanion, in the form so called 'constitution water' (1.5H_2O for $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ and 2H_2O for $H_4PMo_{11}VO_{40}$). Above 450-500 ºC, only mixtures of oxides are characterized (typically by IR). The TG curves (Fig. 2) are consistent with published results[19,23]. As for the copper salt $Cu_{1.5}PMo_{12}O$, the figure shows the loss of weight as soon as the temperature increased until the its total decomposition into oxides.



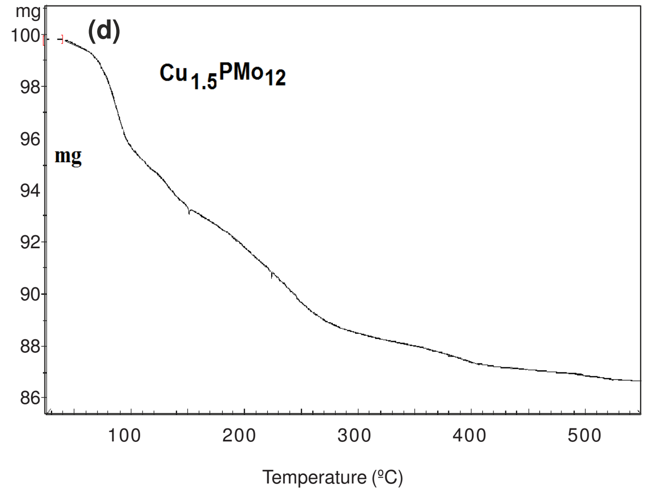
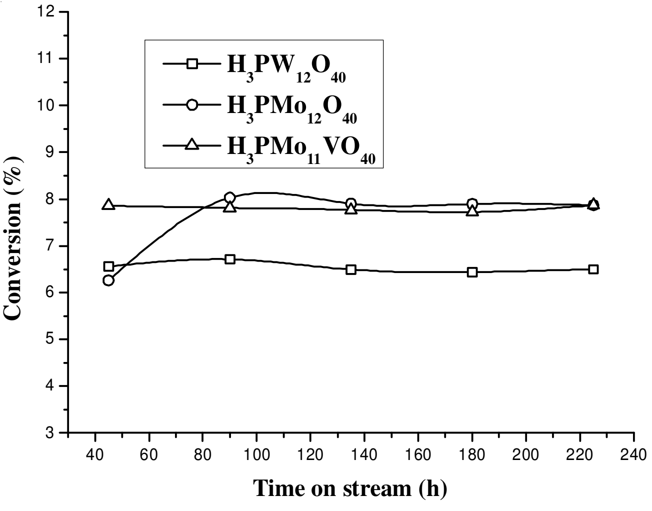


Fig. 2. Thermogravimetric profile in nitrogen of a) $H_3PMo_{12}O_{40}$; b) $H_4PMo_{11}VO_{40}$; c) $H_3PW_{12}O_{40}$ d) $Cu_{1.5}PMo_{12}O_{40}$ (Heating rate 5 ºC/min)

Effect of addenda atoms (W, Mo and V): Fig. 3. shows the effect of the addenda atom (W, Mo and V) on the conversion and the product selectivities. It can be seen from the figure that the activity is stable during the reaction time for all the heteropolyacids tested. The conversion obtained over $H_3PW_{12}O_{40}$, H_3PMoO_{40} and $H_4PMo_{11}VO_{40}$ heteropolyacids are respectively (6.5 %), (7.9 %) and (7.9 %). This result indicated that these three heteropolyacids have almost the same activity. Nevertheless, $H_3PW_{12}O_{40}$ was slightly less active. As for the selectivity, it was found that $H_3PW_{12}O_{40}$ and H_3PMoO_{40} led to the same selectivity value in isomerization reaction (14.9 %). Whereas, that obtained over $H_4PMo_{11}VO_{40}$ (15.7 %) was slightly greater. This difference in isomerization selectivity might be due to the difference in the number of protons in the heteropolyacids ($H_4PMo_{11}VO_{40}$ has more protons than $H_3PW_{12}O_{40}$ and H_3PMoO_{40}). The selectivity of cracking and cyclization reaction obtained over $H_3PW_{12}O_{40}$ and H_3PMoO_{40} are 74.2 % and 77.1 %. This result indicated that Mo as addenda atoms favoured the cracking reaction to the detriment of that of cyclization. Isomerization selectivity remained unchanged (14.9 %) when W was replaced with Mo.



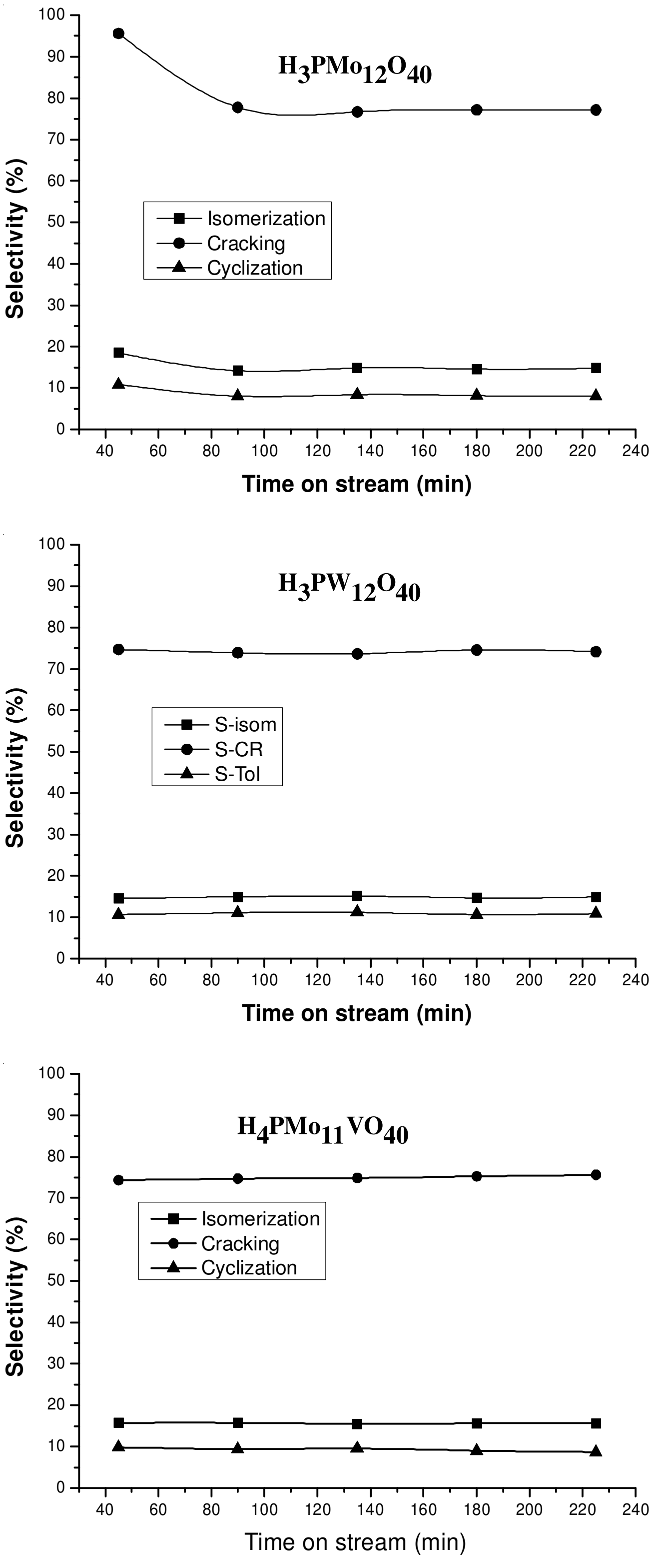
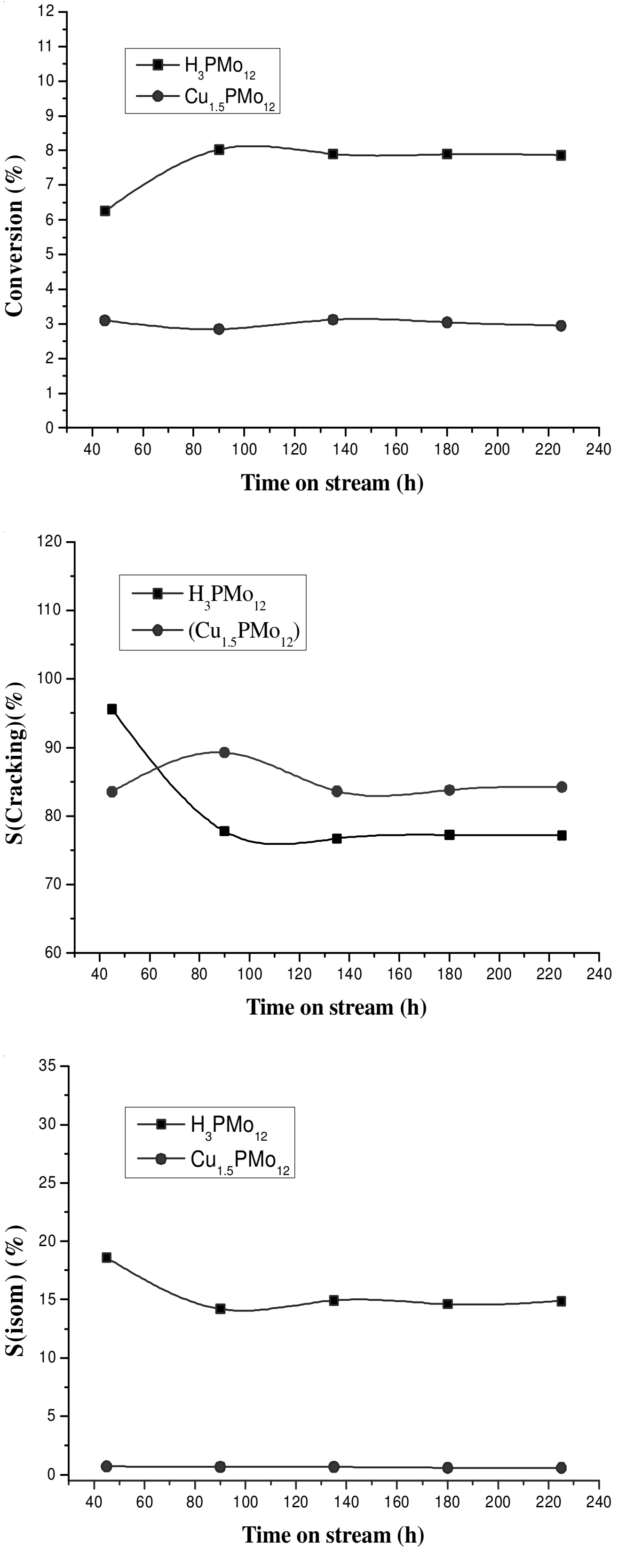


Fig. 3. Conversion of *n*-heptane and products selectivity *versus* time on stream at 300 °C and H_2/C_7H_{16} = 0.2 over $H_3PMo_{12}O_{40}$, $H_4PMo_{11}VO_{40}$, $H_3PW_{12}O_{40}$ and $Cu_{1.5}PMo_{12}O_{40}$

Effect of the counter cation (H^+ and Cu^{2+}): Since H_3PMo_{12} was (slightly) more active than H_3PW_{12}, it was selected for investigating the effect of the counter cation on the *n*-heptane conversion. The activity of the heteropoly acid H_3PMo_{12} and the copper heteropolymolybdate salt $Cu_{1.5}PMo_{12}$ were tested. The results of the effect of the cation (H^+ and

Cu^{2+}) on the conversion and on the selectivity are shown in Fig. 4. It can be seen that H_3PMo_{12} (7.9 %) was more active than $Cu_{1.5}PMo_{12}$ (2.9 %). As for the selectivity, it has been found that the selectivity obtained over $Cu_{1.5}PMo_{12}$ are (0.6 %) in isomerization, (84.2 %) in cracking and (15.2 %) in cyclization.



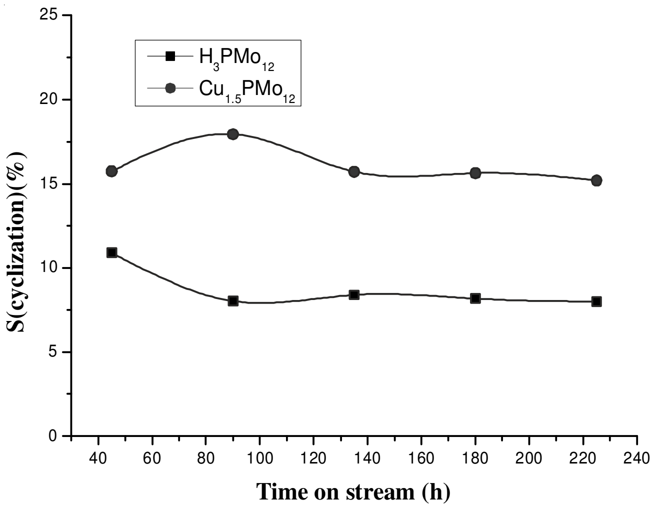


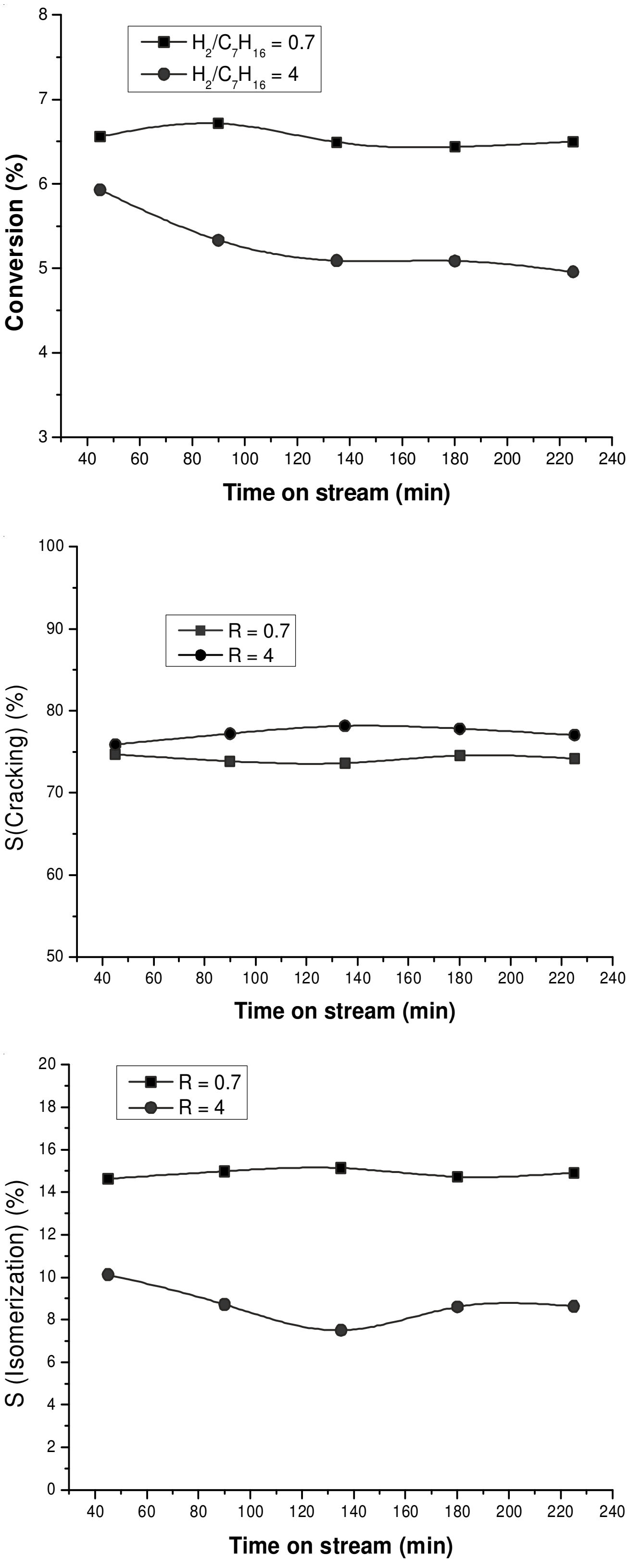
Fig. 4. Conversion of *n*-heptane and product distribution *versus* time on stream at 300 °C and H_2/C_7H_{16} = 0.2 over $H_3PMo_{12}O_{40}$ and $Cu_{1.5}PMo_{12}O_{40}$

Effect of hydrogen: The variation of the conversion and the selectivities for both H_2/C_7H_{16} molar ratios equal to 0.2 and 4 are shown in Fig. 5. It can be seen from the figure that both the conversion and the selectivities are stable during the time of the catalytic tests for the two molar ratios. The conversion and the selectivities values obtained when the hydrogen pressure was increased showed that the conversion remained constant, whereas the selectivities were significantly changed. In fact, when the H_2/C_7H_{16} molar ratio was increased from 0.2 to 4, the conversion was decreased from 6.5 to 5.0 %. As for the selectivities, it has been found that increasing the molar ratio from 0.2 to 4 decreased the isomerization selectivity from 14.9 to 8.6 %. In contrast, the selectivity of cracking and cyclization products increased from 74.2 to 77.1 % and from 10.9 to 14.3 %, respectively. This result is in agreement with that of K. Na *etc.*[16]. In fact, in their study of *n*-butane isomerization, they found that cracking products increased when hydrogen increased. In the point of view of the authors, this cracking is not the hydrogenolysis catalyzed by Pt, but is acid-catalyzed cracking of oligomerized butenes. It is generally recognized that isomerization reactions should be carried out on a bifunctional catalyst, consisting of protonating acid function and a hydrogenating/dehydrogenating metal function[24]; alkane is dehydrogenated on a metal phase and the alkene formed is protonated at Bronsted acid sites, yielding an alkylcarbenium ion. After C-C bond rearrangement, the isomeric alkylcarbenium ion desorbs as the product alkene that is hydrogenated at the metal phase to yield the product alkane. According to this mechanism, the hydrogen pressure affects the concentration of carbenium ions by the equilibrium reaction below. Consequently the selctivity of isomerization will be reduced.

$$R^+ + H_2 \rightarrow RH + H^+$$

Conclusion

In this research work the effect of the addenda atoms (W, Mo and V) and the counter cation (H^+ and Cu^{2+}) in heteropoly compounds was investigated. By comparing three heteropolyacids namely, $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_4PMo_{11}VO_{40}$, it has been found that using Mo as addenda atoms increased the conversion and favoured the cracking reaction to the detriment of that of cyclization. Isomerization selectivity remained unchanged when W atoms were replaced with Mo ones but increased when one Mo atom in the keggin unit was replaced with a V atom. This result indicated that isomerization reaction is strongly dependent on the acidity strength.



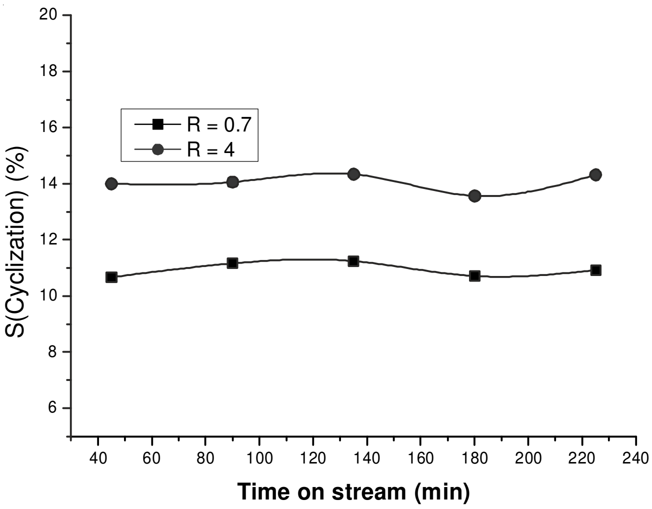


Fig. 5. Conversion and selectivities versus time on stream with H_2/C_7H_{16} molar ratios of 0.7 and 4 over $H_3PW_{12}O_{40}$ at 300 ºC

The results of the effect of the cation (H^+ and Cu^{2+}) on the *n*-heptane conversion showed that the 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$) is more active and more selective in isomerization reaction compared to its corresponding copper salt ($Cu_{1.5}PMo_{12}O_{40}$). Substituting H^+ with Cu^{2+} in the Keggin-type heteropoly compound decreased the selectivity of isomerization in favour of that of cracking and cyclization.

Heteropoly compounds permit the design of the catalysts at the molecular level by controlling their structures. Therefore there are promising solids for *n*-alkanes conversion. In fact, the choice of the counter cation and the addenda atoms can orientate the conversion towards the desired reaction (isomerization, cracking, or cyclization).

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