

Catalytic Reactivity of 12-Molybdophosphoric Acid and its Copper and Zinc Salts in CO₂ Methanol Reforming

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The CO₂ methanol reforming reaction over Keggin type heteropoly compounds catalysts was investigated. The catalysts prepared, H₃PMo₁₂O₄₀ and its salts Cu_{1.5}PMo₁₂O₄₀ and Zn_{1.5}PMo₁₂O₄₀ were characterized by means of IR, XRD and TG. Catalytic tests were carried out under atmospheric pressure at 573 K in a continuous flow system using a glass reactor. The results obtained showed that the unsupported H₃PMo₁₂O₄₀ is more active than its copper and zinc salts. As for the alumina-supported H₃PMo₁₂O₄₀, it has been observed that, besides methyl formate (MF), formaldehyde (HCHO) and dimethyl ether (DME), the dimethyl carbonate (DMC) was obtained. The formation of the latter, observed only on the supported catalysts, seems to indicate that its formation requires both, Lewis-acid and redox sites. Brønsted-sites reduce its formation in favour of dimethyl ether (DME) and strong redox sites in favour to formaldehyde (HCHO).

Key Words: Methanol conversion, Heteropoly compound, Solid acid, Dimethyl carbonate, Bifunctional catalyst.

INTRODUCTION

Research and development of processes for upgrading natural gas to more valuable chemicals have attracted more attention in the last decades. Two routes can perform the natural gas upgrading: direct conversion of methane and indirect conversion *via* methanol. In fact, methanol, which is manufactured by the steam reforming of methane, has its high capacity of the worldwide production mainly from natural gas. It is considered as a chemical carrier to transport hydrogen¹⁻³ an easily transportable fuel and alternative source for fuels. It is also regarded as one of the keys for producing various organic and raw materials for the chemical industry. For example, methanol is a starting material in the production of dimethyl ether (DME), methyl formate (MF) and formaldehyde (HCHO)⁴⁻⁶. So it is obvious that methanol is one of the promising routes for upgrading natural gas. Therefore, many efforts have been recently made to develop catalysts for methanol transformations.

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The transformation of methanol can lead to various products depending on the reaction conditions and on the catalyst used⁷⁻⁹. Selectivities are strongly influenced by acid-base and redox character of both the active component and the support. In this work we have studied the methanol transformation in presence of carbon dioxide over Keggin-type heteropoly compound catalysts. It has been well recognized that carbon dioxide is an important resource of carbon, abundant, inexpensive, which can be involved in many organic compounds synthesis^{10, 11}. Keggin-type heteropoly compounds were selected as catalysts because they are well known as oxidative and acidic catalysts in which the redox and acid-base properties can be adjusted by choosing the counter-cation, the heteroatoms and the addenda atoms. Due to their unique combination of acid-base and redox properties, heteropoly compounds have been used successfully as catalysts, for acid and redox catalyzed reactions, either in their acidic form or in their cationic exchanged or substituted form^{12, 13}. Additionally these materials provide suitable model structures with structural flexibility for catalyzing multifunctional pathways required for methanol transformations. For these reasons, methanol conversion has been extensively studied over Keggin heteropoly compounds.

EXPERIMENTAL

Preparation of the Catalysts

The $H_3PMo_{12}O_{40}$ heteropolyacid was prepared according to the methods of Deltcheff *et al.*¹⁴. The salt forms were obtained from the acidic $H_3PMo_{12}O_{40}$, as precipitates, by adding slowly the required amount of $Ba(OH)_2 \cdot 8H_2O$ (to neutralize the three proton) to the aqueous solution of $H_3PMo_{12}O_{40}$, then the required amount of $MSO_4 \cdot xH_2O$ ($M = Cu$ and Zn) was added. After eliminating the formed $BaSO_4$ precipitate, the obtained solution was allowed to stand for few days at 4°C. The $M_{1.5}PMo_{12}O_{40}$ salt was recovered from the solution by filtration.

The series of alumina-supported catalysts, $H_3PMo_{12}O_{40}/Al_2O_3$, was prepared by incipient-wetness impregnation of Al_2O_3 (GF 254 type 60/E Merck) with aqueous solutions of $H_3PMo_{12}O_{40}$ at high enough concentration to avoid its degradation¹⁵.

Physico-chemical techniques

The purity and the Keggin structure of 12-molybdo-phosphoric acid $H_3PMo_{12}O_{40}$ and its Cu and Zn salts were checked by infrared and X-ray diffraction. The number of protons of 12-molybdophosphoric acid $H_3PMo_{12}O_{40}$, was checked by means of thermogravimetry.

IR spectra were recorded with an infrared spectrometer Genesis-II FTIR (4000–400 cm^{-1}) as KBr pellets. TGA was performed in a flow of argon in a thermogravimeter (Perkin-Elmer, TGA/DSC). 10 mg of 12-molybdophosphoric acid was heated at 5 K per min up to 793 K. The XRD powder patterns were recorded on a Philips X PERT, PRO diffractometer using CuK_{α} radiation.

Catalytic measurements

Catalytic tests were carried out at atmospheric pressure using a fixed-bed continuous-flow reactor made of a Pyrex tube. The catalyst (250 mg) packed in the reactor, was preconditioned under air flow for 2 h with a rate of 10 mL/min at 300°C. After the pretreatment the reagent mixture, which consisted of methanol and carbon dioxide mixture with molar ratio $CO_2/CH_3OH = 0.25$, was admitted into the reactor at a rate of 55 $cm^3 \text{ min}^{-1}$. Liquid methanol admission was carried out

automatically and continuously by microinjection through a syringe. The reaction was conducted at 300°C. 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

Characterization of catalysts

Infrared spectra: The spectra of the catalysts used are shown in Fig. 1. The IR spectra have been assigned^{15,16}. The main characteristic features of the Keggin structure are observed at 1080–1060 cm^{-1} $\nu_{\text{asym}}(\text{P-O}_a)$, at 990–960 cm^{-1} $\nu_{\text{asym}}(\text{Mo-O}_d)$, at 900–870 cm^{-1} $\nu_{\text{asym}}(\text{Mo-O}_d\text{-Mo})$ and at 810–760 cm^{-1} $\nu_{\text{asym}}(\text{Mo-O}_c\text{-Mo})$.

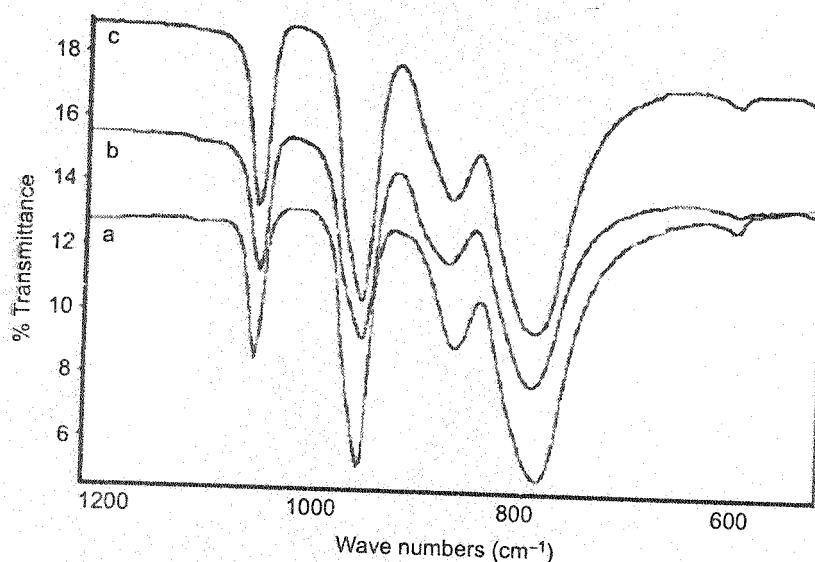


Fig. 1. IR spectra of fresh samples of (a) $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, (b) $\text{Cu}_{1.5}\text{PMo}_{12}\text{O}_{40}$, (c) $\text{Zn}_{1.5}\text{PMo}_{12}\text{O}_{40}$ at ambient conditions

X-Ray diffraction: According to the crystal structure of $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$, determined by d'Amour and Allmann¹⁷, the powder diffractogram of this solid can be unambiguously indexed with triclinic symmetry (Fig. 2).

Thermogravimetric analysis: The number of hydrogen atoms and water molecules in $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ can be determined by thermogravimetric analysis through the loss of weight as soon as the temperature is increased. The TG curve shows that there are two steps of mass loss. The first which is observed between 140 and 270°C, is the loss of hydration water (13-hydrates), followed by a plateau corresponding to the anhydrous acid and the second is the loss of structural water ($1.5\text{H}_2\text{O}$) observed at 350–450°C. With a further increase of the temperature, above 450–500°C, only mixtures of oxides are characterized (typically by IR). The TG curve (Fig. 3) is consistent with published results^{15,18}.

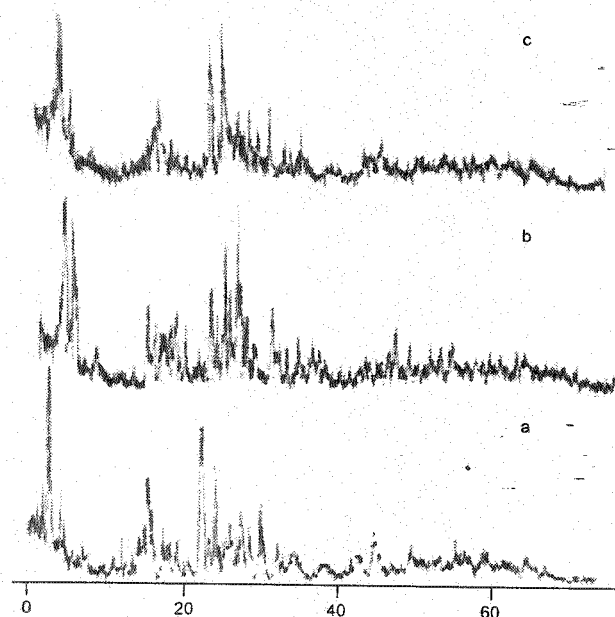


Fig. 2. XRD diagrams of initial samples of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{Cu}_{1.5}\text{PMo}_{12}\text{O}_{40}$ and $\text{Zn}_{1.5}\text{PMo}_{12}\text{O}_{40}$ at ambient conditions

Catalytic reactions

Unsupported catalyst behaviour: The progress of the conversion and the product selectivities have been followed during the reaction time on samples of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{Cu}_{1.5}\text{PMo}_{12}\text{O}_{40}$ and $\text{Zn}_{1.5}\text{PMo}_{12}\text{O}_{40}$. The results of the catalytic behaviour for the CO_2 /methanol reforming with the $\text{CO}_2/\text{CH}_3\text{OH}$ ratio equals 0.25, are shown in Figs. 4 and 5. The total conversion values (Fig. 4) show that the heteropolyacid $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ was more active than its corresponding salts. This result is in agreement with those reported in literature where it has been mentioned that the overall methanol oxidation depends on the number of protons per Keggin unit. The lack of protons decreases the concentration of protonated methanol and the amount of the common intermediate between DME and dehydrogenation products, which leads to a decrease in the conversion^{19, 20}. The conversion obtained over $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ is equal to 41.9%, whereas those obtained over $\text{Cu}_{1.5}\text{PMo}_{12}\text{O}_{40}$ and $\text{Zn}_{1.5}\text{PMo}_{12}\text{O}_{40}$ are 24.7 and 4.4% respectively. As for the selectivity, the results obtained (Fig. 5) showed that the high selectivity of HCHO (87.8%) was obtained with $\text{Zn}_{1.5}\text{PMo}_{12}\text{O}_{40}$. As expected, the high selectivity in DME (48.4%) was obtained over the heteropolyacid. It is worth mentioning that the MF was observed with a selectivity less than 5% for all the sets of catalysts. The DMM was not observed at all in this reaction condition (in absence of O_2). This result agrees with what was mentioned in literature, that the formation of the DMM requires the oxygen presence. Its formation occurs by activation of C---H bond in methoxy group to form HCHO. This latter can react in subsequent reaction with methanol to form either dimethoxymethane or methyl formate^{21, 22}. Each one of these products requires redox sites.

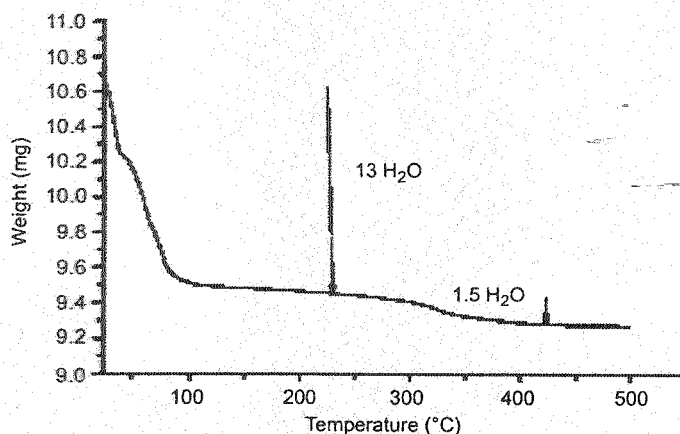


Fig. 3. Thermogravimetric curve of initial sample of $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$ at ambient conditions (heating rate: $5^\circ\text{C}/\text{min}$)

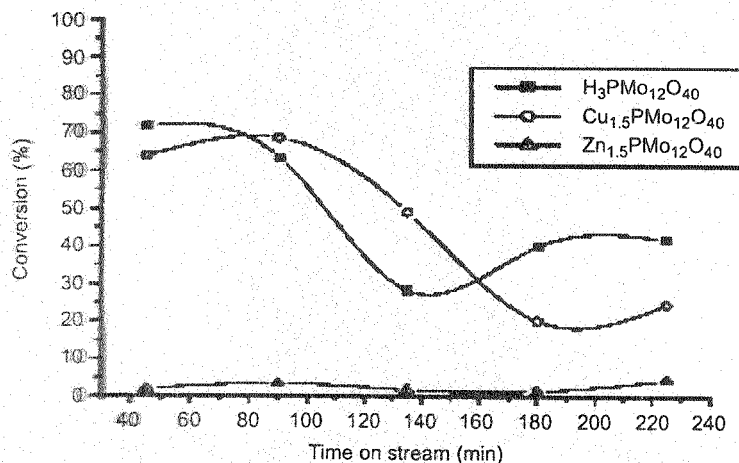


Fig. 4. Variation of methanol conversion vs. time on stream over the series of prepared catalysts (Tests conducted at 573 K with a $\text{CO}_2/\text{CH}_3\text{OH}$ ratio of 0.25)

Alumina-supported $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ behaviour: The alumina-supported $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ at different contents was also tested in the $\text{CO}_2/\text{methanol}$ reforming reaction. In Fig. 6, the conversions are plotted against the amounts of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ on alumina. The results showed that the conversion value depends on the heteropoly acid loading. The conversion increases with the catalyst loading. This is in agreement with literature findings, that the overall methanol oxidation depends on the number of protons per Keggin unit. As mentioned before for the unsupported catalysts, the lack of protons decreases the concentration of protonated methanol and hence the amount of common intermediate between DME and dehydrogenation products, which leads to a decrease in the conversion^{19, 20}. As for the selectivities, it is worthy to note that besides MF, HCHO and DME, the DMC formation was observed for the supported heteropolyacid catalysts. It has been noticed that, for the heteropolyacid, the selectivity of DMC and MF decreases when the load of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ on the support increases in favour of the DME and HCHO. For $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ contents $\geq 10\%$ heteropoly crystals are predominant and the catalyst behaves as unsupported $\text{H}_3\text{PMo}_{12}\text{O}_{40}$,²² catalysis is mainly acidic, with formation

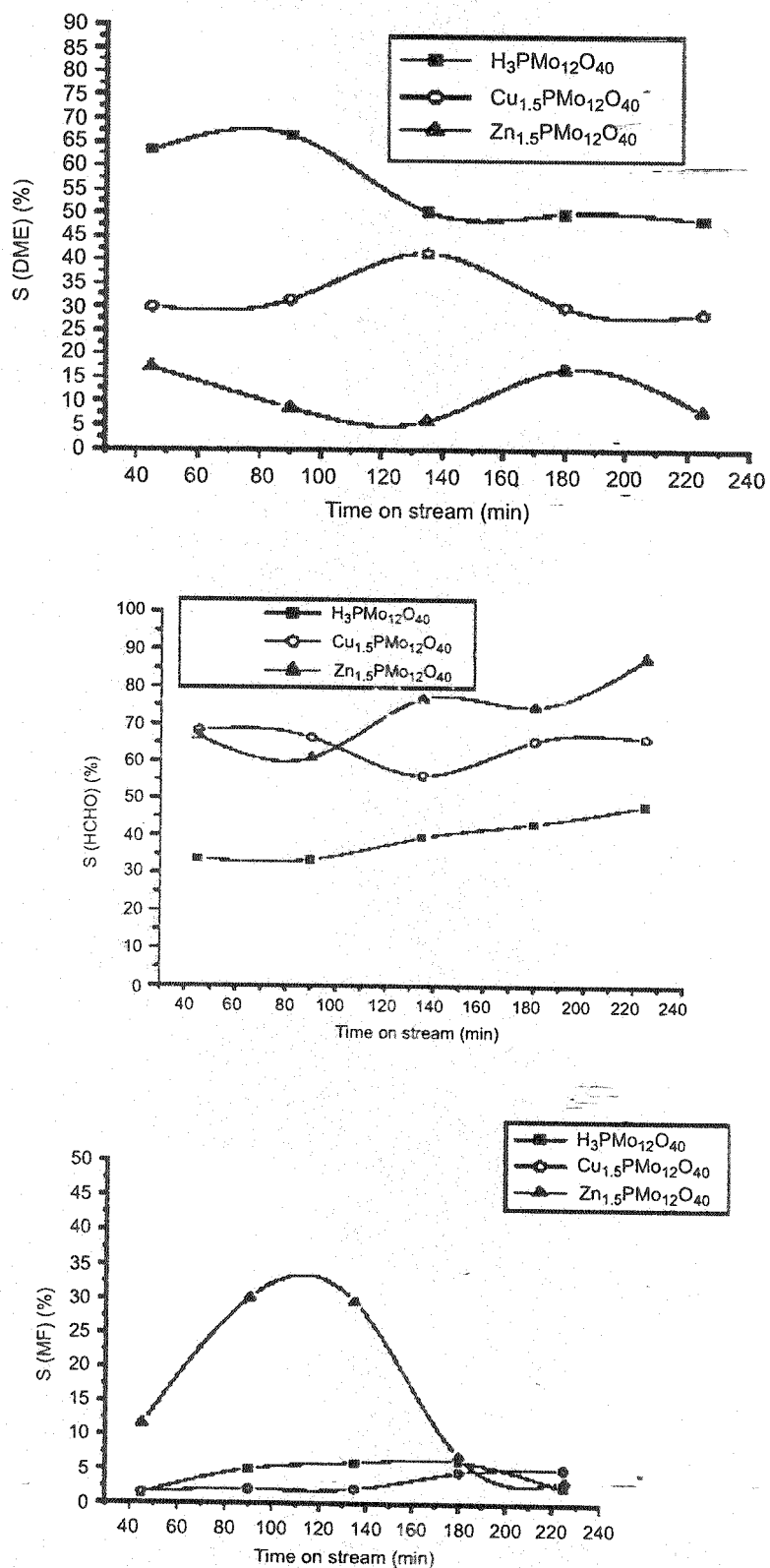


Fig. 5. Variation of the selectivities vs. time on stream over the series of prepared catalysts (Tests conducted at 573 K with a $\text{CO}_2/\text{CH}_3\text{OH}$ ratio of 0.25)

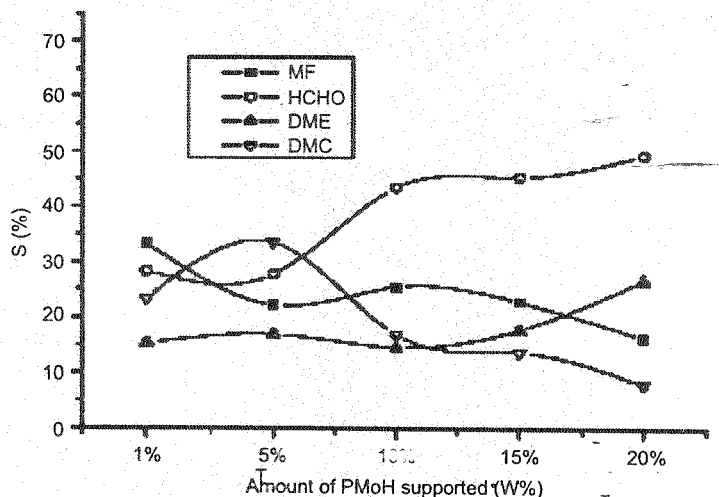


Fig. 6. Variation of methanol conversion vs. the amount of $H_3PMo_{12}O_{40}$ loaded (Tests conducted at 573 K with a CO_2/CH_3OH ratio of 0.25)

of DME at the expense of DMC. As expected, the selectivity of DME decreases as loading decreases. In fact, at lower coverages, all the protons are more and more trapped through an HPA-support interaction and the number of Brønsted-acid sites decreases, inducing the decrease of the Brønsted-acid character leading to a decrease of DME selectivity in favour of DMC selectivity. The formation of the latter requires both Lewis acid and redox sites, whereas the formation of DME requires only Brønsted-acid sites. This result agrees with that reported in literature²¹, where it is mentioned that DMC synthesis is facilitated by interactions of C and O atoms in CO_2 with Lewis acid-base pairs of sites. The mechanism can be envisaged to occur *via* the sequence of these steps: methanol binds to the Lewis acid sites and releases an H atom, which then rapidly reacts with the surface OH group to form H_2O . CO_2 is then inserted into the $M(-O)$ bond of the CH_3O-M species to produce $CH_3O-COO-M$.

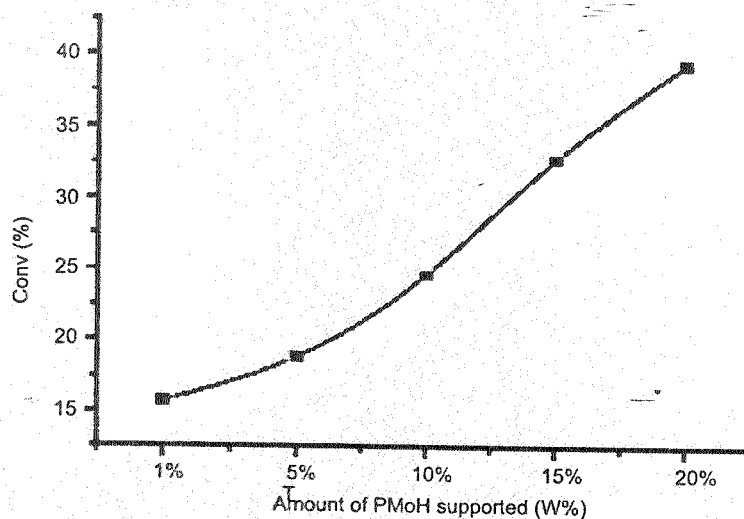


Fig. 7. Variation of the selectivities vs. the amount of $H_3PMo_{12}O_{40}$ loaded (Tests conducted at 573 K with a CO_2/CH_3OH ratio of 0.25).

Conclusion

This study allows us to draw the following conclusions. First, the methanol transformation reaction in presence of CO₂ over unsupported 12-molybdophosphoric acid and its unsupported zinc and copper salts leads to the products: HCHO, MF and DME. MF was obtained as a main product for both unsupported catalysts. When these heteropoly compounds were supported on alumina, DMC formation was observed, as well as the previous products. The support effect reveals that the formation of DMC required both Lewis acid and redox sites. The conversion increases with increasing heteropoly acid loading, suggesting that the conversion depends on the amount of Brønsted acid sites available on the catalyst surface. The selectivity of DMC decreases when Brønsted acid character increases while the selectivity of DME increases. The formation of DME is at the expense of DMC.

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