

Dehydration of ethanol over copper and cerium phosphotungstates supported on MCM-41

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The selective dehydration of 80% ethanol to diethyl ether on copper and cerium phosphotungstates supported on MCM-41 was carried out; the latter showed higher activity.

The production of diethyl ether and ethylene from bioethanol is of interest for the synthesis of petrochemicals from nonpetroleum environmentally friendly feedstock.¹ Diethyl ether can be mixed with ethanol as a fuel blending oxygenate.² The catalytic dehydration of ethanol was investigated using transition metal oxides,³ Na₂O-doped Mn₂O₃/Al₂O₃,⁴ or acidic catalysts such as zeolite,⁵ HZSM-5, silicoaluminophosphate (SAPO-34) and Ni-substituted SAPO-34.⁶ Phosphorus- and lanthanum-modified HZSM-5 catalysts were reported to show resistance to coke formation.^{7,8} Due to their higher activity in comparison with that of conventional solid acid catalysts, heteropoly acids (HPAs) were used in the dehydration reaction of alcohols.^{9–11} As HPAs have very low surface areas (<1 m² g⁻¹) and high solubility in polar solvents, in order to improve these limitations, studies were focused on the synthesis of supported catalysts.^{12,13} Catalytic activities for the dehydration of alcohols on HPAs supported on montmorillonite,¹⁴ SiO₂, TiO₂ and Nb₂O₅ were described.¹⁵ MCM-41 is a mesoporous silica molecular sieve with uniform tubular channels with a tunable pore diameter varying from 5 to 30 nm, and it is a suitable host for the Keggin structure of HPAs.¹⁶ HPA on MCM-41 synthesized using impregnation suffered from leaching.¹⁷ The supported catalyst synthesized by a direct method possessed a larger surface area and dispersed better than the impregnated sample.^{18,19} The activities of Ag₃PM₁₂O₄₀ (M = W or Mo) in the dehydration of ethanol depend on humidity, the Ag₃PM₁₂O₄₀ gave 99% selectivity for ethylene at 220 °C.²⁰ The Ag_xH_{3-x}PW₁₂O₄₀ and K_xH_{3-x}PW₁₂O₄₀ (x = 1–3) supported on SiO₂ showed decreasing activity in dehydration of ethanol with increasing x at a temperature below 200 °C. This silver salt provided a 99% conversion of ethanol at 200 °C.⁹ Cu_{0.5x}H_{3-x}PMo₁₂O₄₀ (x = 1–3) showed ~82% selectivity for diethyl ether. The conversion decreased in the order Cu_{0.5}H_{2.5}PMo₁₂O₄₀ > CuHPMo₁₂O₄₀ > Cu_{1.5}PMo₁₂O₄₀ at 350 °C.²¹

The aim of this work was to study the effect of the replacement of protons in H₃PW₁₂O₄₀ by Cu and Ce cations in an MCM-41 support on the selective dehydration of ethanol into diethyl ether. The supported catalysts were synthesized by a two-step impregnation method.[†] In the synthesis of the supported catalysts, the thermal pretreatment was conducted at 220 °C to prevent HPW on MCM-41 from aggregation and dissolution during the second

[†] MCM-41 was impregnated with aqueous solutions of H₃PW₁₂O₄₀ (HPW, Fluka, 20 and 30 wt%). It was heated at 220 °C for 2 h in a flow of N₂. Then, the secondary impregnation was carried out with an aqueous solution of Cu(NO₃)₂ or Ce(NO₃)₃. For each loading, the Cu (or Ce):HPW molar ratio was 0.5. The mixture was stirred for 2 h. Then, the metal-impregnated MCM-41 was filtered off, washed with ethanol, dried at 100 °C and calcined at 300 °C for 2 h in a flow of N₂.

Table 1 Chemical analysis and textural parameters of catalysts.

Catalyst	HPW (%) ^a analyzed	S _{BET} / m ² g ⁻¹	Pore volume/ cm ³ g ⁻¹	Cu (or Ce):P:W ^b molar ratio
MCM	0	987	0.96	0
20CuHPW/MCM	19.2	780	0.63	1.1:1.0:11.9
30CuHPW/MCM	25.6	747	0.57	1.2:1.0:11.8
20CeHPW/MCM	19.8	795	0.68	0.6:1.0:12.1
30CeHPW/MCM	28.4	758	0.60	0.7:1.0:12.0

^a Deduced from the chemical analysis of W by ICP. ^b From the ICP and XRF chemical analysis.

impregnation of metal solution.²² The thermal treatment in the second impregnation was conducted in an atmosphere of N₂ to keep the stable Keggin structure of HPW salts over MCM-41. Table 1 shows that the amount of HPW salts supported on MCM-41 is close to the loading amount except the CuHPW/MCM. This indicates that the CeHPW/MCM, similar to the CsHPW/MCM-41,¹³ is less soluble than the CuHPW/MCM.²³

The measured Cu (or Ce):P:W ratios in the catalysts revealed the presence of Cu and Ce in the catalyst. The loadings of Cu (or Ce) HPA caused a decrease in the surface area (SBET) and pore volume of the supported catalysts. This is due to the inclusion of Cu (or Ce) HPW into the one-dimensional mesopores of MCM-41 or by the agglomeration on the external surface of the support. The N₂ adsorption–desorption of the supported catalysts (Figure 1) is similar to MCM-41, and the reversible type IV isotherm is typical of mesoporous materials.

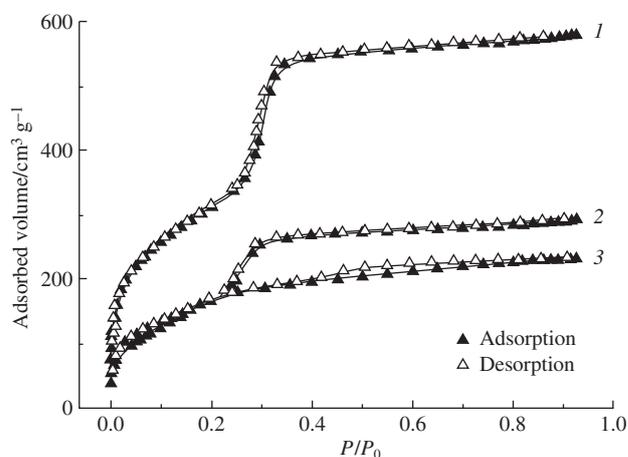


Figure 1 N₂ adsorption–desorption isotherms of (1) MCM, (2) 30CuHPW/MCM and (3) 30CeHPW/MCM.

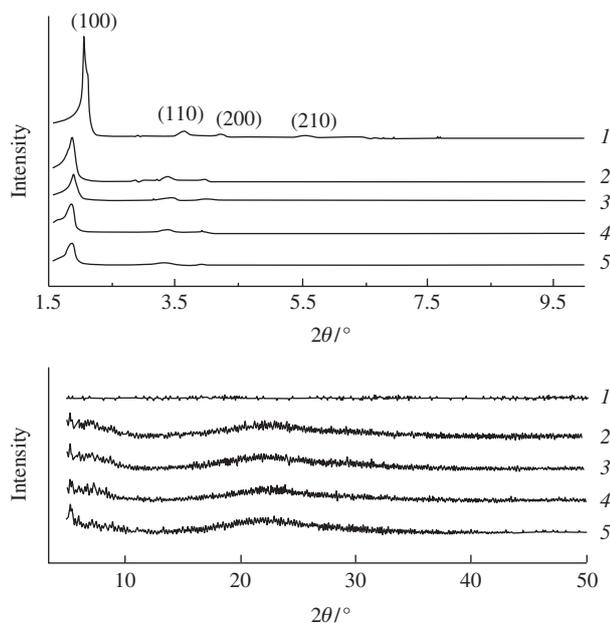


Figure 2 XRD patterns of (1) MCM, (2,3) CuHPW/MCM (20 and 30%, respectively) and (4,5) CeHPW/MCM (20 and 30%, respectively).

The XRD patterns of the supported catalysts are depicted in Figure 2.[‡] The MCM-41 showed a typical hexagonal pattern with four distinct peaks, $d_{100} = 35.9 \text{ \AA}$, $d_{110} = 21.5 \text{ \AA}$, $d_{200} = 18.8 \text{ \AA}$ and $d_{210} = 13.4 \text{ \AA}$. These peaks remain unchanged in the process of loading. There is no peak related to the crystals of Cu (or Ce) HPW, indicating the high dispersion of Cu (or Ce) HPW on the support.

The acidic properties of the catalysts were determined by NH_3 -TPD (Figure 3). The peak temperatures of the supported catalysts are much higher than that of MCM-41, which testify to higher acidity. The acidity increases with the loading of Cu (or Ce) HPW. The curve area of CeHPW/MCM is more than that of CuHPW/MCM, indicating more acid sites. The representative IR spectra of the CeHPW/MCM catalysts at $400\text{--}2500 \text{ cm}^{-1}$ (Figure 4) show a peak at 891 cm^{-1} (W–O–W) only in the 30% loading catalyst, revealing the heteropoly acid salt on the support. Other characteristic bands of the heteropoly acid salts at $1070\text{--}1080$ (P–O), $980\text{--}986$ (W=O) and $800\text{--}803$ (W–O–W) cm^{-1} overlap with the framework bands of MCM-41. Similar spectra were obtained for the CuHPW/MCM catalysts.

Catalytic activity of the supported catalysts in dehydration of ethanol[§] at 300°C was compared (Table 2). The CeHPW/MCM catalyst exhibited higher activity than the CuHPW/MCM one. The 30CeHPW/MCM catalyst, which possesses the highest acidity, displayed the highest conversion of ethanol (88.3%) with 85.0%

Table 2 Ethanol dehydration at 300°C (catalyst weight, 6 g; 80% ethanol; WHSV, 1 h^{-1}).

Catalyst	Conversion (%)	Selectivity for diethyl ether (%)
20CuHPW/MCM	75.4	77.1
30CuHPW/MCM	81.0	78.3
20CeHPW/MCM	83.2	84.5
30CeHPW/MCM	88.3	85.0

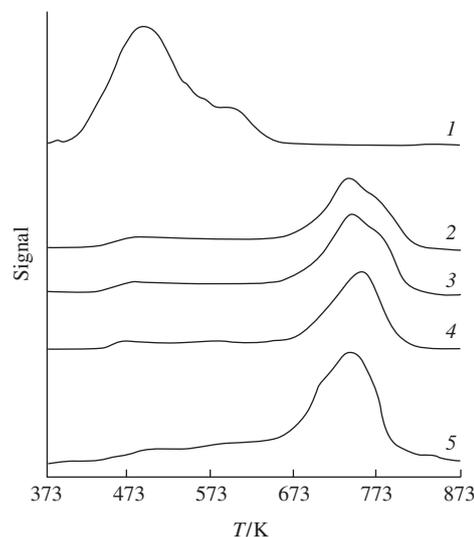


Figure 3 NH_3 -TPD profiles of (1) MCM, (2,3) CuHPW/MCM (20 and 30%, respectively) and (4,5) CeHPW/MCM (20 and 30%, respectively).

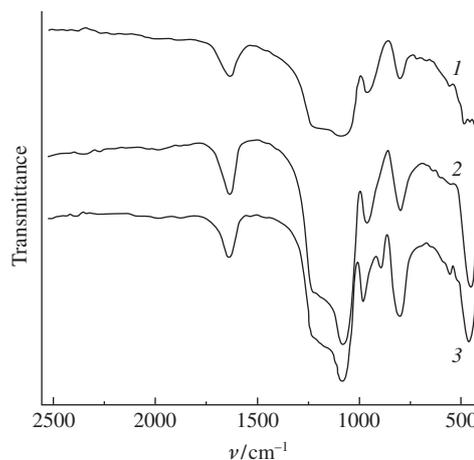


Figure 4 FTIR spectra of (1) MCM-41, (2) 20CeHPW/MCM and (3) 30CeHPW/MCM.

selectivity for diethyl ether at 300°C . The high activity of the heteropoly acid salt supported catalysts might be due to the flexible nature of the secondary structure of heteropoly acid salt and mesoporosity of the support, which allow polar ethanol to penetrate to the bulk of the solid. For comparison, at the same temperature (300°C), $\text{Cu}_{0.5}\text{H}_{2.5}\text{PMo}_{12}\text{O}_{40}$ was reported to show 88.0% conversion at 82.3% selectivity for diethyl ether,²¹ while the 18% $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ gave 86% conversion compared to 72% from $\text{AgH}_2\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ with ethylene as the main product.⁹ In addition, the catalytic activity in gas-phase isopropanol dehydration over HPW supported on different supports was reported to decrease in the order $\text{HPW}/\text{SiO}_2 > \text{HPW}/\text{TiO}_2 > \text{HPW}/\text{Nb}_2\text{O}_5 > \text{HPW}/\text{ZrO}_2$, in line with the acid strength.²⁴

The variation in the catalytic activity as a function of reaction temperature over the 30CeHPW/MCM and 30CuHPW/MCM catalysts is presented in Figure 5. Conversion increases with

[‡] Specific surface areas were measured using the BET method on a BELSORP-mini instrument. XRD measurements were performed on a Rigaku DMAX 2002/Ultima Plus powder X-ray diffractometer. The FTIR spectra were obtained on a Nicolet FT-IR Impact 410 spectrophotometer with a pressed KBr pellet. The amounts of Cu, Ce and W were determined by inductively coupled plasma atomic emission spectrometry (ICP, Perkin Elmer model PLASMA-1000), and the P content was determined using an ARL 8410 X-ray fluorescence spectrometer (XRF).

[§] *Dehydration of ethanol*: 0.5 g of the catalyst was placed in a fixed-bed flow reactor (10 mm i.d.) and supported by quartz wool from both ends. It was activated at 250°C in the presence of N_2 (30 ml min^{-1}) for 2 h. Then, bioethanol (80%) was fed using a syringe pump into N_2 stream, at a weight hourly space velocity (WHSV) of 1 h^{-1} and atmospheric pressure. Each reaction was performed for a period of 5 h. The temperature was varied in a range of $200\text{--}350^\circ\text{C}$. The products were condensed and analyzed off-line using a gas chromatograph (Hewlett Packard-6890) with a Porapak T column and a TCD detector.

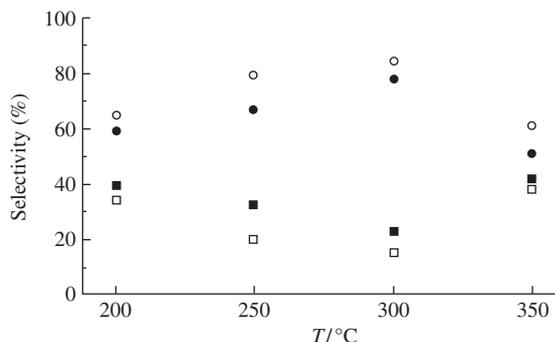


Figure 5 Effect of reaction temperature on the selectivity for diethyl ether (○,●) and ethylene (□,■) of the (○,□) 30CeHPW/MCM and (●,■) 30CuHPW/MCM catalysts.

temperature to reach 91.5 and 86.6% for 30CeHPW/MCM and 30CuHPW/MCM, respectively, at 350 °C. Even though the synthesized catalysts were calcined at 300 °C but the reaction was performed at 350 °C, the catalysts were stable. The HPW salts on silica were reported to be stable at <400 °C.²²

Dehydration of ethanol can occur by two competitive paths. The first one is the intramolecular dehydration of ethanol to ethylene, whereas the second is the intermolecular dehydration of ethanol to diethyl ether.²⁵ At 200 °C, diethyl ether is the main product. This may be attributed to the requirement of intermolecular dehydration of ethanol (needs 2 mol) to form diethyl ether at a lower energy than the intramolecular dehydration of ethanol to form ethylene. With an increase in the temperature to 350 °C, the conversion of ethanol grew but the selectivity for diethyl ether decreased and the selectivity for ethylene increased due to the decomposition of diethyl ether. The 30CeHPW/MCM catalyst gave higher selectivity for diethyl ether. The $\text{Cu}_{0.5}\text{H}_{2.5}\text{PMo}_{12}\text{O}_{40}$ was reported to show low conversion (65.8%) and selectivity for diethyl ether (67.1%) at 200 °C but a much higher activity at 250 °C (90.5% conversion with 81.1% selectivity).²¹

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