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Mendeleev Commun., 2014, 24, 167-169

Mendeleev Communications

Platinum/phosphotungstic acid/(Zr)MCM-41 catalysts in glycerol dehydration

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DOI: 10.1016/j.mencom.2014.04.015

MCM-41 and ZrMCM-41 impregnated with 2% Pt and 30–40% phosphotungstic acid exhibit catalytic activity in the dehydration of glycerol to acrolein, and Pt doping increases the stability.

Glycerol dehydration to acrolein is an attractive sustainable alternative to the conventional acrolein process (oxidation of propene with Bi/Mo-mixed oxide catalyst).¹ Solid acid catalysts including sulfates, phosphates and zeolites have been tested for the dehydration of glycerol in either gaseous or liquid phases.²⁻⁴ Heteropoly acids, which have strong Brønsted acidity, showed decreasing activity in the liquid phase dehydration of glycerol to acrolein in the order $H_4SiW_{12}O_{40} > H_3PW_{12}O_{40} > H_3PMo_{12}O_{40}$. Due to their very low surface area and high solubility in polar solvents, the synthesis of supported catalysts was focused on activated carbon-supported H₄SiW₁₂O₄₀ (10% loading, yield of 68.5 mmol h⁻¹ g⁻¹),⁶ ZrO₂-supported H₃PW₁₂O₄₀ (10-40% loading, 42-54% yield, 65-71% selectivity),7 alumina- and aluminosilicate-supported H₄SiW₁₂O₄₀ (20% loading, 75% selectivity)⁸ and SiO₂-supported H₄SiW₁₂O₄₀ (30% loading, >85% selectivity).⁹ The major drawback to the gas-phase dehydration of glycerol on acid catalysts is catalyst deactivation due to coke deposition. Addition of alkaline and alkaline earth cations improved the catalytic performance, but they still deactivated over a short reaction time.¹⁰ The decrease in glycerol conversion was reported: >60% after 8 h (zeolite),³ >20% after 10 h (ZrO_2-supported $H_3PW_{12}O_{40})$ and 40% after 5 h (SiO_2-supported $H_3PW_{12}O_{40}$).⁷ The catalyst deactivation is overcome by cofeeding O_2 ,¹¹ or doping with noble metals and co-feeding H_2 , with the order of activity Ru, $Pt < Pd.^{12}$ Zr doped mesoporous silica catalysts are more thermally stable and have high selectivity for acrolein.13 H₄SiW₁₂O₄₀ supported on SBA-15 grafted with ZrO₂ was reported to have a long-time performance.¹⁴ Mixed Zr-Nb oxide exhibited stability (82% glycerol conversion after 177 h).¹⁵ Previously, we used MCM-41-supported Cu and Ce phosphotungstates for the dehydration of ethanol¹⁶ and MCM-41supported H₃PW₁₂O₄₀ for the esterification of palm fatty acids distillate.17

The aim of this work was to improve the long-time stability of MCM-41-supported catalysts for selective dehydration of glycerol into acrolein. The supports and catalysts were synthesized^{\dagger} and characterized.^{\ddagger}

| Table | 1 | Chemical | analysis, | textural | parameters | and | acidity | of catalysts. | |
|-------|---|----------|-----------|----------|------------|-----|---------|---------------|--|
|-------|---|----------|-----------|----------|------------|-----|---------|---------------|--|

| | HPW ana- lyzed ^a (%) | $\frac{S_{\rm BET}}{{ m m}^2{ m g}^{-1}}$ | Pore | Pore | Total | Acidity ^c | | |
|-------------------------|--|---|--|-------------|--|----------------------|--------------|-----|
| Catalyst | | | volume/ cm ³ g ⁻¹ | size/ nm | acidity ^b / mmol g ⁻¹ | <i>I</i> (B) | <i>I</i> (L) | B/L |
| MCM-41 | 0 | 993 | 0.80 | 3.8 | 0 | _ | _ | _ |
| ZrMCM-41 | 0 | 792 | 0.71 | 3.6 | 0.26 | 0.19 | 0.23 | 0.8 |
| 35% HPW/ MCM-41 | 34.6 | 722 | 0.64 | 3.1 | 0.63 | 0.83 | 0.72 | 1.1 |
| Pt/30% HPW/ MCM-41 | 29.4 | 765 | 0.70 | 3.4 | 0.55 | 0.70 | 0.66 | 1.0 |
| Pt/35% HPW/ MCM-41 | 34.4 | 753 | 0.67 | 3.5 | 0.67 | 0.83 | 0.72 | 1.1 |
| Pt/40% HPW/ MCM-41 | 38.8 | 736 | 0.65 | 3.5 | 0.71 | 1.09 | 0.80 | 1.4 |
| Pt/30% HPW/ ZrMCM-41 | 29.0 | 712 | 0.69 | 3.5 | 0.51 | 0.74 | 0.68 | 1.1 |
| Pt/35% HPW/ ZrMCM-41 | 32.8 | 686 | 0.67 | 3.5 | 0.68 | 0.85 | 0.71 | 1.2 |
| Pt/40% HPW/ ZrMCM-41 | 36.6 | 680 | 0.65 | 3.3 | 0.73 | 1.12 | 0.80 | 1.4 |

^{*a*} Deduced from the chemical analysis of W by ICP AES. ^{*b*} Measured by NH₃-TPD techniques. ^{*c*} Measured from pyridine adsorption FTIR.

Table 1 summarizes the specific surface area, pore volume, pore size and acidity of the support and the catalysts.[‡] The decreases of specific surface area, pore volume and pore size with Pt and HPW loadings indicate that the HPW was either introduced in the porosity, filling the pores and/or being deposited on the external surface of the mesoporous material.

material was filtered off and dried at 80 °C for 12 h. The sample was calcined at 500 °C for 6 h. The determined Si/Zr molar ratio was 8.9.

[†] MCM-41 was synthesized as follows: 1.988 g of cetyltrimethylammonium bromide (CTAB) was dissolved in 120 g of water; 8 ml of aqueous NH₃ (conc.) and 10 ml of tetraethyl orthosilicate (TEOS) were added with vigorous stirring. The solution became milky and slurry formed. After 1 h, the material was filtered off and dried at 80 °C for 12 h. The sample was calcined at 500 °C for 6 h. ZrMCM-41 with the molar ratio Si/Zr = 10 was synthesized as follows: 12.2 g of CTAB was dissolved in 110 ml of water and 110 ml of aqueous NH₃ (conc.). A solution prepared from 5.5 ml of zirconium *n*-propoxide (70% in propanol) and 22.8 ml of TEOS was then dropwise added with vigorous stirring. After 2 h, the

MCM-41 or ZrMCM-41 was first impregnated with an aqueous solution of H₂PtCl₆·6H₂O (2 wt% Pt). The sample was dried overnight at 110 °C and calcined in air at 300 °C for 3 h. Then, it was impregnated with H₃PW₁₂O₄₀ solutions (30, 35 and 40 wt%), dried overnight at 110 °C and calcined at 350 °C for 2 h. 35% HPW/MCM-41 without Pt was also prepared for comparison.

[‡] Specific surface areas were measured using the BET method on BELSORP-mini. XRD measurements were performed on a Rigaku DMAX 2002/Ultima Plus powder X-ray diffractometer. The acidity of the catalysts was studied by the temperature-programmed desorption of ammonia (NH₃-TPD). To evaluate the types of acid sites, pyridine adsorption on the samples was performed on a 170-SX FTIR spectrometer. The FTIR spectra were obtained on a Nicolet FT-IR Impact 410 spectrophotometer with a pressed KBr pellet. The amounts of Zr and W were determined by inductively coupled plasma atomic emission spectrometry (ICP, Perkin Elmer model PLASMA-1000). The carbon content of spent catalysts was determined from combustion analysis.



Figure 1 Pyridine-adsorption FTIR spectra of (1) Pt/35% HPW/ZrMCM-41 and (2) Pt/35% HPW/MCM-41.



Figure 2 N₂ adsorption–desorption isotherms of (1) Pt/35% HPW/MCM-41 and (2) Pt/35% HPW/ZrMCM-41.

The FTIR spectra of pyridine adsorption on the supported catalysts (Figure 1) show Brønsted (B) and Lewis (L) acidities, the integrated areas of the absorbance bands at 1444 (B) and 1542 (L) cm⁻¹ are quantified.¹⁸ The total acidity and B/L ratios are given in Table 1. The incorporation of Zr into the MCM-41 framework weakens the SiO–H bond, generates Brønsted acid sites and increases the total acidity.¹⁹ The supported catalysts had a larger amount of acid sites than pure supports. With increasing acid loading, not only the total acidity but also both Lewis and Brønsted acidities increase. Compared with Pt/HPW/MCM-41 catalysts (30–35% HPW loadings), the B/L ratio of Pt/HPW/ZrMCM-41 catalysts is a little higher. It was reported that Pt/HPW/ZrMCM-41 support than MCM-41.²⁰

The N_2 adsorption–desorption isotherms of the MCM-41and ZrMCM-41-supported catalysts are similar (Figure 2). They exhibit a reversible type IV isotherm with a hysteresis loop typical of mesoporous materials.

The powder XRD patterns[‡] of MCM-41 and ZrMCM-41 exhibit a low-angle diffraction peak due to the (100), (110), (200) and (210) planes characteristic of the MCM-41 structure. The



Figure 3 XRD patterns of (1) HPW, (2) MCM-41 and (3)–(5) Pt/HPW/ MCM-41 (30, 35 and 40% HPW, respectively).



Figure 4 FTIR spectra of (1) HPW, (2)-(4) Pt/HPW/MCM-41 (30, 35 and 45% loading, respectively) and (5) MCM-41.

peak intensities decreased with the loading amount of HPW. The XRD patterns of the MCM-41-supported catalysts (Figure 3) show diffraction peaks corresponding to HPW at 2θ angles of 25.3, 29.3, 34.6 and 37.7° (PDF#38-0178). The XRD patterns of the ZrMCM-41-supported catalysts are similar but with a slight shift of the (100) peak position towards smaller angle resulting from an increase in the lattice cell parameter from the substitution of Zr.

The FTIR spectra of the MCM-41 and Pt/HPW/MCM-41 catalysts are depicted in Figure 4. The IR spectrum of HPW in the region of 600–1300 cm⁻¹ contains characteristic bands at 960 (W=O), 886 and 811 cm⁻¹ (W–O–W). A tiny band at 886 cm⁻¹ still appears in the spectra of the supported catalyst, which confirmed the retention of the HPW structure after impregnation. However, the bands at 960 and 811 cm⁻¹ are not clearly evident, as well as the bands at 1065–1100 cm⁻¹ attributed to v_{as}(P–O) vibration were obscured by an intense and broad band of MCM-41. The FTIR spectra of the Pt/HPW/ZrMCM-41 catalysts are similar except that the tiny band at 886 cm⁻¹ was observed only in case of the 40% HPW loaded catalyst.

The catalytic activity[§] is given in Table 2. The main product is acrolein with minor amounts of acetaldehyde, hydroxyacetone, propanal and trace amounts of others. In Scheme 1, when protonation occurs at the secondary hydroxy group of glycerol **1**, a water molecule and a proton are eliminated from the protonated glycerol, and then 3-hydroxypropanal **2** is produced by tautomerism. Since this 3-hydroxypropanal intermediate is unstable, readily dehydrated into acrolein **3**, it was not detected, similarly to that reported for TiO₂-supported HPW catalyst.¹⁸ When protonation proceeds



 $^{\$}$ Dehydration of glycerol was carried out in a vertical tubular fixed-bed quartz reactor (20 cm in length and 10 mm in internal diameter). The catalyst (20–40 mesh, 0.4 g) was put into the center of the reactor between quartz wool. The catalyst was first reduced under H₂ flow (15 ml min⁻¹) for 1 h at 250 °C. Then, a 10% aqueous solution of glycerol was fed into an evaporator at 250 °C with a flow rate of 0.14 ml min⁻¹ (or WHSV of 2.1 h⁻¹). Then, the gas stream was transported into the reactor in 15 ml min⁻¹ N₂ flow under atmospheric pressure and reacted at different reaction temperatures (300–400 °C).

Table 2 Glycerol dehydration (5 h).

| Entry | Catalyst | T/°C | Conver- sion (%) | Acrolein selectivity (%) | Ref. |
|-------|--|------|---------------------|--------------------------------|------------------------|
| 1 | MCM-41 | 300 | 10 | 30 | This work ^a |
| 2 | ZrMCM-41 | 300 | 66 | 28 | This work ^a |
| 3 | 35% HPW/MCM-41 | 350 | 70 | 79 | This work ^a |
| 4 | Pt/30% HPW/MCM-41 | 300 | 68 | 74 | This work ^a |
| 5 | | 350 | 76 | 78 | This work ^a |
| 6 | Pt/35% HPW/MCM-41 | 300 | 76 | 77 | This work ^a |
| 7 | | 350 | 82 | 80 | This work ^a |
| 8 | | 400 | 80 | 69 | This work ^a |
| 9 | Pt/40% HPW/MCM-41 | 300 | 79 | 73 | This work ^a |
| 10 | | 350 | 83 | 77 | This work ^a |
| 11 | Pt/30% HPW/ZrMCM-41 | 300 | 70 | 76 | This work ^a |
| 12 | | 350 | 80 | 78 | This work ^a |
| 13 | Pt/35% HPW/ZrMCM-41 | 300 | 79 | 76 | This work ^a |
| 14 | | 350 | 87 | 81 | This work ^a |
| 15 | | 400 | 76 | 69 | This work ^a |
| 16 | Pt/40% HPW/ZrMCM-41 | 300 | 80 | 77 | This work ^a |
| 17 | | 350 | 86 | 77 | This work ^a |
| 18 | 20% HPW/SiO2 ^b | 300 | 67 | 71 | 8 |
| 19 | 20% HPW/SiO ₂ (in N ₂) ^c | 275 | 60 | 95 | 12 |
| 20 | $2\% \text{Pd}/20\% \text{HPW/SiO}_2$ (in H ₂) ^c | 275 | 72 | 94 | 12 |
| 21 | $ZrMCM-41 (Si/Zr = 10)^d$ | 325 | 73 | 24 | 13 |

 a Catalyst 0.4 g, 10% glycerol feed at 0.14 ml min⁻¹ flow rate, 15 ml min⁻¹ N₂. b Catalyst 0.3 g, 10% glycerol feed at 0.028 ml min⁻¹ flow rate, 30 ml min⁻¹ N₂. c Catalyst 0.3 g, 10% glycerol feed at 0.14 ml min⁻¹ flow rate, 15 ml min⁻¹ H₂ or N₂. d Catalyst (2.7 nm pore size) 0.3 g, 10% glycerol feed at 0.05 ml min⁻¹ flow rate, 30 ml min⁻¹ N₂.

at a terminal hydroxy group of glycerol, hydroxyacetone **4** is produced through dehydration and deprotonation accompanied by tautomerism.²¹ Other by-products include acetaldehyde, propanal and trace unidentified compounds (each less than 4%).

MCM-41 and ZrMCM-41 produce significantly low glycerol conversion and selectivity for acrolein (Table 2, entries 1, 2). The supported catalysts provide much higher glycerol conversion and selectivity for acrolein. The 35% HPW/MCM-41 shows 70% conversion with 79% selectivity. When loaded with Pt, under the same reaction condition, a higher conversion (82%) was achieved (entry 3 vs. 7). This reveals the higher catalyst stability attributed to the role of Pt in reducing coke formation.

At the same temperature, the increasing loading of HPW on both supports leads to an increase in glycerol conversion (cf. entries 4-10 and 11-17). It was reported that the formation of acrolein is related to Brønsted acid sites, while Lewis acid sites show higher selectivity for hydroxyacetone.14 Increasing HPW loading results in a higher B/L ratio (Table 1); therefore, the selectivity for acrolein increased. Among the test catalysts, Pt/35% HPW/ZrMCM-41 shows the best performance (82% conversion with 80% selectivity, entry 7). As for other by-products over the Pt-loaded catalysts, the selectivity for hydroxyacetone is 11-18%, along with acetaldehyde (<8%) and propanal (<5%). There is a difference in the selectivity for hydroxyacetone between Pt/35% HPW/MCM-41 and 35% HPW/MCM-41 (16% vs. 7%), similarly to a result reported for Pt/SBA-15 and SBA-15.22 Selectivities for hydroxyacetone and acetaldehyde from the bare support are almost equal.

The glycerol conversion increased with the reaction temperature (300-400 °C). However, the selectivity for acrolein decreased at 400 °C (entries 8 and 15) due to the formation of acrolein oligomers or the cracking of acrolein. The experimental results showed that both the reaction temperature and the acid loading affected the conversion of glycerol and the selectivity for acrolein.



Figure 5 Time dependence of glycerol dehydration at $350 \degree C$ over (x) Pt/35% HPW/ZrMCM-41, (o) Pt/35% HPW/MCM-41 and (D) 35% HPW/MCM-41.

The long term stability of the catalysts was tested with Pt/35% HPW/ZrMCM-41 and Pt/35% HPW/MCM-41 compared to the Pt-free catalyst at 350 °C (Figure 5). Both Pt loaded catalysts retain conversion until 40 h; at 50 h, the glycerol conversion decreased to 78–80%, while the Pt-free catalyst demonstrated a drastic decrease in conversion (60% in 20 h). This might be due to coke deposition (7.5%). A lower coke deposition was found for the Pt loaded catalysts ($\leq 1.0-1.5\%$). The Pt reduces catalyst coking by hydrogenating coke precursors.

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Received: 13th May 2013; Com. 13/4119