**BULLETIN**
OF THE
KOREAN CHEMICAL SOCIETY

ISSN 0253-2964 BKCSDE 21(10) 947-1054
Volume 21, Number 10 October 20, 2000

# Communications

## Deprotection of Acetals and Ketals over Hexagonal Mesoporous Molecular Sieve as a Reusable, Heterogeneous Catalyst

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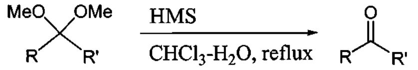
*Received July 4, 2000*

In recent years, organic reactions on solid supports[1] such as zeolites[2] or mesoporous molecular sieves[3] have attracted much attention because of advantages such as mild acidic properties, shape-selectivities, environment-friendly nature of catalysts, the easy work-up, the high purity of the products, and the recycling of catalysts. In 1995, the preparation of a new type of hexagonal mesoporous molecular sieves (HMS) by neutral assembly pathways was reported by Tanev and Pinnavaia.[4] This HMS was reported to possess physical and catalytic properties different from those of MCM-41 prepared by electrostatic assembly pathways.[5] Even though HMS can be prepared much more easily than MCM-41 or other zeolites and has certain advantages such as thicker framework walls, superior thermal stability, and a smaller crystalline size, HMS itself has not yet been fully exploited as a new catalyst.[6,7] Therefore we undertook a study aimed at discovering reactions that can be catalyzed by HMS. Here we present our finding that HMS can act as a recyclable solid acid catalyst for the deprotection[8] of acetals and ketals, as shown in Table 1.

Dimethyl acetals and ketals could be deprotected into the carbonyl compounds by simply heating with HMS[9] in the presence of water (5 equiv) in purified $CHCl_3$ solvent. The work-up was simple: the filtration of HMS followed by the removal of solvent gave a product in an excellent yield and in a high state of purity. Deprotection of dimethyl acetal of $\alpha,\beta$-unsaturated aldehyde (entry 1), aromatic aldehydes (entries 2, 4), and simple ketones (entries 7-9) was completed within a few hours, except for entries 3, 9 and 10.[10] In contrast, dimethyl acetals of aliphatic aldehydes required a longer reaction time (entries 5, 6).[11] Deprotection of dimethyl ketal of 4-*tert*-butylcyclohexanone (entry 10) and camphor (entry 11) required a longer time than that of less bulky

**Table 1**. HMS-Mediated Deprotection of Acetals and Ketals to Carbonyl Compounds



| Entries[a] | Substrates[b] | Reaction Conditions[c] | Yield (%)[d] |
|---|---|---|---|
| 1a | (*E*)-Ph-CH=CH-CH$(OMe)_2$ | 0.1 g, 4 h | 94 |
| 1b | (*E*)-Ph-CH=CH-CH$(OMe)_2$ | 0.2 g, 16 h | 95 |
| 2a | $PhCH(OMe)_2$ | 0.1 g, 1 h | 92 |
| 2b | $PhCH(OMe)_2$ | 0.1 g, 7 h | 94 |
| 3 | *m*-$NO_2C_6H_4CH(OMe)_2$ | 0.2 g, 20 h | 98 |
| 4 | *o*-$ClC_6H_4CH(OMe)_2$ | 0.1 g, 1 h | 98 |
| 5 | $Me(CH_2)_4CH_2CH(OMe)_2$ | 0.1 g, 11 h | 93 |
| 6 | $Me(CH_2)_5CH_2CH(OMe)_2$ | 0.1 g, 18 h | 94 |
| 7 | $MeC(OMe)_2CH_2(CH_2)_4Me$ | 0.1 g, 1 h | 94 |
| 8 | Dimethyl ketal of cyclohexanone | 0.1 g, 4 h | 95 |
| 9 | $PhC(OMe)_2Me$ | 0.1 g, 2 h | 97 |
| 10 | Dimethyl ketal of 4-*tert*-butylcyclohexanone | 0.1 g, 10 h | 96 |
| 11 | Dimethyl ketal of (±)-camphor | 0.2 g, 24 h | 92 |
| 12 | 1,3-Dioxolane of 2-octanone | 0.2 g, 10 h | 91 |
| 13 | 1,3-Dioxolane of PhCHO | 0.2 g, 10 h | 91 |
| 14 | 1,3-Dioxolane of octanal | 0.5 g, 2 days | 50[e] |
| 15 | 1,3-Dioxolane of heptanal | 0.5 g, 2 days | 20[e] |

[a] In entries 1b and 2b, non-calcined HMS was used. [b] Dimethyl acetals and ketals were prepared by heating a solution of carbonyl compound and $(MeO)_3CH$ in MeOH solvent in the presence of Amberlyst-15 (Patwardhan, S. A.; Dev. S. *Synthesis* **1974**, 348) and characterized by NMR spectroscopy. Dioxolanes were prepared by heating a solution of carbonyl compound and glycol in the presence of *p*-TsOH. [c] Deprotection was performed by refluxing 1.0 mmol of the substrates dissolved in 10 mL of purified chloroform in the presence of 90 mg of $H_2O$ (5 mmol) and HMS under $N_2$ atmosphere. The weight represents the amount of HMS. [d] Isolated yields. [e] The rest is the starting compound.

ones. This is probably due to the bulky shape of ketals and their product, which impedes the formation and diffusion in the pore channel of HMS. Also, 1,3-dioxolanes, especially those of aliphatic aldehydes (entries 14, 15) were less reactive than dimethyl acetals or ketals, even in the presence of a larger amount of HMS. Non-calcined HMS was less active as catalyst than calcined HMS, as shown in b series in Table 1. We speculate that the increased surface area resulting from the complete removal of the neutral template during calcination[5] may be responsible for the increased activity of calcined HMS. Next, we studied the recycling of HMS. Thus, HMS catalyst used in entry 1 was recovered by filtration and was reused without calcination for the next run, which was finished in 3 hr, giving 96% yield. Third run using the recovered HMS from the second run gave 97% yield in 3 h. These results show that HMS can be recycled for many times without loss of the activity.

The reduced reactivity[12] of 1,3-dioxolanes was employed in the chemoselective deprotection of dimethyl acetals. Thus, when an equimolar mixture (1 mmol each) of dimethyl acetal and 1,3-dioxolane of heptanal was refluxed with HMS (0.1 g) in chloroform (10 mL) in the presence of water (5 mmol) for 10 h, 1,3-dioxolane was recovered nearly intact, while dimethyl acetal was completely deprotected to aldehyde, as evidenced by $^1$H NMR spectroscopy.[13] In comparison with other zeolites such as H-mordenite,[14] HMS employed here shows a similar catalytic reactivity toward acetals and ketals except 1,3-dioxolanes of aliphatic aldehydes. However deprotection with HMS requires lower temperature and less amount of water than H-mordenite.

In conclusion, we have shown that HMS can serve as a reusable solid acid for the deprotection of the dimethyl acetals and ketals in high yields.

## References and Notes

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9. HMS used in this experiment was prepared according to the literature method[5] using dodecyl amine as template and tetraethyl orthosilicate (TEOS) as silicon source. Template removal was achieved by ethanol extraction. Thus, neat TEOS (44.6 mL, 0.20 mol) was added to a well-stirred solution of dodecyl amine (10.0 g, 0.054 mol) in EtOH (105.5 mL) and $H_2O$ (106.7 mL) all at once at rt. The whole mixture was stirred for 18 h at rt and the solid product was filtered, washed with deionized water (800 mL), and air-dried for 1 day. The pale yellow solid (21.4 g) was extracted with EtOH (500 mL) in a Soxhlet extractor for 4 h. The solvent-extracted material was dried at 80 °C for 3 h and calcined in air at 630 °C for 4 h (heating rate 2 °C/min) to give 9.60 g of white solid. The physicochemical parameters of HMS prepared thus are as follows: BET surface area 1142 ± 19 $m^2$/g, average pore diameter 41 Å, micropore volume 0.67 mL/g.
10. The less reactivity observed in entry 3 is probably due to the electronic effect.
11. Generally, dimethyl acetals are less reactive than ketals in the acid-catalysed cleavage. See *Ref.* 8a.
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