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Highly Effective Acetalization of Aldehydes and Ketones with Methanol on Siliceous Mesoporous Material

Yasuhiro Tanaka, Naoki Sawamura, and Masakazu Iwamoto*

Catalysis Research Center, Hokkaido University, Sapporo 060-0811, Japan

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Abstract

Aromatic and linear aldehydes as well as cyclohexanone could be converted to the corresponding dimethylacetals in yields of *ca.* 90-100% at ambient or refluxing temperature in the titled reaction.

Keywords: acetals; catalysis; mesoporous silica

Acetalization has widely been used to protect the carbonyl group of aldehydes and ketones. Various kinds of acids are well known to catalyze the reaction in homogeneous and heterogeneous phases.[1] Several problems, however, remain to be solved. For example, the formation of dimethylacetals in the homogeneous phase is frequently carried out by using trimethyl orthoformate as the reagent, but use of methanol for the reaction is to be desired. In the case of the typical methanol/HCl system, many kinds of by-products are often produced because of the strong acidity of HCl. On the other hand, some solid catalysts such as silica gel,[2] alumina,[2] zeolite,[3] resins,[4, 5] clays,[6,7] hydrous zirconium oxide[8] and mesoporous aluminosilicate[9] have been reported to be active for the acetalization. Trimethyl orthoformate is again employed as the dimethylacetalization reagent on all of the solid catalysts except Ce^{3+}-exchanged montmorillonite[7] (abbreviated as Ce-mont). On Ce-mont, cyclohexanone, its derivatives, and aromatic aldehydes can be converted into the corresponding dimethylacetals with methanol whose yields were roughly 94-99%.

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Much attention has been focused on the siliceous mesoporous material termed MCM-41.[10, 11] The MCM-41 possesses well-ordered hexagonal arrays of uniform channels and a high surface area; therefore, it can be used for the catalysis of organic molecules. In fact, aluminosilicate MCM-41 showed catalytic activities for aldol condensation,[12] Friedel-Crafts acylation,[13, 14] and Diels-Alder reaction.[15] The present authors have also reported the high activity of MCM-41 supporting Mn^{2+} [16] for the epoxidation of stilbene and its derivatives.[17] During the study we have found the siliceous MCM-41 itself shows excellent catalytic activity for the acetalization with methanol. We wish here to report the high yields of dimethylacetals from aldehydes and ketones.

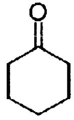
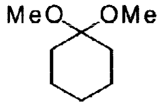
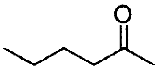
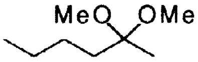
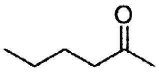
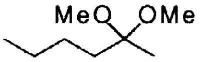
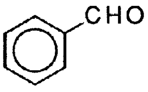
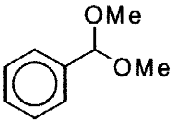
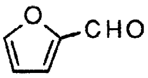
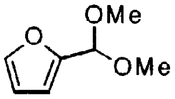
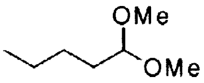
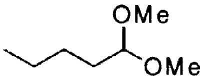
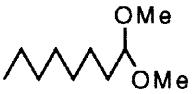
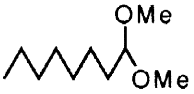
The MCM-41 used was prepared from colloidal silica and dodecyltrimethylammonium bromide by the method described previously.[18] The as-synthesized MCM-41 obtained was washed with deionized water and calcined at 873 K for 6 h in air to remove organic components. The calcined MCM-41 was vigorously stirred in a 0.1 N HNO_3 aqueous solution for 0.5 h, washed with water until the filtrate became neutral, dried at 353 K for 2 h, and then preserved in air at ambient temperature. The hexagonal structure of the resulting MCM-41 was confirmed by the appearance of $2\theta = 2.580$, 4.476, and 5.124° peaks in the X-ray diffraction pattern, which correspond to (100), (110), and (200), respectively. The N_2 adsorption-desorption and the BET measurements gave the pore diameter of 2.24 nm and the surface area of 1,016 m^2 g^{-1}. The content of aluminum, which was derived from impurities in the colloidal silica, was very low and the Al/Si ratio was 0.00114.

Carbonyl compounds of 2.0 mmol were reacted on 30 mg of MCM-41 in 5.0 cm^3 of methanol All of the experiments were performed in air at ambient or refluxing temperature. Methanol was of commercially available, non-anhydrous grade and used without further dehydration treatment. The MCM-41 contained *ca.* 11 wt% of water just before use in the acetalization run but was used without any drying. Yields were determined by GC-MS using *n*-decane as an internal standard.

Acetalization of cyclohexanone was first measured on the MCM-41 as a function of reaction time. The acetalization reached an equilibrium within 40 minutes and the yield of 1,1-dimethoxycyclohexane was 89%. No other product than acetal was detected by careful GC-MS and ^1H NMR analyses of the reaction mixture. Silica gel (Merck, Silica gel 60), treated with 0.1 N HNO_3 in the above manner, shows no production of acetal even after 24 h reaction. In addition, the filtrate of 7 h stirred mixture of the MCM-41 and methanol showed no catalytic activity at all. This rules out the possibility that some components eluted from the MCM-41 in methanol might be active for the reaction. It follows that the acetalization is indeed catalyzed by the MCM-41.

Table 1

Acetalization of aldehydes and ketones with MeOH on MCM-41.

Entry	Substrate	Temperature	Time (h)	Products	Yield (%)	Unchanged (%)
1		ambient	1		89	11
2		ambient	1		18	82
3		reflux	0.5		18	82
4		ambient	24		97	3
5		ambient	4		93	6
6		ambient	24		34	63
7		reflux	5		quant.	0
8		ambient	48		25	75
9		reflux	5		quant.	0

Five kinds of carbonyl compounds in addition to cyclohexanone were next investigated. The respective reaction rates and conversion levels were greatly dependent on the substrates and the reaction temperature. The reaction of 2-hexanone reached an equilibrium within 1 h at ambient temperature, but the conversion was low (entry 2). Raising the reaction temperature did not improve the yield (entry 3). On the other hand, aldehydes could be converted in excellent yields. The aromatic aldehydes gave the corresponding acetals at ambient temperature. It should be noted that 2-furancarboxaldehyde yielded the dimethylacetal in 93% yield (entry 5), because the substrate is acid-sensitive and many side reactions often proceed in the presence of acid. The reactions of linear aldehydes with methanol at ambient temperature were not so fast (entries 6 and 8). At refluxing temperature, pentanal and octanal gave their acetals in quantitative yields (entries 7 and 9).

The yields in entries 1, 4, 6, and 8 are comparable to those on Ce-mont,[7] while the excellent yields in entries 5, 7, and 9 have never been reported. It follows that the siliceous MCM-41 is an excellent solid catalyst for the acetalization of carbonyl compounds including linear aldehydes. No other reagent than methanol and no strict anhydrous condition, *e.g.*, use of dehydrated methanol or drying the catalyst *in vacuo*, was required to achieve the good yields. The easiness of removing the catalyst from the reaction mixture would also be convenient for chemists wanting to protect carbonyl groups by using acetalization.

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