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Preparation of an MCM-41/Nafion® composite material; a selective catalyst for α-methylstyrene dimerization

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A MCM-41/Nafion® composite prepared from tetraethoxysilane and Nafion gel solution with cetyltrimethylammonium surfactant, is a highly selective catalyst for α-methylstyrene dimerization to form the corresponding acyclic dimer.

The synthesis of mesoporous materials is one of the most important subjects in modern chemistry. MCM-41 obtained by the utilization of surfactant micelles[1] is actively studied for applications to catalysts. Recently organically modified MCM-41 materials using alkyl-substituted silane compounds have been prepared for use as catalysts and other applications.[2] On the other hand, DuPont has recently reported amorphous silica/Nafion composites which were effective solid acid catalysts.[3] It is thought that the combination of the new technology for fabricating mesoporous materials and Nafion resin creates a novel class of functional solid acid materials.[4] Here, we report the first preparation (to our knowledge) of a MCM-41/Nafion composite material and its applications as a solid acid catalyst.

The MCM-41/Nafion composite was obtained by the following procedure; 0.1 g of Nafion gel obtained from a 5% Nafion solution (Aldrich) in ethanol was dissolved in 1.5 mL of ethanol. This solution was added slowly to a mixture of tetramethylammonium hydroxide (8 mmol) and cetyltrimethylammonium bromide (4.5 mmol) in distilled water (15 mL) with vigorous stirring. Then, tetraethoxysilane (30 mmol) was added dropwise with stirring to the resulting mixture. Finally, the mixture was transferred to a Teflon beaker and crystallized in a stainless steel autoclave at 130 °C under autogeneous pressure for 24 h. The white solid obtained was washed twice with 200 mL of distilled water and dried at 60 °C. The removal of the template and acidification of the Nafion resin were performed by refluxing in concentrated sulfuric acid (3 mL) in ethanol (300 mL) for 18 h. After two further refluxes in ethanol (300 mL), the recovered solid was dried at 150 °C for 20 h.

Fig. 1 shows the XRD pattern of the MCM-41/Nafion composite obtained.† A clear peak at $2\theta = 2.15°$ was observed which was assigned to the (100) reflection of MCM-41 type materials.[1] The (110) and (200) reflections from MCM-41 appeared as broad peaks at $2\theta \approx 4.1°$. The BET surface area and pore volume were estimated at 619 $m^2\ g^{-1}$ or 0.64 $cm^3\ g^{-1}$, respectively. The diameter of the main pore type (*ca.* 90%) was 2.8 nm in accord with an organically modified MCM-41.[2] The minor pore type had a diameter of 3.8 nm and corresponded to MCM-41.[1] From the IR spectrum, it was confirmed that the template was removed because of the absence of alkyl adsorptions of the template around 2900 cm^{-1}. All these results indicate that the preparation of the MCM-41/Nafion composite was successful.

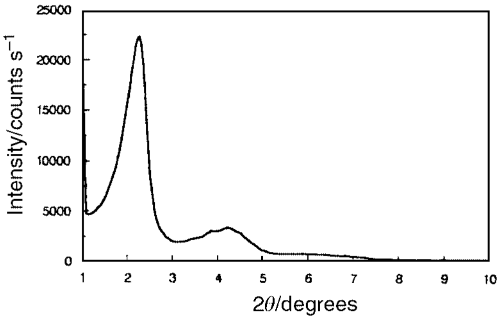
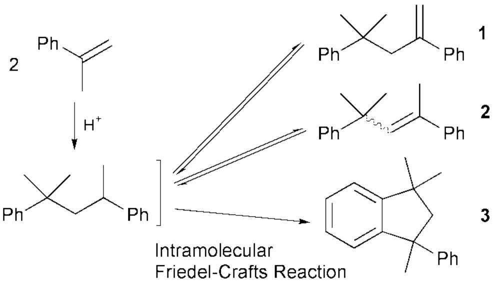


Fig. 1 X-Ray diffraction pattern of the MCM-41/Nafion composite.

This novel composite material was applied to the dimerization of α-methylstyrene (AMS) to produce the corresponding acyclic dimer, 4-methyl-2,4-diphenylpent-1-ene **1**, which is a chain transfer agent amongst other uses.[5] Although this reaction using solid sulfuric acid has been actively studied,[5] the significant side reaction to form the cyclic dimer, 1,1,3-trimethyl-3-phenylindan **3**, often results in low production of **1** (Scheme 1). The yields of the desired dimer **1** [Fig. 2(a)] and of the undesired dimer **3** [Fig. 2(b)] as a function of time are shown using the MCM-41/Nafion composite, as well as for Nafion NR-50, Nafion SAC-13 (silica/Nafion composite),[3] Amberlyst® 15 (all obtained from Aldrich) and Al-MCM-41.[6]† Although SAC-13 and Amberlyst 15 had high activity, the yields of **1** drastically decreased with time and substantial increases of the bicyclic dimer **3** were observed. For NR-50, the reaction rate was quite slow as reported[3] and **3** was formed in considerable yield even at a low conversion of AMS. On the other hand, when the MCM-41/Nafion composite was used, the yield of **1** was about 70% and scarcely decreased with reaction time. Furthermore, the formation of **3** was low even after 1000 min. This high selectivity shown by the MCM-41/Nafion composite is not simply derived from the mesoporous channel structure since **3** was obtained in high yield using Al-MCM-41 which was reported as an acid catalyst.[6] Furthermore, other types of MCM-41/Nafion composite obtained from impregnating Nafion solution to MCM-41[7] also afforded **3** in 30% yield with a lower yield of **1** (25%) after 300 min. As expected, MCM-41 itself (silica material without Nafion resin or other metals) showed no activity for this dimerization under our conditions (no conversion of AMS even after 1500 min). Thus, the MCM-41/Nafion composite prepared in this work was an excellent catalyst to produce **1** *via* the dimerization of AMS.



Scheme 1

The low yield of **3** for our MCM-41/Nafion composite suggests poor catalytic activity for Friedel–Crafts reactions.[8] The conversion of **1** to **3** at 60 °C scarcely proceeded with the MCM-41/Nafion composite (3% after 24 h), whereas SAC-13 considerably catalyzed this reaction (17% after 6 h and 56%

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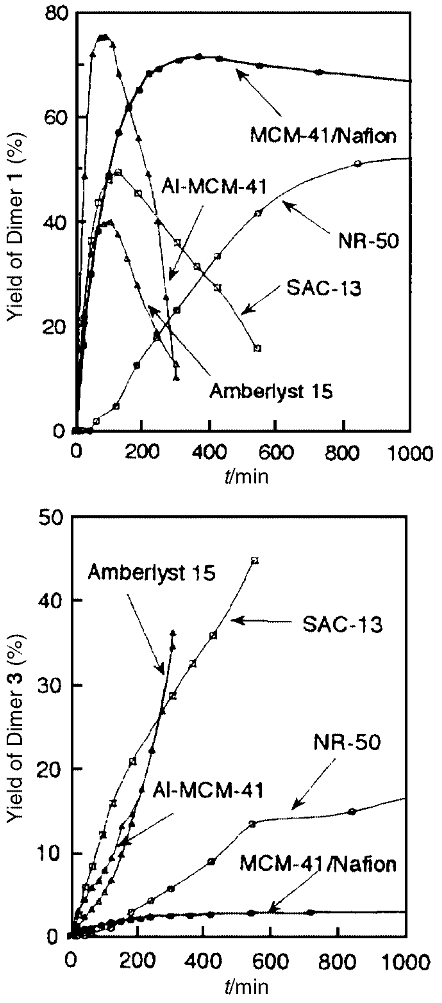
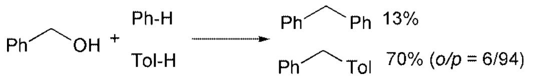


Fig. 2 Yields of **1** (a) and **3** (b) as a function of time using various catalysts.

after 24 h). The clear difference of the catalytic activity between the MCM-41/Nafion composite and SAC-13 in another Friedel–Crafts type reaction was also observed.[9] While SAC-13 catalyzed the reaction of styrene with toluene to form 1-phenyl-1-tolylethane in 27% yield with complete conversion of styrene at 70 °C for 6 h, MCM-41/Nafion composite gave only a trace of the product even after 24 h (styrene conversion: 37%). Therefore, it is thought that the low activity of the MCM-41/Nafion composite to Friedel–Crafts reaction at 60 °C results in the high selectivity towards dimer **1** from AMS. However, it is noteworthy that AMS afforded **3** in 91% yield using the MCM-41/Nafion composite at 100 °C after 3 h, and that the reaction of benzyl alcohol with toluene at 100 °C for 3 h afforded 87% of phenyltolylmethane, *cf.* trace amounts at 60 °C even after 24 h. Moreover, the competitive reaction of benzene and toluene with benzyl alcohol [eqn. (1)] at 90 °C showed a



(1)

higher selectivity towards toluene (toluene/benzene = 5.4) than NR-50 (toluene/benzene = 3.6).[10] These results indicate that the catalytic properties of sulfuric acid in the MCM-41/Nafion composite are crucially influenced by the reaction temperature and the reactivity of the substrate. It is expected that some novel selective reactions can be carried out using this characteristic catalytic activity, and further studies are under investigation.

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Notes and references

† To a solution of AMS (5 mmol) in toluene (5 mL) a solid catalyst (50 mg) was added under argon atmosphere and the resulting mixture stirred at 60 °C. Remaining AMS and all products were determined by capillary GC.

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