

Selective Hydrogenation of 2-Methylbenzaldehyde Using Palladium Particles Generated in situ in Surfactant Exchanged Fluorotetrasilic Mica

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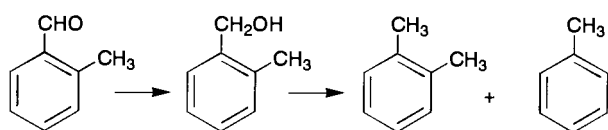
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(Received May 31, 2001; CL-010511)

Palladium intercalated surfactant-exchanged fluorotetrasilic mica (Pd-HDP-TSM) was synthesized by ion exchange of surfactant with TSM, intercalation and in situ reduction of palladium. This catalyst showed the highest selectivity to 2-methylbenzyl alcohol for the title reaction when compared with supported catalysts. Interestingly, in contrast with the supported catalysts, Pd-HDP-TSM catalysts do not favor the consecutive reaction yielding the hydrogenolysis products such as xylene and toluene.

The interlayer regions have been recently the subject of study in the area of catalysis as they are the active reaction centers to selectively catalyze various reactions. Hence number of attempts such as pillaring of metal oxide precursors, immobilization of either the metal complex or metal ion and in situ generation of nano particles with or without steric stabilizers have been made to control, expand the interlammellar space and intercalate the active component.¹⁻⁶

Selective hydrogenation reactions have recently received growing attention since it is an important step in the preparation of fine chemicals, advanced polymers, dyes, drugs, flavors, herbicides and pesticides.⁷⁻¹² The selective hydrogenation of aromatic aldehydes to aromatic alcohols is difficult since concurrent ring hydrogenation and/or hydrogenolysis of C-C bond also occur. Hence the hydrogenation of 2-methylbenzaldehyde is generally followed by consecutive hydrogenolysis of C-C bond yielding toluene and xylene (Scheme 1).



Scheme 1.

Recently, we have found that palladium intercalated surfactant-modified fluorotetrasilic mica (Pd-HDP-TSM) was highly selective (> 95%) towards 2-methylbenzyl alcohol without the formation of the hydrogenolysis products such as xylene and toluene. In this communication, we report the synthesis and catalytic activity of Pd-HDP-TSM.

Fluorotetrasilic mica (Na-TSM) with chemical formula $\text{Na}[\text{Mg}_{2.5}\text{Si}_4\text{O}_{10}\text{F}_2]$ is a swelling type mica with a cation exchange capacity of 2.54 mEq/g. Na-TSM possesses some interesting properties such as (i) the silicate sheets are non-acidic and (ii) it swells in water enabling diffusion of bigger organic surfactants for easy exchange with Na ions. It has been well proved that metal ion-exchanged TSM catalysts are very good

catalysts for a variety of reactions.¹³⁻¹⁸ The easily exchangeable interlayer Na^+ ions were exchanged in an aqueous solution containing slightly larger amounts of 1-hexadecylpyridinium bromide (Kanto Chemical) with vigorous stirring for 14 h. After the completion of exchange, the precipitate obtained (HDP-TSM) was washed well with distilled water and dried at 423 K. HDP-TSM (0.5 g) was taken in 20 mL of toluene and refluxed for 1 h at 338 K in argon atmosphere (flow rate = 65 mL/min). To prepare different intercalated levels of Pd, different volumes of palladium acetate in toluene were added and the mixture was refluxed for another 1 h. Then 20 mL of ethanol:toluene (5:95) was added and refluxed for 1 h.⁴ The suspension obtained was washed several times with toluene, filtered and dried at 423 K. To compare the catalytic activity of Pd-HDP-TSM with supported catalysts, Pd/SiO₂, Pd/Al₂O₃, Pd/TiO₂, Pd/TSM were also prepared either by ion exchange or by impregnation. Supported Pd/Al₂O₃ and Pd/TiO₂ catalysts were prepared by impregnation of Al₂O₃ or TiO₂ with Pd(CH₃COO)₂ in acetone solution. The acetone was allowed to evaporate with continuous stirring at 333 K. The resulting solid was dried overnight at 383 K, and calcined at 573 K in air for 3 h, whereas Pd/SiO₂ was prepared by an ion-exchange method with an ammoniacal solution of [Pd(NH₃)₄]Cl₂. The solids obtained after 24 h of thorough stirring were filtered and dried in an air oven overnight at 383 K. The samples were then characterized by XRD (Rigaku RAD-1B) and XRF (Shimadzu EDX-800) to determine the basal spacing (d_{001} was 1.23 and 4.16 nm respectively for Na-TSM and HDP-TSM) and palladium content, respectively.

The catalysts (0.035 g) were tested for their catalytic activity towards the hydrogenation of 2-methylbenzaldehyde using a pulse reactor (Pyrex with an internal diameter of 4 mm) connected to a gas chromatograph (Hitachi GC-163) fitted with a flame ionization detector and PEG 6000 column. The supported catalysts were pretreated with hydrogen at 573 K for 2 h whereas the intercalated catalysts were pretreated with hydrogen at 423 K for 2 h. A pulse size of 1 μL was injected in hydrogen stream. The flow rate of hydrogen was 60 mL/min. The products were identified by using GC-MS (Hitachi M-80B). The main products were found to be 2-methylbenzyl alcohol, xylene and toluene. Although all the palladium catalysts tested in the temperature range between 373 and 573 K do not show any ring hydrogenation, the supported catalysts behave differently with that of intercalated catalysts (Pd-HDP-TSM). Conversion was found to increase with temperature for all the catalysts but the selectivity to alcohol decreased beyond 423 K yielding the hydrogenolysis products. Pd/SiO₂ and Pd/TSM were found to be selective towards alcohol (> 75%) in the temperature range of 373 to 423 K, whereas the intercalated Pd-HDP-TSM maintained more than 75% selectivity to alcohol even up to 498 K. The intercalated catalysts exclusively cat-

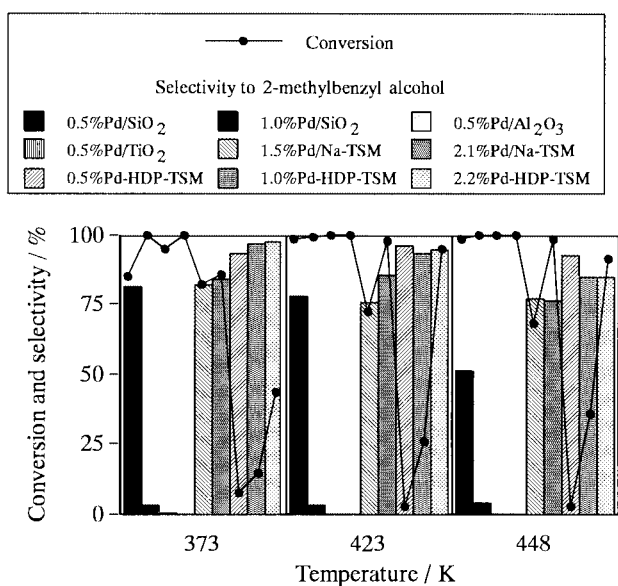


Figure 1. Effect of reaction temperature on conversion and alcohol selectivity over various Pd catalysts.

alyzed alcohol in the temperature range of 373 to 423 K with very high selectivity (> 95% selectivity) which was the unique phenomenon observed with Pd-HDP-TSM (Figure 1). Interestingly, increasing the palladium loading in the silica support decreased the selectivity drastically but significant improvement in the selectivity was observed both in Pd/Na-TSM and Pd-HDP-TSM. The first hydrogenolysis product namely xylene increased up to 473 K in the case of Pd/SiO₂ and 448 K in the case of Pd-HDP-TSM catalysts and decreased thereafter as the second hydrogenolysis of the methyl group on the aromatic ring took place yielding toluene. This suggests that the scission of C–C bond of 2-methylbenzylalcohol is more favored at high temperature than C–O bond. With increase in temperature, decrease in both conversion and selectivity to the alcohol were observed with Pd-HDP-TSM, whereas, decrease in only selectivity to the

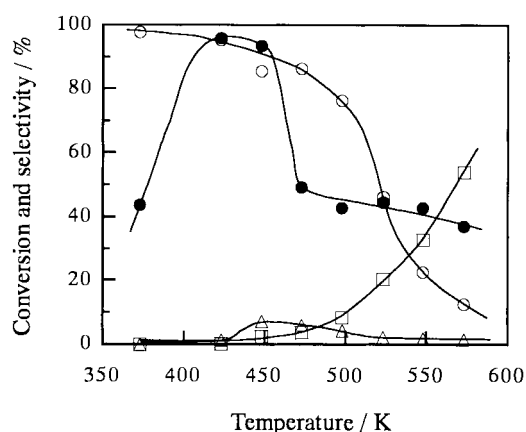
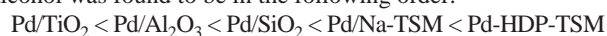


Figure 2. Effect of temperature on conversion of 2-methylbenzaldehyde over 2.2% Pd-HDP-TSM. Conversion (●), selectivity to 2-methylbenzyl alcohol (○), xylene (△) and toluene (□).

alcohol was seen with Pd/SiO₂, Pd/TiO₂, Pd/Al₂O₃ catalysts (Figure 2). The decrease in conversion at high temperature (> 448 K) observed in Pd-HDP-TSM is due to both the decomposition of HDP resulting in blocking of active sites and the thermodynamic limitation of hydrogenation at high temperatures. TGA studies of Pd-HDP-TSM also confirm the decomposition of HDP beyond 473 K. Alumina and titania supported catalysts do not produce the alcohol in the entire temperature range studied and mainly produce xylene at low reaction temperature and toluene at high reaction temperature suggesting concurrent hydrogenolysis. High conversion with zero selectivity to the alcohol was observed with alumina and titania supported catalysts. Appreciable conversion and significant selectivity to the alcohol were observed with Pd/SiO₂ and Pd/TSM catalysts but very good conversion and the highest selectivity was seen only in the case of Pd-HDP-TSM catalysts. The selectivity to the alcohol was found to be in the following order:



Further studies on the effect of TSM as support and the effect of HDP on the increased selectivity are underway.

T. Sivakumar wishes to thank UNESCO for the award of a research fellowship.

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