

Selective hydrogenation of maleic anhydride to γ -butyrolactone over Pd/Al₂O₃ catalyst using supercritical CO₂ as solvent

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A selective hydrogenation of maleic anhydride to either γ -butyrolactone or succinic anhydride over simple Pd/Al₂O₃ catalyst under supercritical CO₂ medium is described for the first time which has considerable promise for both lab-scale as well as industrial selective hydrogenations of low vapor pressure compounds without employing environmentally harmful organic solvents.

Hydrogenation of maleic anhydride (MA) is an important industrial reaction as all its products *viz.*, succinic anhydride (SAH), succinic acid (SA), γ -butyrolactone (GBL) and tetrahydrofuran (THF), are commodity chemicals of considerable industrial importance.¹ GBL is currently one of the most valuable alternatives to the environmentally harmful chlorinated solvents, which have been widely used in the polymer and paint industries. Hydrogenation of MA is the most direct way to produce GBL and it does not involve the use of hazardous materials. GBL is currently being manufactured by the vapor phase hydrogenation of MA using reduced copper chromite catalysts containing some physical and chemical promoters.² Cr-containing catalysts are getting increasingly difficult to use owing to their toxicity. Hydrogenation of MA over different noble metal and Cu based catalysts both in vapor and liquid phases have been reported by many research groups.³ Recent patent literature suggests that Al-containing catalysts may represent an interesting and promising alternative to the chromite catalysts.^{4a-c} A recent study reports a two-stage liquid phase hydrogenation of MA to GBL over supported Pd catalyst followed by a homogeneous ruthenium catalyst system consisting of Ru(acac)₃, P(octyl)₃ and toluene *p*-sulfonic acid.^{5a} However, the activity is low besides the fact that homogeneous catalytic systems suffer from the problem of catalyst separation from the reaction mixture. Another drawback with the reported efficient catalytic transformation of MA to GBL is the use of expensive solvents like ethylene glycol dimethyl ether and polyethylene glycol dimethyl ether.^{5b}

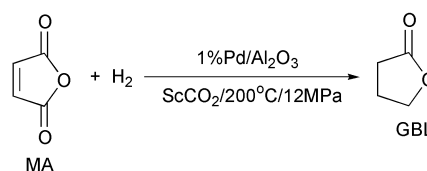
In the past decade, supercritical carbon dioxide (Sc-CO₂) has been increasingly used as an environmentally friendly reaction medium. The ability of the Sc-CO₂ to dissolve many of reactive gases like H₂, O₂ and also a variety of organic compounds facilitates oxidation and hydrogenation reactions in this medium, thereby eliminating interphase mass transfer limitations and enhancing the reaction rate.⁶ The fact that slight changes in temperature and pressure near the critical point can change the activity and selectivity significantly provides remarkable potential for its use as a reaction medium. Several recent publications have demonstrated the potential of Sc-CO₂ as an alternative reaction medium for a variety of synthetic transformations.^{6,7} However, relatively few studies have been reported on hydrogenation reactions in supercritical fluid media.⁸⁻¹³ MA has been reported to have a fairly good solubility in liquid CO₂ (7.5%).¹⁴ It is expected to show a much higher solubility at higher temperatures and pressures. Therefore we decided to investigate the hydrogenation of MA in Sc-CO₂ medium. This communication presents the first example of organic solvent-free hydrogenation of a low vapor pressure compound under supercritical conditions over a simple alumina supported palladium catalyst. Supported Pd catalysts are highly efficient

hydrogenation catalysts, but are not known to be effective as partial/selective hydrogenation catalysts like Pt or Rh.¹⁵ Nevertheless, selectivities different from those obtained under normal liquid phase hydrogenations in organic solvents are reported here under supercritical conditions.

A 1% Pd/Al₂O₃ (w/w) catalyst was prepared by wet impregnation of alumina pellets (1400 μ , Aldrich) with a solution (0.02 M) of palladium chloride (Aldrich). After the impregnation step, the catalyst was dried at 110 °C over night and then calcined in air at 450 °C for 5 h followed by reduction in flowing hydrogen at 450 °C for 5 h.

Isothermal hydrogenation of MA was conducted in a 500 mL stainless steel batch reactor using 2.45 g MA (25 mmol) and 0.5 g catalyst loaded into a spinning dynamic basket. The reactor was then heated to the desired temperature while being filled with known amounts of hydrogen and carbon dioxide based on the set pressure. After the reaction, the reactor was cooled to room temperature and vented slowly. The products were collected and analyzed by a Hewlett-Packard 6890 gas chromatograph using a HP-5 5% phenyl methyl siloxane capillary column (30 m \times 320 μ m \times 0.25 μ m) and a quadruple mass filter equipped HP 5973 mass selective detector. Quantification of the products was obtained using a multi-point calibration curve for each product.

The results of the hydrogenation experiments in Sc-CO₂ medium are shown in Table 1. MA conversion and product yields are also compared with the conventional liquid phase reaction under similar conditions, using commonly employed solvents such as polyethylene glycol (PEG), ethylene glycol dimethyl ether (EGDME), acetone as well as with the reaction under N₂ pressure. A 100% MA conversion with approximately 80% yield to GBL was obtained at 200 °C and at a pressure of 2.1 MPa H₂ and 12 MPa CO₂ (Scheme 1). The high conversions (~100%) obtained irrespective of the variations in pressure and temperature or the type the reaction medium could be the result of Pd being a good hydrogenation catalyst and the high catalyst-to-substrate ratio. Product selectivity, however, varied significantly with changes in temperature, pressure as well as the reaction medium (Table 1). It was seen that GBL selectivity increased with increase in CO₂ pressure. Temperature was critical in obtaining the desired GBL yield or selectivity. GBL yield/selectivity increased with increase in reaction temperature. A high GBL yield could not be obtained at 150 °C even at pressures higher than 12 MPa. It is obvious from the results that the desired product selectivity can be obtained by controlling the temperature and pressure. On the other hand, hydrogenation in the presence of organic solvents produced the double bond hydrogenated product, SAH, selectively. In the case of liquid phase reaction, there is an additional requirement



Scheme 1

Table 1 Maleic anhydride hydrogenation over 1% Pd/Al₂O₃ under supercritical CO₂ medium^a

Temperature/°C	CO ₂ pressure/MPa	Organic solvent	Duration/h	Conversion (%)	Yield (%) ^b	
					GBL	SAH + SA
200	12	No solvent	2	100	~80 ^c	ND
200	8.3	No solvent	2	100	56	44
200	8.3	No solvent	2	100	42	58 ^d
200	8.3	No solvent	1	100	35	65
200	3.5	No solvent	2	100	48	52
200	2.1	No solvent	2	100	30	70
200	12 (N ₂)	No solvent	2	100	30	60 ^e
180	12	No solvent	2	100	28	63
150	12	No solvent	2	100	5	95
200	--	PEG (10 mL) ^f	2	100	2	78
200	--	EGDME (10 mL) ^g	2	100	7	80
200	--	Acetone (10 mL)	2	100	2	96

^a Reaction conditions: MA = 25 mmol, catalyst = 0.5 g, H₂ = 2.1 MPa, stirrer = 350 rpm, duration = 2 h, ND = below the method detection limit of GC-MS. ^b GC yield. ^c Exact values could not be ascertained above 80% as the GC-MS signals for SAH and SA at these concentrations were close to their method detection limits. ^d 0.25 g catalyst. ^e Under N₂ pressure. ^f PEG = polyethylene glycol. ^g EDGME = ethylene glycol dimethyl ether.

of removing the high boiling solvents (PEG, EGDME) from the reaction mixture. The gas phase reaction under pressurized nitrogen, at 200 °C, yielded better GBL selectivity than the organic liquid phase reactions, but much lower than the selectivity obtained under Sc-CO₂ medium at the same temperature. However, carrying out the hydrogenation reaction under N₂ medium poses an explosion hazard due to the possibility of sudden temperature shoot-out and therefore is not very safe. This, however, is not the case with Sc-CO₂ medium as it possesses high heat capacity and hence can act as a good heat sink. The unusual GBL selectivity obtained over Pd/Al₂O₃ may be a consequence of the enhanced reactant-product solubility as well as different reaction energetics in Sc-CO₂, which require further studies in detail.

Phase behavior experiments of MA in Sc-CO₂ were conducted at 150 °C using a 75 mL stirred high pressure view cell containing 0.5 g MA, in the presence of a constant H₂ pressure of 2.1 MPa and varying CO₂ pressure in the range 5.5 to 14 MPa. MA showed no miscibility at 5.5 MPa. However, the miscibility increased with increase in CO₂ pressure and showed complete miscibility at 11 MPa CO₂ pressure (a homogeneous and uniform single phase was visible). The solubility experiments could not be conducted at 200 °C due to the temperature limitation of the pressure view cell. Nevertheless, the above studies tend us to believe that MA should be completely miscible with Sc-CO₂ at the experimental conditions employed in the hydrogenation studies. Phase behavior calculation of a mixture of CO₂, H₂, and MA, conducted using the Peng-Robinson equation of state subroutine built in to ASPEN plus software, showed that the reactor composition is a single phase at 200 °C. The loss of any product during venting of the reaction vessel was tested by passing the cooled reactor vent through a chilled methanol trap and later analyzing the methanol solution. However, no reactant or products were detected by GC, which suggests no appreciable volatile compound loss during the venting of the autoclave. Also, no significant leaching of Pd by Sc-CO₂ was evident as a regenerated catalyst (calcination and reduction of the spent catalyst) showed almost similar activity and GBL selectivity. Some studies have reported the potential deactivation of hydrogenation catalysts due to the formation of carbon monoxide or metal formate.^{8,10} In this study no significant deactivation of the Pd sites was observed for the two-cycle two hour run tests. Similarly, other researchers observed little deactivation after an extended period of tests.¹³

In conclusion, this study demonstrates that selective hydrogenation of a low vapor pressure compound like MA can be successfully carried out in Sc-CO₂ medium using a simple supported metal catalyst thereby accomplishing the goal of green chemistry cost effectively. It further demonstrates the potential of Sc-CO₂ medium for tuning the reaction to the

desired end by a simple maneuver of the reaction temperature and pressure. A more systematic investigation is underway to determine the phase behavior of the mixture and the reaction kinetics to understand the physicochemical processes, which will help in addressing issues like reactor design, process development and product separation.

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