Hydrous Zirconia as a Selective Catalyst for the Meerwein–Ponndorf–Verley Reduction of Cinnamaldehyde

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Hydrous zirconia was found to be active in the Meerwein–Ponndorf–Verley (MPV) reduction of cinnamaldehyde with 2-propanol. An initial selectivity to cinnamyl alcohol of higher than 97% was measured. At longer reaction times, etherification between cinnamyl alcohol and 2-propanol decreased the selectivity. The activity decreased sharply when the hydrous zirconia was calcined to higher temperatures. Surface hydroxyl groups are postulated to be important for the activity. They are required for ligand exchange with 2-propanol. Zirconium 1-propoxide grafted on silica, siliceous MCM-41, and Al-MCM-41 were also active in the MPV reaction. In contrast, zeolite beta, although active in the conversion of cinnamaldehyde, showed poor selectivity toward the desired product, cinnamyl alcohol. Instead, the main product formed was cinnamyl 2-propyl ether.   © 2002 Elsevier Science (USA)

Key Words: hydrous zirconia; grafted zirconium 1-propoxide; MPV reduction; cinnamaldehyde; hydroxyl concentration; zeolite beta; etherification.

1. INTRODUCTION

α,β-unsaturated alcohols are important starting materials for the production of fine chemicals and versatile intermediates in organic synthesis. The selective hydrogenation of α,β-unsaturated aldehydes over heterogeneous catalysts was extensively studied. Supported metals such as osmium, iridium, ruthenium, rhodium, platinum, nickel, and cobalt catalyze the reaction with gaseous hydrogen, usually under pressure (1–9). The selectivity to the unsaturated alcohols depends on the competitive C=C and C=O adsorption of the α,β-unsaturated aldehydes on the metal surfaces (10).

As an alternative to hydrogenation with nascent hydrogen, the Meerwein–Ponndorf–Verley (MPV) reaction provides a highly selective reduction of the C=O functional group in the presence of other reducible sites (11, 12). A secondary alcohol such as 2-propanol acts as the hydrogen donor. Originally, the reaction was carried out in the homogenous phase with metal alkoxides such as aluminium 2-propoxide as the catalysts. The reaction mechanism for the homogenous MPV reaction involves a cyclic six-membered transition state in which both the reducing alcohol and the carbonyl compound are coordinated to the same metal center. The reaction proceeds by a hydride transfer from the alcohol, bound to the metal center as an alkoxide, to the carbonyl compound (Scheme 1).

Heterogeneous catalysts have the advantage of ease of separation from the reaction mixture. Various metal oxides with either Lewis acidic and/or basic properties have been found to be active in the MPV reaction. Ivanov *et al.* (13) investigated the MPV reaction over magnesium oxide, zirconia, silica, alumina, chloride- and sodium-modified alumina and found that basic oxides were better than acidic ones in terms of stability and selectivity. Acidic catalysts frequently lead to secondary products that form by alcohol dehydration or condensation of the aldehyde. Mg–Al hydrotalcites were also reported to be active in the MPV reduction where the coexistence of weak acidic and strong Lewis basic sites is important (14–18). The reducing alcohol adsorbs with the oxygen and hydrogen of the hydroxyl group to the Lewis basic metal ion and the *oxo*-ion site, respectively. The carbonyl group coordinates by hydrogen bonding to this surface hydroxyl group rather than to the metal. The reaction proceeds again via a cyclic six-membered transition state (Scheme 2). The MPV reaction can also be catalyzed by zeolites (19, 20). Zeolite X which has been ion-exchanged with bulky Cs^+ ions catalyzes the reduction of citronellal to citronellol in the gas phase while LiX, NaX, and CaX, containing smaller cations, promote the cyclization of citronellal to isopulegol (19). Recently, Creyghton *et al.* (20) reported that zeolite beta catalyzed the reduction of 4-*tert*-butylcyclohexanone to 4-*tert*-butylcyclohexanol in the liquid phase with a stereoselectivity of >95% to the *cis*-alcohol. The activity of the catalysts could be increased by pretreatment at higher temperature, showing the role of Lewis acidic aluminum sites. The authors propose that both the alcohol, as an alkoxide, and the ketone/aldehyde coordinate to the same metal site, as in homogenous catalysis.

Cinnamaldehyde (3-phenyl-2-propenal, C_9H_8O) is an α,β-unsaturated aldehyde which is used in the fragrance

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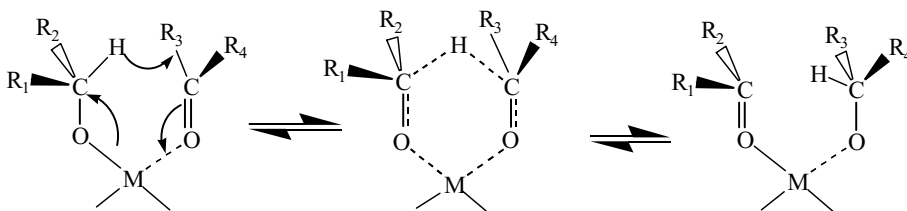
SCHEME 1.   Transition state for MPV reduction over metal alkoxide.

industry to give spicy and oriental notes (21). It is also an important intermediate in the synthesis of cinnamyl alcohol and dihydrocinnamyl alcohol, both of which are also used in the perfume industry. Cinnamyl alcohol is used for its flowery notes and is itself a starting material for several cinnamyl esters, which are important fragrance compounds. In addition, cinnamyl alcohol finds applications in the formulation of animal repellant compositions and insect attractants, production of photosensitive polymers, and multicolor ink formulation.

Industrially, cinnamyl alcohol is prepared by selective catalytic hydrogenation of the carbonyl group using an osmium carbonyl catalyst, or by MPV reduction of cinnamaldehyde using aluminum 2-propoxide (22). Besides aluminum 2-propoxide, several other homogeneous catalysts, e.g., zirconocene and hafnocene complexes such as bis(η^5-cyclopentadienyl)zirconium or hafnium dihydrides (23) and a macrocyclic nickel complex (24) have also been described for the selective reduction with hydrogen. All these catalysts suffer the problem of separation of the products from the catalyst.

In this paper, we report on the use of hydrous zirconia as heterogeneous catalyst for the reduction of cinnamaldehyde to cinnamyl alcohol. Hydrous zirconia is a polymeric material with the general formula $[ZrO_x(OH)_{4-2x} \cdot yH_2O]_n$ where the amount of hydroxyl and water groups depends on the conditions of preparation (25). It has been reported as a very active catalyst for MPV reduction and the reverse Oppenauer oxidation of secondary alcohols with ketones (26–29). The activity reached a maximum over catalysts that were calcined at 300°C but decreased with higher calcination temperature, which could be correlated with a drop in the surface area. It was postulated that most of the pores in hydrous zirconia calcined below 300°C were too small to allow the reactants to access the catalytic sites (30). The patent disclosure (31) reports that active hydrous zirconia
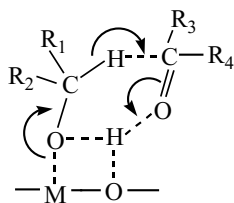
is formed by heating at 300°C for 1 h under atmospheric pressure, which leads to a weight reduction of about 17%. The resulting compound is X-ray amorphous and has a low acidity. Silica-supported hydrous zirconia is claimed to be superior to the unsupported material in the MPV reduction of various carbonyl compounds to the corresponding alcohols (32). Low loadings of zirconia ranging from 0.5 to 11.8 wt% gave high conversions of >97% and a selectivity to the allyl alcohol of more than 87%. However, if alumina instead of silica was used as the support, the yield of the allyl alcohol was lower. A recent patent assigned to Lonza AG (33) also claims catalysts based on partially dehydrated hydrous zirconia. Zirconia doped with 0.01 to 20 atom% copper and/or nickel is active in the reduction of quinuclidin-3-one to 3-hydroxyquinuclidine. Thus, the high activity of hydrous zirconia as compared to the dehydrated oxide for the MPV reaction has been observed by several groups. A satisfactory explanation for the phenomenon has, however, not been advanced.

In this study, the effect of the calcination temperature on the activity and the relation of the textural, structural, and chemical properties of zirconia on the MPV reduction of cinnmaldehyde are investigated. In addition, zirconium 1-propoxide was supported on silica gel and siliceous and aluminated MCM-41, and the activity of these supported catalysts was compared with the unsupported hydrous zirconia.

2. EXPERIMENTAL

Catalyst Preparation and Characterization

Hydrous zirconia was prepared by the precipitation of a 10 wt% zirconium chloride solution with excess 5 M ammonium hydroxide (34). One portion of the precipitate was removed immediately and washed free of chloride. The remaining precipitate was left in the mother liquor and subjected to open reflux at 100°C for 2 days before filtering and washing. Samples were dried overnight at 100°C before they were calcined for 12 h at temperatures ranging from 200 to 500°C. These samples were labeled ZrO_2-D-T, where D stands for the number of days of digestion (0 or 2) and T for the temperature of calcination.

The supports used for grafting of zirconium 1-propoxide were silica gel 60 (Merck), siliceous MCM-41, and

SCHEME 2.   MPV transition state over basic catalyst.

aluminated MCM-41 (Si/Al 10). A narrow-pore MCM-41 was prepared as described in Ref. (35) using a molar composition of the reactant silica, tetraethylammonium hydroxide, decyltrimethylammonium bromide, and water in the ratio 1.00 : 0.21 : 0.28 : 24. After hydrothermal treatment at 150°C for 2 days, the product was recovered by filtration and washed free of bromide. The solid was calcined in a muffle furnace at 550°C for 8 h with a heating rate of 1°C/min. The aluminated MCM-41 was prepared using aluminium propoxide as the aluminium source in the synthesis gel. The grafting of zirconium 1-propoxide (Alfa) onto the supports was carried out following Ref. (36). The support was first dried at 150°C overnight. After cooling down in vacuum, zirconium 1-propoxide in hexane was introduced, and the mixture was refluxed for 12 h. A stoichiometric amount of zirconium 1-propoxide to surface hydroxyl groups was used in the grafting, based on an approximate density of 1.4 OH/nm^2. The product was recovered by filtration and washed with hexane to remove any unreacted precursor. It was transferred to a vacuum desiccator and dried under vacuum for 6 h. This sample is referred to as $Zr(OR)_4$/support.

Zeolite beta (Si/Al 13.0) was prepared according to Ref. (37). The product was calcined at 550°C to remove the template. The zeolite was ion-exchanged with three portions of 1 M NH_4NO_3 at 80°C and subsequently calcined at 500°C to give the H-form. In addition, a commercial zeolite beta with Si/Al 50 (Zeolyst CP 814E) was used for catalytic testing.

The surface area, pore size distribution, and pore volume were determined using a Quantachrome NOVA 2000. Different degassing conditions were used to dry the samples. Hydrous zirconia samples were degassed at 120°C in a flow of nitrogen for 4 h prior to measurements. Supports (silica gel, MCM-41, and Al-MCM) and zeolite beta were dried under nitrogen at 300°C. For the supported catalysts, a number of procedures were used to remove water and any remaining solvent without destroying the grafted zirconium propoxide. These include drying under vacuum at room temperature and heating at 100 and 250°C under nitrogen flow. The crystalline phase of the samples was determined by powder X-ray diffraction using a Siemens D5005 diffractometer (Cu anode) equipped with variable primary and secondary beam slits. The loading of hydrous zirconia on the supported catalysts was measured using inductively coupled plasma–atomic emission spectroscopy (ICP–AES) and X-ray fluorescence (Link 200). Diffuse reflectance spectra of the samples were recorded on a Shimadzu UV-1610 spectrometer with integrating sphere, using $BaSO_4$ as a reference material.

Thermogravimetric analyses on hydrous zirconia were performed on a Dupont SDT 2960 apparatus to determine the concentration of hydroxyl groups. To ensure that the sample was thoroughly dry and free of physisorbed water, it was kept at 100°C for 30 min in a flow of air (80 ml/min) before ramping up to 1000°C at 20°C/min. The weight loss was attributed to the removal of water (34). To determine the presence of 2-propoxide groups on hydrous zirconia, the sample was refluxed in 2-propanol for 3 h, dried under vacuum, and subjected to thermogravimetric analysis. Infrared (IR) spectroscopy was also used to detect the presence of the organic group. A self-supporting wafer of hydrous zirconia was placed in an evacuable Pyrex IR cell with NaCl windows. The sample was first degassed at 100°C for 3 h before cooling down to room temperature and recording the spectrum. A Bio-Rad spectrometer (FTS 3000) was used with a resolution of 2 cm^{-1}. The sample was then removed from the IR cell and treated for 30 min in 2-propanol at 50°C. It was returned to the IR cell and evacuated before further IR measurements.

Catalytic Testing

Cinnamaldehyde (Fluka) was used as received. A reaction mixture of 30 ml (390 mmol) 2-propanol (dried over molecular sieve 4A), 0.1 g nonane (internal standard), and 1.5 mmol cinnamaldehyde was placed in a three-necked round-bottomed flask equipped with a magnetic stirrer and a condenser with a calcium chloride guard tube. To this was added 300 mg of the dried catalyst. The mixture was refluxed with stirring at a temperature of 80°C. Aliquots were taken during the reaction and analyzed by gas chromatography using an HP-Innowax cross-linked PEG capillary column (30 m × 0.25 mm i.d.). The various reaction products were identified by GC/MS using a similar column and by comparison with reference compounds.

The grafted catalysts were tested for leaching of zirconium 1-propoxide. Three hundred milligrams of the grafted catalyst was refluxed with 30 ml 2-propanol for 1 h followed by centrifugation to remove the catalyst. Cinnamaldehyde was added to the clarified supernatant, and the reaction mixture was again heated to reflux. Samples were withdrawn at regular intervals and tested for any catalytic activity.

3. RESULTS

Textural Properties

The surface area of hydrous zirconia decreased with increasing calcination temperature (Fig. 1). Hydrous zirconia calcined for 12 h below 350°C have surface areas higher than 200 m^2/g. Above this temperature, the surface area decreased as the hydrous zirconia transformed to zirconia (34). The digested hydrous zirconia, ZrO_2-2-T, had better thermal stability than the undigested sample. This may be explained by the incorporation of some silica from the glassware during the digestion. The stabilizing effect of silica in silica–zirconia aerogels has been reported previously (38). From X-ray fluorescence and ICP–AES results, the
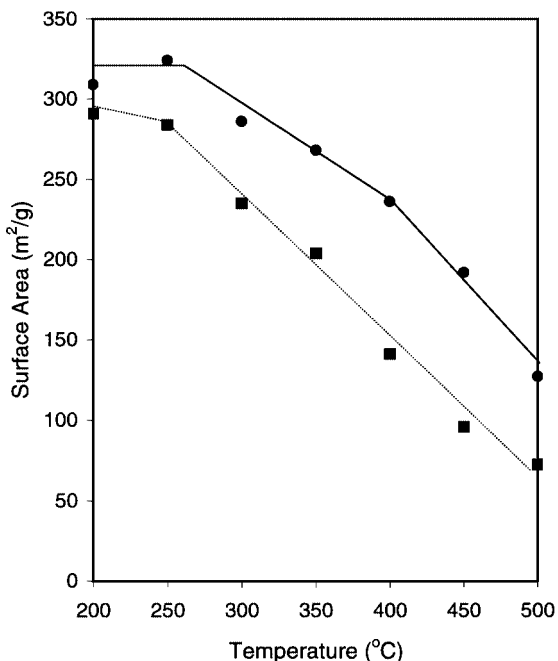
FIG. 1. Surface area of (■) ZrO_2-0 and (●) ZrO_2-2 versus calcination temperature.

amount of silica in ZrO_2-2-T was less than 0.2 wt%. However, even at low concentration, silica is clearly able to stabilize the surface area relative to the silica-free hydrous zirconia. Another factor for the better retention of surface area is the removal of surface defect sites responsible for grain growth during the digestion process (34, 39). Hence, the surface area of zirconia from the digested hydrous zirconia, ZrO_2-2–500, was 127 m^2/g, while that of ZrO_2-0–500 was only 72.3 m^2/g. Hydrous zirconias have a range of pore sizes from microporous to mesoporous (Fig. 2). Calcination at 500°C removed the micropores so that pores in the range of 20 to ~400 Å were present. The mean pore diameter in ZrO_2-0–500 was ~150 Å, while smaller pores with a mean diameter of ~100 Å were present in ZrO_2-2–500.

The sample, ZrO_2-0-T, remained X-ray amorphous after calcination to a temperature of 350°C. After calcination at 400°C, the sample changed from amorphous to a mixture of tetragonal and monoclinic phases. The monoclinic phase increased relative to the tetragonal with heating at higher temperatures. In contrast, the digested sample, ZrO_2-2-T, remained X-ray amorphous even after calcination at 400°C. Crystallinity developed in this sample only after calcination at 450°C when the pure tetragonal phase was formed.
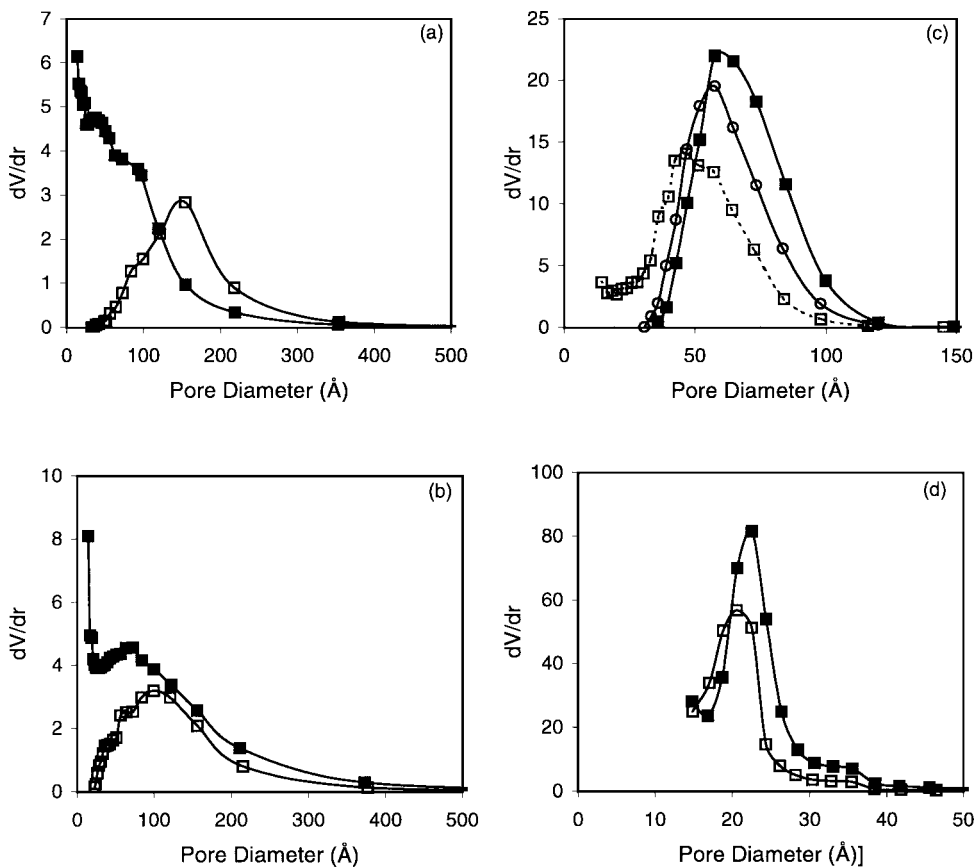

FIG. 2. Pore size distribution of (a) (■) ZrO_2-0–250, (□) ZrO_2-0–500; (b) (■) ZrO_2-2–250, (□) ZrO_2-2–500; (c) (■) SiO_2, (□) $Zr(OR)_4/SiO_2$ dried at 100°C, (○) $Zr(OR)_4/SiO_2$ dried at 250°C; and (d) (■) MCM-41, (□) $Zr(OR)_4/MCM-41$.

TABLE 1

Textural Properties of the Samples

Catalyst	Surface area (m^2/g)	Pore volume (ml/g)	H_2O/ZrO_2 (mol/mol)	Zr/Si (mol/mol)
ZrO_2-0–250	284	0.48	1.04 ± 0.02	
ZrO_2-2–250	324	0.69	0.94 ± 0.02	
ZrO_2-0–500	72.6	0.31		
ZrO_2-2–500	127	0.41		
SiO_2	311	0.74		
$Zr(OR)_4/SiO_2$	220^a	0.34^a		0.032
	243^b	0.38^b		
	270^c	0.60^c		
MCM-41	960	0.57		
$Zr(OR)_4/MCM$-41	661^a	0.37^a		0.054
AlMCM	1075	0.98		
$Zr(OR)_4/Al$-MCM	647^a	0.51^a		0.080
Zeolite beta	550	0.45		

Drying conditions: ^{a}vacuum, 4 h; ^{b}100°C in N_2 flow; ^{c}dried at 250°C in N_2 flow.

The supported catalysts had lower surface area and porosity than the supports themselves (Table 1). The pore size distribution curves indicated that the mean pore diameters were reduced after grafting. Figure 2c shows the distribution for the SiO_2 support and $Zr(OR)_4/SiO_2$ after different drying conditions. Pores larger than 50 Å were considerably reduced in number after vacuum drying $Zr(OR)_4/SiO_2$ at 100°C. Drying at a higher temperature of 250°C led to an increase in the pore volume and surface area (Table 1). In contrast, the porosity of the MCM-supported sample was not affected much by the degassing conditions. The MCM support used in this study was prepared using a C10-template and has a narrow pore size. After grafting with zirconium 1-propoxide, the average pore diameter decreased only slightly from 22.5 to 20.6 Å, but the pore volume decreased from 0.57 to 0.37 ml/g. These results can be explained if the incorporation of zirconium propoxide into pores is restricted to pores bigger than 20 Å. Smaller pores are not accessible for grafting because the kinetic diameter of zirconium 1-propoxide is about 13 Å. Hence, the pore size distribution curve remains almost unchanged and is only shifted to smaller diameter. The measured decrease in pore volume agrees well with that expected for the zirconium loading (Zr/Si = 0.054). From the elemental analysis, the zirconium 1-propoxide coverage on the support amounted to only half a monolayer. In agreement with the low coverage, no X-ray peaks of zirconium compounds could be observed, and the X-ray spectrum showed only the diffraction peaks of the supports.

UV–Visible Diffuse Reflectance Spectroscopy

UV–visible spectroscopy can be used to study the domain size of the grafted zirconium propoxide on the supports. For particles below 10 nm, the band gap energy increases with decreasing domain size (40). The Kubelka–Munk plot of pure hydrous zirconia is shown in Fig. 3. Two absorption edges are observed: one at 250 nm and another at 347 nm. In zirconia, the low-energy step is attributed to $O^{2-} \rightarrow Zr^{4+}$ charge–transfer transitions from O^{2-} in low coordination sites at the surface of small particles, while the step at higher energy is due to the direct band gap of the bulk tetragonal zirconia phase. On the grafted catalysts, the low-energy step was not observed while the edge position of the high-energy absorption shifted to lower wavelength (higher energy) compared to hydrous zirconia. This verified that the zirconium propoxide supported on the silica and MCM-41 was well dispersed and formed very small crystallites.

Thermogravimetric and FTIR Measurements

The thermogravimetric analysis (TGA) curve of hydrous zirconia showed that the sample lost weight from 100 to 600°C with the main loss occurring at around 300 to 500°C (Fig. 4a). The weight loss is associated with the removal of water during the condensation to zirconia. Hence, the degree of hydration of the hydrous zirconia can be calculated. It was found that ZrO_2-0–100 had 1.04 ± 0.02 mol H_2O/mol ZrO_2 while ZrO_2-2–100 contained 0.94 ± 0.02 mol H_2O/mol ZrO_2 (Table 1). The smaller water content in ZrO_2-2–100 has been explained previously (34). We reported that freshly precipitated hydrous zirconia consists of a loose agglomeration of hydroxylated primary particles. During digestion, cross-links form between these particles by condensation of surface hydroxyl groups. We observe a clear trend of decreasing water content and therefore a higher degree of cross-linking of the hydrous zirconia with digestion time.
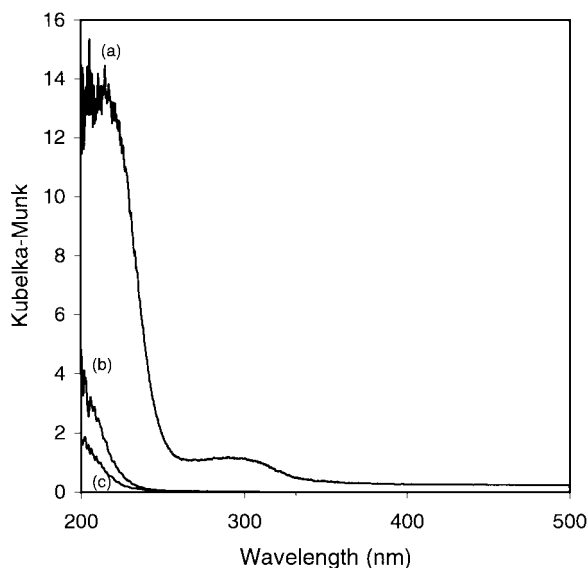

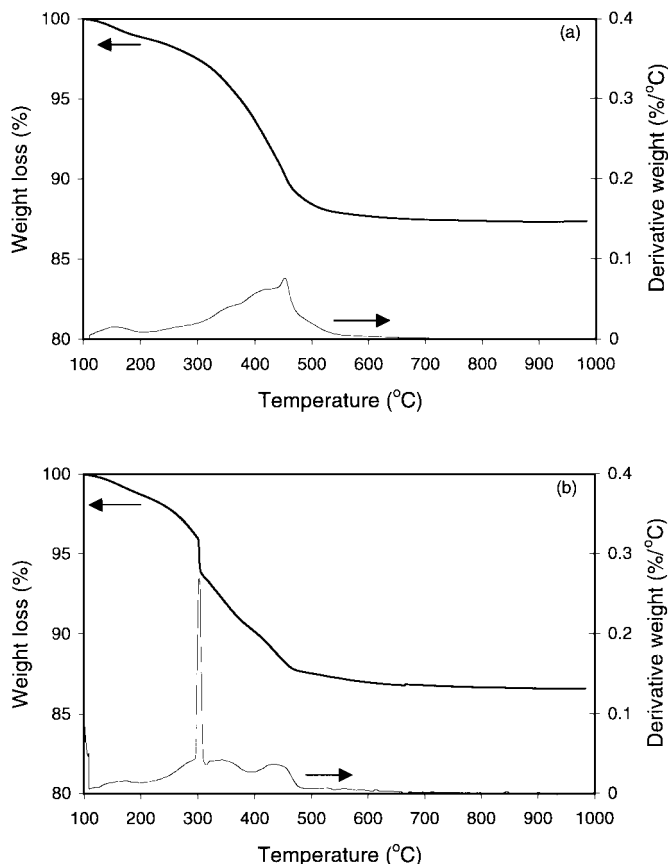**FIG. 3.** Uv–vis spectra of (a) ZrO_2-0–250, (b) $Zr(OR)_4/SiO_2$, and (c) $Zr(OR)_4/MCM$-41.

FIG. 4.   TGA curves of (a) ZrO_2-2–100 and (b) ZrO_2-2–100 after re-
fluxing in 2-propanol.

The TGA curve of ZrO_2-2–100, which was refluxed in
2-propanol showed a sharp weight loss at around 300°C in
addition to the broad weight loss occurring below 500°C
(Fig. 4b). During reflux, the hydroxyl groups on hydrous
zirconia undergo ligand exchange with 2-propanol to form
2-propoxide species. The weight loss at 300°C can be at-
tributed to the decomposition of 2-propoxide groups on
the sample. From the results, the concentration of the 2-
propoxide is about 3.2 μmol/m^2. The actual concentration
of 2-propoxide on hydrous zirconia during reaction could
be higher as the sample would be partially hydrolyzed by
ambient moisture during preparation for the TGA mea-
surement.

The presence of 2-propoxide species on the hydrous zir-
conia was confirmed by FTIR (Fig. 5). In ZrO_2-2–100, a
broad band in the hydroxyl stretching region was measured.
After exposure to 2-propanol, a new band at 2980 cm^{-1} was
observed, which can be assigned to the C-H stretching.

Catalytic Studies

The rate of conversion of cinnamaldehyde over hydrous
zirconia, ZrO_2-0, was initially very high, and almost com-
plete conversion was reached within 5 h (Fig. 6). For ZrO_2-0
catalysts calcined from 200 to 300°C, the conversion of
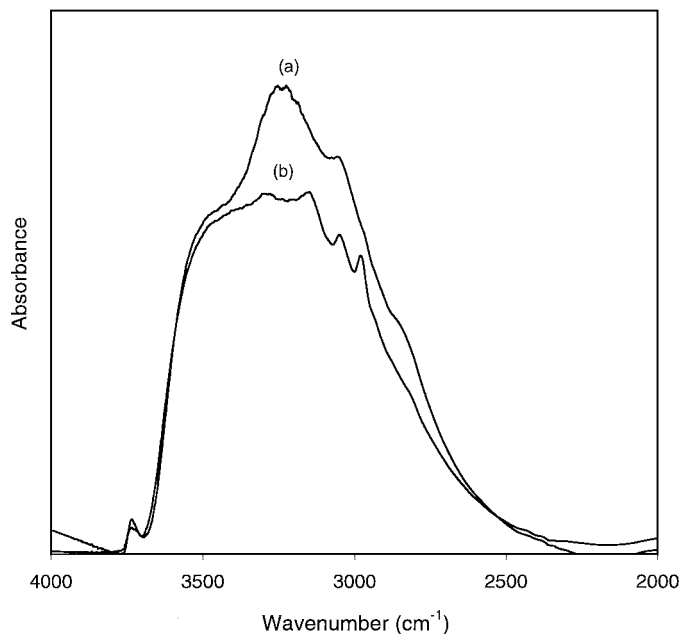

FIG. 5.   FTIR spectra of (a) ZrO_2-2–100 dried at 100°C and (b) after
immersing in 2-propanol at 50°C for 1 h and evacuating for 4 h.

cinnamaldehyde was higher than 80% after 4 h. However,
if the catalyst had been calcined at 400°C or higher, a steep
drop in the activity was observed, so that even after 24 h,
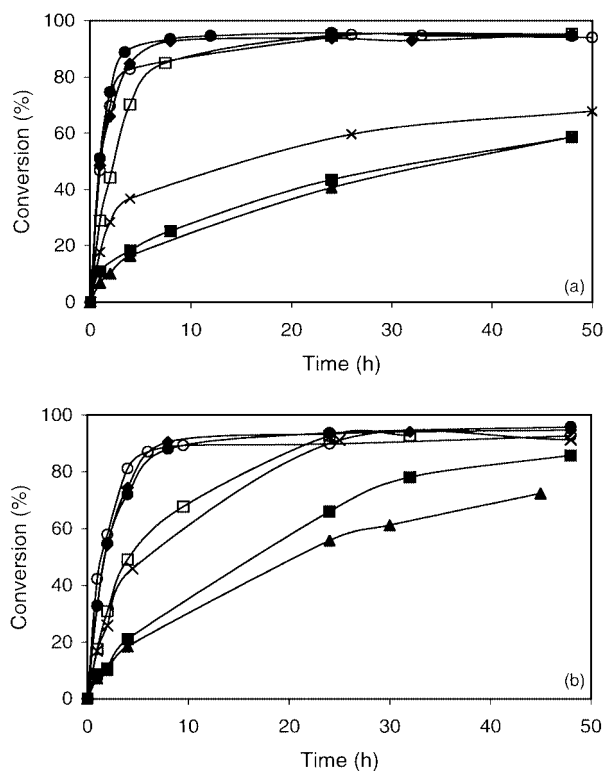the conversion was less than 50%. The digested hydrous

FIG. 6.   Conversion (%) versus calcination temperature for (a) ZrO_2-
0 and (b) ZrO_2-2. (○) 200°C, (●) 250°C, (◆) 300°C, (□) 350°C, (×) 400°C,
(■) 450°C, and (▲) 500°C.

TABLE 2

MPV Activity of Zirconium-Containing Catalysts

Catalyst	Initial rates[a] (mmol/$g_{cat} \cdot$ h)	Conversion[b] (%)	Selectivity[b] (%)
ZrO_2-0–250	2.55	75	96
ZrO_2-2–250	1.64	55	100
ZrO_2-0–500	0.34	10	100
ZrO_2-2–500	0.36	12	100
$Zr(OR)_4$/SiO_2	2.72	80	100
$Zr(OR)_4$/MCM-41	3.68	94	100
$Zr(OR)_4$/Al-MCM	2.94	71	100

[a] Rates calculated for the first hour.
[b] Conversion and selectivity to cinnamyl alcohol after 2 h reaction.

zirconia, ZrO_2-2–250, was slightly less active than the ZrO_2-0–250 with an initial rate of 1.64 mmol/$g_{cat} \cdot$ h as compared to 2.55 mmol/$g_{cat} \cdot$ h for the latter (Table 2). However, the decrease in conversion with increasing calcination temperature was less pronounced than that with the undigested hydrous zirconia. After 24 h, ZrO_2-2–500 had a conversion of 61.2% compared with only 40.7% over ZrO_2-0–500.

The selectivity to cinnamyl alcohol was high over all hydrous zirconia catalysts. For ZrO_2-0–200, the initial selectivity to cinnamyl alcohol was 97%. A small amount of 1-cinnamyl 2-propyl ether was formed by etherification of cinnamyl alcohol and excess 2-propanol. After 24 h of reaction, the selectivity to 1-cinnamyl 2-propyl ether increased to 7.8% (Fig. 7). The formation of the ether requires strong acidic sites on hydrous zirconia. These could be hydroxyl
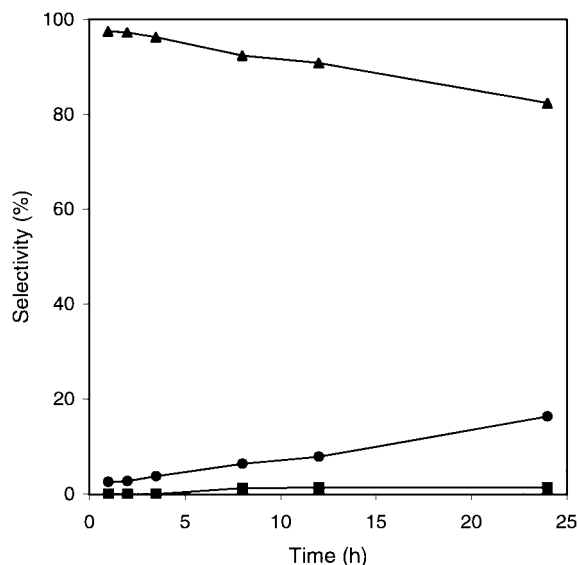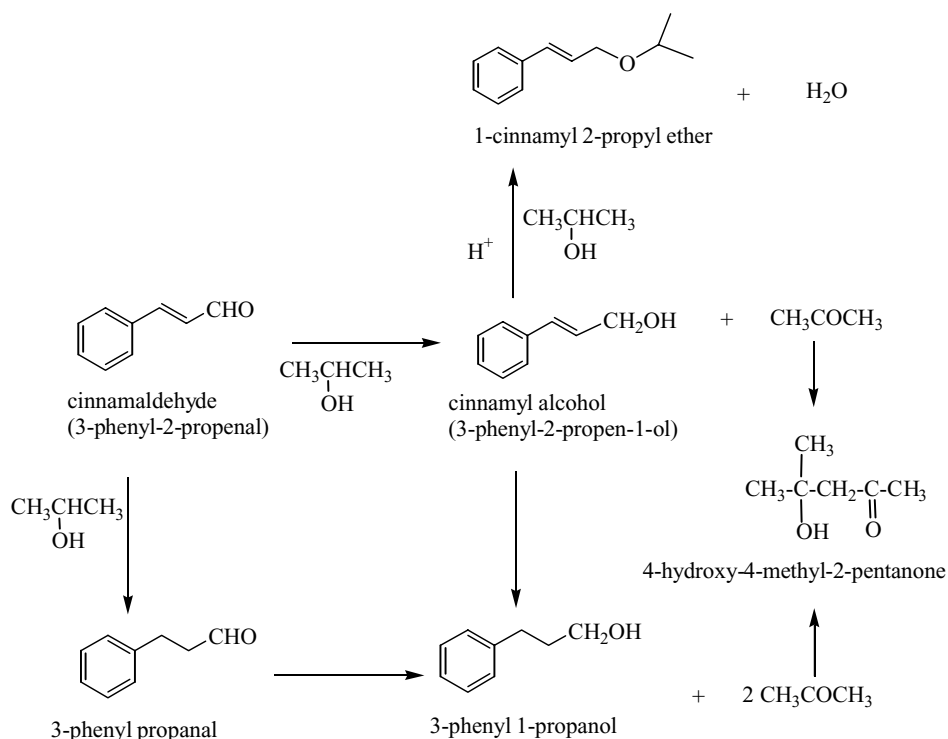

FIG. 7. Reaction products: (▲), cinnamyl alcohol; (●), 1-cinnamyl 2-propyl ether; (■), 3-phenyl 1-propanol formed over ZrO_2-0–250 versus reaction time.

groups located at edges or kink sites. Another side product, 3-phenyl 1-propanol, was also detected (Scheme 3). This product appeared after 4 h reaction time and constituted about 1.3% of the reaction products. The selectivity remained almost constant up to 24 h reaction time. Hydrous zirconia calcined at temperatures above 400°C formed only cinnamyl alcohol although the activity was low (Table 3). The absence of 1-cinnamyl 2-propyl ether shows that the

SCHEME 3. MPV reduction of cinnamaldehyde to cinnamyl alcohol and other side products.

TABLE 3

Selectivity to Cinnamyl Alcohol versus Calcination Temperature for ZrO$_2$-0 and ZrO$_2$-2 Catalysts

Calcination temperature (°C)	Reaction time (h)					
	ZrO$_2$-0			ZrO$_2$-2		
	1	8	24	1	8	24
200	97.0	92.0	89.5	100	94.0	93.6
250	97.5	91.0	88.0	100	97.3	87.8
300	97.5	94.6	91.7	100	97.6	88.6
350	98.4	96.8	95.3	100	100	100
400	100	100	100	100	100	100
450	100	100	100	100	100	100
500	100	100	100	100	100	100

acidic sites required for etherification were removed during calcination of the hydrous zirconia at higher temperatures. Similarly, the digested hydrous zirconia shows a high selectivity toward cinnamyl alcohol with only a small concentration of side products, 1-cinnamyl 2-propyl ether and 3-phenyl 1-propanol.

The catalysts prepared by grafting zirconium 1-propoxide on a support were also active in the MPV reduction of cinnamaldehyde. The initial rate over Zr(OR)$_4$/SiO$_2$ was 2.72 mmol/g$_{cat}$ · h as compared to 2.55 mmol/g$_{cat}$ · h over ZrO$_2$-0–250 (Table 2). After 2 h reaction, the conversion was ∼80% with a selectivity of 100% to cinnamyl alcohol. When zirconium 1-propoxide was supported over a high-surface-area support, MCM-41, the resulting catalyst had a higher activity with a rate of 3.68 mmol/g$_{cat}$ · h. This is due to the higher surface concentration of zirconium 1-propoxide. The only product formed over the grafted catalysts supported on silica or MCM-41 was cinnamyl alcohol, even at long reaction times. This is in contrast to that over hydrous zirconia where side products of 1-cinnamyl 2-propyl ether and 3-phenyl propanol were observed. A slightly lower rate of reaction was observed over the acidic Al-MCM-41, with ∼71% conversion after 2 h reaction. The selectivity decreased from 100% after 1 h to 92% after 4 h due to the formation of predominantly 1-cinnamyl 2-propyl ether. This is not surprising as the incorporation of aluminium into silica MCM-41 increased the acidity of Al-MCM-41. Zirconium 1-propoxide did not leach from the grafted catalysts into the reaction mixture. No conversion was observed when cinnamaldehyde was added to the supernatant solution after refluxing the grafted catalyst with 2-propanol.

In contrast to the zirconium catalysts, zeolite beta (Si/Al 13) although active, showed a selectivity to cinnamyl alcohol of only 1.9% at a conversion of 69% after 12 h. The predominant product was 1-cinnamyl 2-propyl ether (82%). Other products found were 3-phenyl propanal and 3-phenyl 1-propanol resulting from hydrogenation at the C=C bond and 4-hydroxy-4-methyl-2-pentanone—an aldol condensa-

tion product of acetone. The commercial zeolite beta (Si/Al 50) was similarly active with a conversion of 90% and a selectivity to the ether product of 82% after 4 h. The poor selectivity over zeolite beta is due to its highly acidic nature with both Lewis and Brønsted acidity. The formation of 1-cinnamyl 2-propyl ether may be due to two mechanisms. In the first mechanism, cinnamyl alcohol formed through the MPV reduction reacts with 2-propanol in an acid-catalyzed dehydration reaction (Scheme 3). In the second, the Brønsted acid sites present on zeolite beta catalyze the formation of a hemiacetal followed by a hydride transfer and loss of water to yield the ether. The latter step is postulated to be Lewis acid catalyzed (41). To test this hypothesis, methanol and ethanol were used in place of 2-propanol. No cinnamyl alcohol was formed, which was expected due to the poorer hydride-donating ability of the primary alcohols. More importantly, only trace amounts of hemiacetal was found showing that the cinnamyl propyl ether was unlikely to be formed via this route. Additional support for the first mechanism comes from the presence of 4-hydroxy-4-methyl-2-pentanone. This is a product from the aldol condensation of acetone, catalyzed by the acidic sites of zeolite beta. It could only have formed if 2-propanol was oxidized to acetone in the MPV reduction of cinnamaldehyde.

4. DISCUSSION

The decrease in the activity of hydrous zirconia with calcination temperature suggests that the presence of hydroxyl groups is important in the MPV reaction. We propose that the hydroxyl groups act as sites for ligand exchange with 2-propanol to form 2-propoxide on the catalyst (Scheme 4). Whether the exchange involves the Zr–OH or ZrO–H bond breaking would require additional isotope labeling studies, although it has been reported that hydrous zirconia acts as an anion exchanger (42), thus suggesting that the OH group may be transferred. The reaction mechanism probably involves a cyclic six-membered transition state as has been proposed for zeolite beta (20). The cinnamaldehyde coordinates to the zirconium metal center. This activates the carbonyl group and initiates a hydride transfer from 2-propoxide to the carbonyl. Acetone is formed and subsequent alcoholysis leads to the product, cinnamyl alcohol, and regeneration of the active catalyst. Heating the hydrous zirconia to higher temperatures irreversibly removes the hydroxyl groups, thereby reducing the rate of reaction. Tichit *et al.* (42) reported that a zirconia calcined above 350°C could not be rehydrated in acid medium. Furthermore, the lower rate of reaction over the digested sample, ZrO$_2$-2, as compared to ZrO$_2$-0 may be explained by the effect of digestion which leads to "drier" hydrous oxide. Thermogravimetric analyses showed that the digested hydrous zirconia lost less water than the undigested sample when heated to form zirconia. The similar activity of Zr(OR)$_4$/SiO$_2$ and hydrous zirconia may be explained by
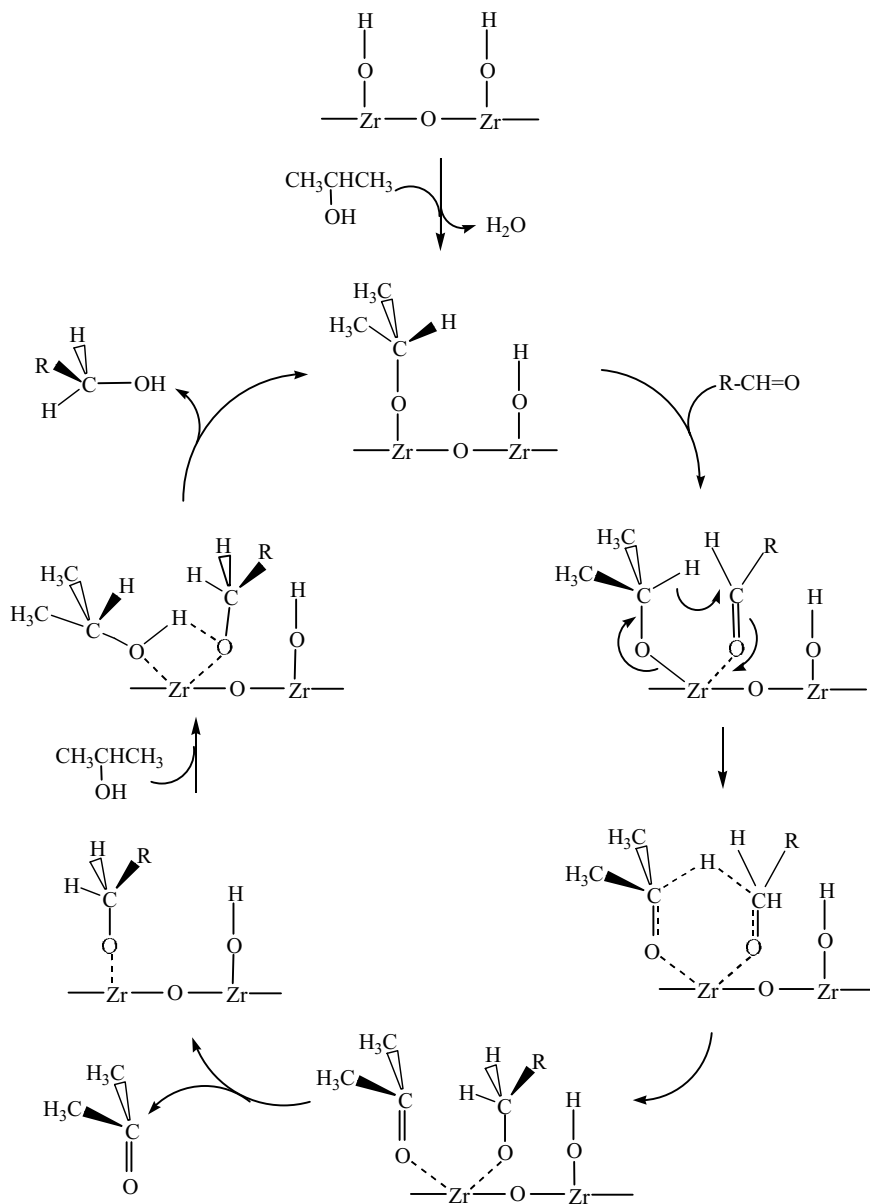
SCHEME 4. Proposed mechanism involving formation of 2-propoxide over hydrous zirconia.

a facile ligand exchange between 1-propoxide or hydroxyl groups, respectively, and 2-propanol. The role of hydroxyl groups in the activity for MPV reduction can be compared to the results of Kunkeler *et al.* (43), who found that mild steaming increased the activity of zeolite beta for the MPV reduction of 4-*tert*-butylcyclohexanone. The authors proposed that the presence of water inverted the coordination geometry of framework aluminum, resulting in its exposure to the zeolite pore. Heating in the presence of water results in the formation of a new tetrahedrally coordinated aluminum bearing a hydroxyl group, which is believed to be the active species reacting with 2-propanol.

The formation of ethers during MPV reduction of a number of substituted cyclohexanones has been reported by Verhoef *et al.* (41). Zeolite MCM-22 with a Si/Al ratio

of 15 was active in the reductive etherification of 4-*tert*-butylcyclohexanone, 4-phenylcyclohexanone, and 4-methylcyclohexanone. In contrast to what we observed, the reaction was found to proceed via the formation of hemiacetals over MCM-22. When 4-*tert*-butylcyclohexanone was refluxed with a 1:1 mixture of methanol and 2-propanol, both dimethyl and mixed methyl isopropyl acetals were formed initially before converting into isopropyl and methyl ethers. As etherification was not observed over other zeolites (20), the authors postulated that H-MCM-22 contained a large number of Brønsted acid sites as compared to the sites responsible for MPV reduction. Therefore, hemiacetals were rapidly formed followed by a slow conversion to ethers. We believe that the etherification observed in this study is likely to be due to the α,β-unsaturated

nature of cinnamyl alcohol. The presence of conjugated double bonds coupled to the benzene ring in cinnamyl alcohol can stabilize the carbocation intermediate formed in etherification, making cinnamyl alcohol more susceptible to a dehydration reaction with excess 2-propanol. Indeed, no 2-propyl ether was formed from the excess 2-propanol. We have previously studied the MPV reaction of 4-*tert*-butylcyclohexanone over the same zeolite beta catalyst but did not observe any etherification products (44).

5. CONCLUSION

Hydrous zirconia calcined below $350°C$ showed good activity for the MPV reduction of cinnamaldehyde. Cinnamyl alcohol was the only product formed at short reaction times, while at long reaction times, etherification occurred between the product cinnamyl alcohol and excess 2-propanol to give cinnamyl 2-propyl ether. The selectivity to cinnamyl alcohol decreased from 97–100% after 1 h to 88–95% after 24 h. Hydrous zirconia calcined above $400°C$ had lower activity. This was attributed to a decrease in the concentration of hydroxyl groups, which are required for binding of 2-propanol. Digested hydrous zirconia was better able to retain its activity despite calcination to high temperatures. Due to the presence of silica in this sample, loss in surface area and porosity was minimized compared to that in pure hydrous zirconia. Zirconium 1-propoxide grafted onto silica and MCM-41 supports were also highly active in the MPV reduction of cinnamaldehyde. The high activity may be partly attributed to a facile ligand exchange between the surface hydroxyl groups on hydrous zirconia and the 2-propanol or 1-propoxide groups on $Zr(OR)_4$/support and 2-propanol. Over zeolite beta, the main product was cinnamyl isopropyl ether, the product of acid-catalyzed etherification between cinnamyl alcohol and 2-propanol.

ACKNOWLEDGMENT

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