Catal Lett (2008) 122:205–209
DOI 10.1007/s10562-008-9480-y

Transesterification Catalysts from Iron Doped Hydrotalcite-like Precursors: Solid Bases for Biodiesel Production

**Gerald S. Macala · Andrew W. Robertson · Charles L. Johnson ·
Zachary B. Day · Robert S. Lewis · Mark G. White ·
Alexei V. Iretskii · Peter C. Ford**

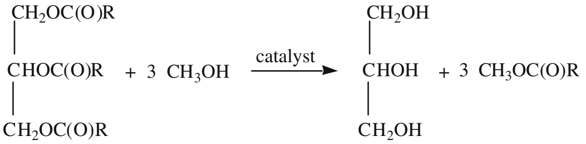
Received: 16 January 2008 / Accepted: 18 March 2008 / Published online: 10 April 2008

Abstract Described are new solid base catalysts for transesterification of seed oil triglycerides to fatty acid methyl esters, a key step in biodiesel production. These were prepared by substituting Fe3+ ions substitute for a fraction of the Al3+ ions in the Mg/Al layered double hydroxide lattices of hydrotalcites (HTC) and calcining to give porous metal oxides (PMOs). These iron-doped PMOs are much stronger bases than those derived from undoped or Ga3+ doped HTCs and are effective catalysts for the methanol transesterification of triacetin (glycerol triacetate) and of soybean oil.

Keywords Catalysis · Biodiesel · Transesterification · Solid base · Hydrotalcite · Iron · Triglycerides

1 Introduction

The base catalyzed transesterification of triglycerides such as seed oils with methanol or ethanol (Eq. 1) produces a non-toxic, biodegradable, renewable, and clean burning fuel that can directly replace petroleum diesel in most applications. Commercial technology for biodiesel production generally employs homogeneous bases such as NaOH in methanol solution as catalysts [1]. Such catalysis requires an aqueous wash to remove the dissolved catalyst and glycerol from the product phase and suffers from separation problems due to emulsion formation and from waste treatment issues. Thus, it is desirable to utilize solid bases to avoid these pitfalls that may be adaptable for use in flow reactors. In this context, there have been several recent reports of base catalysis by solids such as CaO, KF or Eu_2O_3 supported on alumina or silica [2–4]. Here, we report new solid base catalysts prepared from ferric ion doped hydrotalcite (HTC) precursors. Calcination of such HTCs gives porous metal oxides (PMOs) that are effective for the transesterification of triacetin (Eq. 1, $R = CH_3$) and of soybean oil (Eq. 1, $R = C_{16}$ and C_{18} hydrocarbon chains [5]).



$$\begin{array}{l}CH_2OC(O)R\\ |\\ CHOC(O)R\\ |\\ CH_2OC(O)R\end{array} + 3\ CH_3OH \xrightarrow{\text{catalyst}} \begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array} + 3\ CH_3OC(O)R \quad (1)$$

Hydrotalcites are Mg^{2+}/Al^{3+} layered double hydroxides with the general formula $Mg_{1-x}Al_x(OH)_2(CO_3)_{x/2} \cdot nH_2O$, calcination of which gives amorphous PMOs upon evolution of H_2O and CO_2. Earlier reports have shown that Ga^{3+} doped calcined HTCs have enhanced activities for the base-catalyzed Knoevenagel condensation and for CO_2 adsorption [6, 7]. In this context, the present study was initiated with the premise that doping with other trivalent cations, such as those of the transition metals, would lead to PMO catalysts with tunable basicities and higher catalytic activities for triglyceride transesterification. While others have considered the use of calcined Mg:Al

---

G. S. Macala · A. W. Robertson · Z. B. Day ·
R. S. Lewis · A. V. Iretskii (✉) · P. C. Ford (✉)
Department of Chemistry and Biochemistry, University of
California, Santa Barbara, CA 93106-9510, USA
e-mail: airetski@lssu.edu

P. C. Ford
e-mail: ford@chem.ucsb.edu

A. W. Robertson · C. L. Johnson · A. V. Iretskii
Department of Chemistry, Lake Superior State University,
Sault Ste Marie, MI 49783, USA

M. G. White
School of Chemical Engineering, Mississippi State University,
Starkville, MS 39762, USA

hydrotalcites as solid base catalysts for transesterification [8–10], we report here enhanced reactivity of these materials by doping with ferric ion.

2 Experimental Section

2.1 Catalyst Preparation and Characterization

New hydrotalcite solids having a molar ratio Mg/(Al + dopant) of ~3 were prepared by co-precipitation as described for undoped HTCs [11]. Typically, a solution of 300 mL deionized water containing $MgCl_2 \cdot 6H_2O$ (0.15 mole) and $AlCl_3 \cdot 6H_2O$ (0.05 mole) or an mixture of $AlCl_3 \cdot 6H_2O$ and another trivalent metal chloride (0.05 mole total) was slowly added in 10 mL aliquots to a sodium carbonate solution (0.05 moles in 375 mL) at 60 °C with vigorous stirring, resulting in the rapid formation of a precipitate. The pH of this mixture was maintained at ~10 by alternate addition of 10 mL aliquots of 1 M NaOH to the reaction mixture. After addition was complete, the resulting slurry was heated to 80 °C with stirring for 4 days. The precipitate was isolated by filtration and washed first with sodium carbonate solution (0.05 mole in 375 mL distilled water) then deionized water before being dried overnight at 100 °C. The resultant HTC was then calcined overnight in air (typically at 460 °C) to obtain the amorphous Mg/Al or Mg/Al-dopant porous metal oxides.

Elemental analyses were performed by inductively coupled plasma (ICP) using a TJA IRIS HR ICP instrument and by atomic absorption spectroscopy using a Shimadzu AA-6200 atomic absorption flame emission spectrophotometer. Samples were digested in nitric acid and compared to purchased standards. Surface elemental analysis was performed by X-ray photoelectron spectrometry (XPS) using a Kratos Axis Ultra XPS system.

Solid morphologies and crystallite sizes of the HTCs were determined by powder X-ray diffraction (XRD) measurements performed on a Scintag X2 diffractometer using Cu Kα radiation ($k = 1.54060$ Å) and a step size of 0.02 (2θ).

Surface area and pore volume measurements of HTCs and of the PMOs formed by calcination were performed using the BET method by nitrogen adsorption at −196 °C on a Micromeritics Tri-Star 3000 system. Samples were heated for 120 min at 200 °C under flowing nitrogen prior to the measurements.

2.2 Transesterification of Triacetin

Anhydrous methanol (5.6 mL, Acros, <0.002% water) and triacetin (4.4 mL, Acros, 99%) were transferred into a dry 6 dram vial to give a 6:1 molar ratio of methanol to triglyceride. To this mixture was added the PMO catalyst (0.2 to 1%, 95 mg for the latter) and a Teflon coated stir bar, and the vial was sealed and placed in a heated aluminum block at 60 °C. The solution was vigorously stirred and the reaction allowed to proceed for a specified time period (0.5–2 h), after which the mixture was cooled rapidly in an ice bath to arrest the reaction. The extent of the conversion was determined using proton NMR techniques.

2.3 Transesterification of Seed Oil

Anhydrous methanol (2.5 mL) and soybean oil (10.0 mL, Inter-American Products, Inc.) were transferred into a dry 6 dram vial to give a 6:1 molar ratio of methanol to oil. To this mixture was added the PMO catalyst (100 mg, 1 wt%) and a stir bar, and the vial was sealed and placed in a heated aluminum block at 80 °C. The solution was vigorously stirred and the reaction allowed to proceed for a specified time period (0.5–2 h), after which the mixture was cooled rapidly in an ice bath to arrest the reaction. The extent of the conversion was determined using proton NMR techniques.

2.4 Analytical Method

Reaction products were monitored by ^{1}H-NMR spectroscopy. Terminal methyl groups on the fatty acid chains appear at 0.8 ppm for the seed oils and 2.0 ppm for the triacetin, while the methoxy protons of the methyl esters appear at 3.7 ppm. The yield of methyl ester can be calculated from the ratio of the integrated area of the 3.7 ppm peak to the area of that at 0.8 or 2.0 ppm.

3 Results and Discussion

Table 1 summarizes the empirical ratios of metals determined by ICP for the calcined HTCs prepared as described in the Experimental Section [11]. In some cases the dopant was not incorporated in the same ratio as that used in the synthesis scheme. Low amounts of sodium were also detected in both doped and undoped calcined HTC, but sodium levels showed no correlation with catalytic activity. XPS measurements confirmed the relative ratios of Mg and Al as well as the small variable amounts of sodium.

3.1 XRD Experiments

The materials prepared exhibited X-ray diffraction patterns characteristic of hydrotalcite-type structures (Fig. 1). The '*a*' unit cell parameters were determined from the (110) reflection ($a = 2\ d_{110}$) and were plotted (Fig. 2) versus the average radius of the cation: $R = y_{Mg}R_{Mg} + y_{Al}R_{Al} + y_{M}R_{M}$, where M = dopant, y_i is the mole fraction of the cation, and R_i is the

Table 1 Metal ion ratios in calcined HTCs as determined by ICP technique

Doped material[a]	Empirical ratio of metals[b]
Undoped	$Mg_3Al_{1.13}$
Cr 5%	$Mg_3Al_{1.20}Cr_{0.10}$
Cr 10%	$Mg_3Al_{1.28}Cr_{0.13}$
Ga 5%	$Mg_3Al_{1.24}Ga_{0.05}$
Ga 10%	$Mg_3Al_{1.03}Ga_{0.10}$
Fe 10%	$Mg_3Al_{1.03}Fe_{0.13}$
Fe 20%	$Mg_3Al_{0.76}Fe_{0.23}$

[a] The label indicates the dopant and its mole percent in the original mix of M^{3+} salts used in the preparative procedure (see Experimental Section)

[b] The Al and dopant M are normalized relative to $Mg_{3.00}$

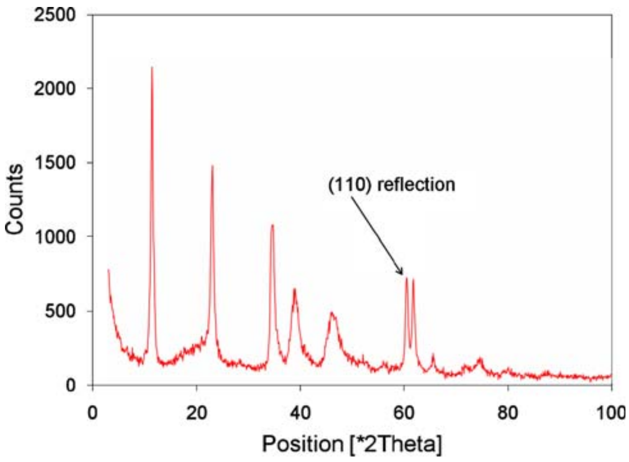


Fig. 1 Mg:Al 3:1 hydrotalcite powder XRD pattern. The (110) reflection at approximately 60° 2-Theta defines the cation–cation distances within the layers

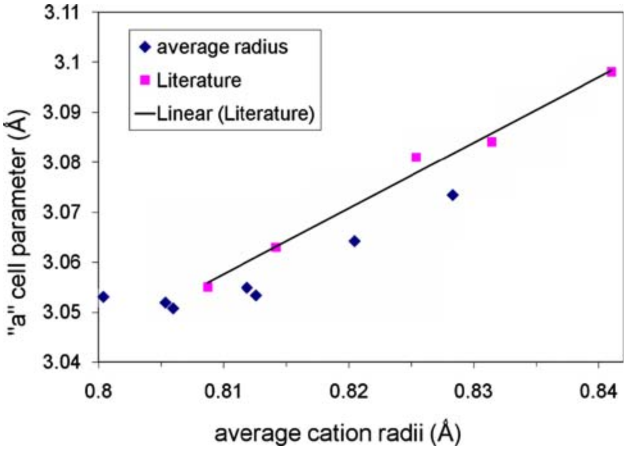


Fig. 2 '*a*' cell parameter as a function of HTC composition in doped HTC, compared to literature values [12] (linear fit is for literature data)

radius of the octahedral metal cation. The abscissa reflects the dopant/Al ratios and the divalent/trivalent cation ratios, which are somewhat variable. Figure 2 also displays analogous data from Bellotto et al. [12]. These data appear to follow Vegard's rule for isomorphous substitution of cations into solids [13] and suggest that the dopant is replacing Al in the layers.

BET isotherm data shows a general increase in surface area upon calcination (Table 2), consistent with the formation of a porous mixed metal oxide on loss of CO_2 and collapse of the HTC lattice. The doped PMOs tended to have larger surface areas than the undoped analogs. The highest surface areas were seen for the 3:1 Mg:Al HTCs, before and after calcination, so the present studies were confined to solids based on 3:1 Mg:(Al + dopant) ratios. Calcining at 480 °C resulted in slightly lower surface areas.

A qualitative assessment of catalyst basicity was made using the Hammett indicator 2,4-dinitroaniline (pKa = 15 in benzene) [14]. Addition of several drops of a benzene solution of this indicator to a benzene suspension of the solid PMO prepared by calcining Fe 10% HTC gave the red color characteristic of the deprotonated 2,4-dinitroaniline thus indicating strong basic sites on the catalyst surface. No such color change was observed with the PMOs prepared by calcining undoped or Ga 10% HTC.

Catalysis tests of doped HTC-derived PMOs (actual compositions in Table 1) were batch reactions of triglycerides and prospective solid base catalysts, modeled after Bancquart's procedure [15]. Higher temperatures were used for the seed oil reactions (80 °C) than for triacetin (glyceryl triacetate) (60 °C). Periodic aliquots were taken and analyzed by ^{1}H-NMR spectroscopy as described in the Experimental Section [16].

Table 2 BET surface areas for HTCs and calcined HTCs

HTC derived materials[a]	BET surface area (m^2/g)
2:1 Mg:Al[b]	51.9
3:1 Mg:Al[b]	87.1
4:1 Mg:Al[b]	89.9
3:1 Mg:Al Fe 10%[b]	68.6
2:1 Mg:Al (460)[c]	75.1
3:1 Mg:Al (460)[c]	111.8
4:1 Mg:Al (460)[c]	67.4
3:1 Mg:Al Ga 10% (460)[c]	122.2
3:1 Mg:Al Fe 10% (460)[c]	123.6
3:1 Mg:Al Fe 10% (440)[c]	124.8
3:1 Mg:Al Fe 10% (480)[c]	112.9
3:1 Mg:Al Fe 20% (460)[c]	161.1

[a] See footnote in Table 1 for labeling scheme

[b] Not calcined

[c] Calcination temperature in °C

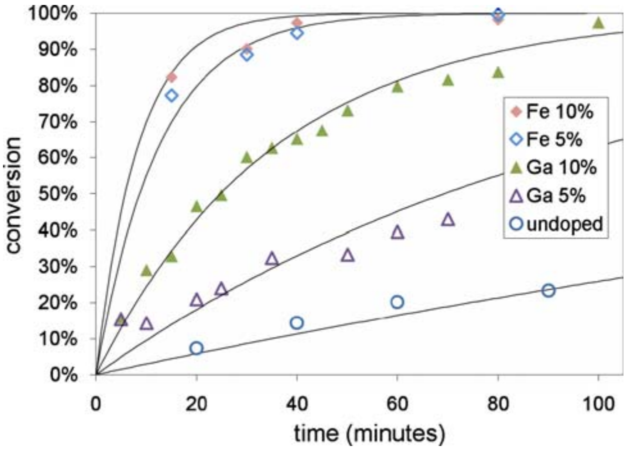


Fig. 3 Comparison of transesterification rates for a mixture of triacetin (10 mmol) and methanol (60 mmol) catalyzed at 60 °C by doped and undoped HTC-derived PMOs (1% by weight loading) as determined by the NMR technique. The lines are fits to the function % conversion = $100(1 - e^{-kt})$. Catalysts were calcined at 460 °C

Figure 3 compares transesterification of triacetin to methyl acetate (Eq. 1) by the various catalysts under otherwise analogous conditions. The undoped PMO shows modest activity, comparable to results previously reported for this reaction [17]. The Ga doped catalysts show enhanced activity with calcined Ga 5% and Ga 10% HTCs giving ~40% and ~80% conversion, respectively, after 60 min. The Fe 5% and Fe 10% doped materials were dramatically more active, with conversion nearly complete in 40 min. The PMO from Fe 20% doped HTC showed similar activity as the Fe 10% PMO. Cr^{3+} doped HTC-derived PMO displayed moderate activity but suffered visible leaching and was not studied further.

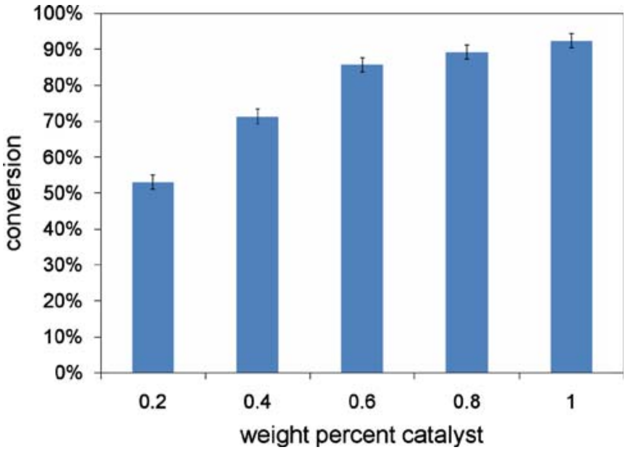


Fig. 4 Triacetin transesterification catalyzed at 60 °C by different % loadings of 480 °C calcined Fe 10% doped HTC. In each case, the reaction was sampled at 30 min and conversion determined by the NMR technique

Figure 4 compares triacetin transesterification for a set of reactions under standard conditions with different catalyst loadings, 0.2 to 1.0 wt% of Fe 10% HTC calcined at 480 °C. For 0.2 wt% loading, 53% conversion was achieved in 30 min (84% after 2 h), and this increased with catalyst loading as expected. An analogous experiment using a 0.2 wt% loading of Fe 10% HTC calcined at 440 °C gave 85% conversion suggesting that a more active catalyst may result from calcination at the lower temperature. Reaction intermediates of triacetin transesterification reactions were further characterized by GC/MS. Mono and diglyceride intermediates were detected in approximately equal amounts along with triacetin in reactions which had gone to ~80% completion.

Transesterification catalysis of soybean oil to fatty acid methyl esters (FAME) was tested for various calcined HTC-derived PMOs at 80 °C. The undoped PMO showed limited activity, giving 8.9% conversion after 60 min at 80 °C and 1 wt% catalyst loading. Previous studies report 35% conversion after 120 min at methanol reflux and 7.5 wt% catalyst loading [17]. HTC-derived PMO has also been used for methanol transesterification of poultry fat [18], with 10% conversion reported after 120 min at 120 °C and 5 wt% catalyst loading.

The catalytic activity of the Ga doped materials for seed oil transesterifications was comparable to that of undoped materials. However, consistent with the data shown above, the calcined Fe doped HTCs proved to be much more active than either the undoped or the Ga doped PMOs. The 10% Fe doped PMO gave 38% conversion after 60 min at 80 °C and 1 wt% catalyst loading. This compares favorably to results previously reported for the solid superbase catalyst Eu_2O_3/Al_2O_3 which gave 63% conversion after 8 h at 70 °C and 6.75 wt% catalyst loading [4].

Catalyst leaching studies were conducted on the calcined Fe 10% doped HTC. Samples were heated to 60 °C with stirring in deionized water for a prescribed time period then removed from heat and subjected to centrifugation. The extracts decanted from the samples were subjected to analysis by ICP. Trace amounts of Mg, Al and Fe (<0.5%) were detected after 24 h of leaching in ratios consistent with the HTC solid sample, possibly due to partial mechanical breakdown of the catalyst into ultrafine particles not separated by centrifugation. No excess Fe was detected in leach extracts.

Catalyst regeneration studies were conducted on the calcined Fe 10% doped PMO. Samples were used for transesterification of triacetin as described above, after which the reaction mixture was subjected to centrifugation. The liquid fraction was decanted and the solid was washed with 10 mL of methanol, followed by further centrifugation and decanting of the methanol extract. The solid was then calcined overnight at 460 °C. The regenerated PMO was half as active as the original catalyst, based on initial turnover frequencies. The regeneration process was repeated and no further degradation of catalyst performance was observed.

In summary, we have prepared and characterized iron-doped hydrotalcites in which Fe^{3+} ions substitute for some Al^{3+} in the Mg/Al layered double hydroxide lattice. Calcination of these HTCs gives new solid bases, which demonstrate a general increase in surface area consistent with the formation of an amorphous porous metal oxide upon evolution of H_2O and CO_2. These new iron doped materials are much stronger bases than PMOs derived from undoped or Ga^{3+} doped HTCs and are very effective catalysts for methanol transesterification of the triglyceride model triacetin and of soy bean oil. Doped HTCs are easily synthesized from inexpensive materials and represent relatively benign precursors for developing PMOs as solid base catalysts for biodiesel production. A variety of dopant cations can be incorporated into the HTC lattice, thus tuning the properties of such catalysts and providing a new platform technology potentially suitable for flow reactor applications. Ongoing studies are directed toward optimizing catalytic properties by examining variable parameters such as metal ion dopants and concentrations, calcination conditions, etc.

Acknowledgments Principal support was the UCSB Partnership for International Research and Education in Electron Chemistry and Catalysis at Interfaces (PIRE-ECCI) under National Science Foundation Grant number OISE-0530268. PCF also acknowledges partial support from the University of California Energy Institute and the University of Washington Center for the Activation of Strong Bonds (NSF CBC).

References

1. Biodiesel Production Fact Sheet, National Biodiesel Board, http://www.biodiesel.org/
2. Bo X, Xiao G, Cui L, Wei R, Gao L (2007) Energy Fuels ACS ASAP
3. D'Cruz A, Kulkarni M, Meher L, Dalai A (2007) J Am Oil Chem Soc 84:937–943
4. Li X, Lu G, Guo Y, Guo Y, Wang Y, Zhang Z, Liu X, Wang Y (2007) Catal Commun 9:1969–1972
5. Torres M, Lloret C, Sosa M, Maestri D (2006) Eur J Lipid Sci Technol 6:513
6. Rousselot I, Taviot-Gueho C, Besse JP (1999) Int J Inorg Mater 1:165
7. White MG, Iretski AV, Chiang RL, Brzozowski JR (2003) Adsorbants, methods of preparation, and methods of use thereof, World Patent WO 2004/000440 A1, 31 December 2003
8. Cantrell DG, Gillie LJ, Lee AF, Wilson K (2005) Appl Catal A: Gen 287:183–190
9. Di Serio M, Ledda M, Cozzolino M, Minutillo G, Tesser R, Santacesaria E (2006) Ind Eng Chem Res 45:3009–3014
10. Di Serio M, Cozzolino M, Giordano M, Tesser R, Patrono P, Santacesaria E (2007) Ind Eng Chem Res 46:6379–6384
11. DiCosimo JI, Diez VK, Xu M, Iglesia E, Apesteguia CR (1998) J Catal 178:499
12. Bellotto M, Rebours B, Clause O, Lynch J, Bazin D, Elkaim E (1996) J Phys Chem 100:8527
13. Vegard L (1921) Z Phys 5:17
14. Forni L (1974) Catal Rev 8:65
15. Bancquart S, Vanhove C, Pouilloux Y, Barrault J (2001) Appl Catal A: Gen 218:1
16. Morgenstern M, Cline J, Meyer S, Cataldo S (2006) Energy Fuels 20:1350
17. Xei W, Peng H, Chen L (2006) J Mol Catal A: Chem 246:24
18. Liu Y, Lotero E, Goodwin J Jr, Mo X (2007) Appl Catal A: Gen 331:138–148