ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 9, pp. 1837–1840. © Pleiades Publishing, Ltd., 2014.

# Montmorillonite K10 and KSF Clays as Acidic and Green Catalysts for Effective Esterification of Phenols and Alcohols under MWI[1]

**O. Marvi, L. Z. Fekri, and M. Takhti**

*Department of Chemistry, Payam Noor University, PO Box 19395-3697 Tehran, Iran*
*e-mail: omid_marvi@pnu.ac.ir*

Received July 19, 2014

**Abstract**—Montmorillonite K-10 and KSF clays catalyze esterification of phenols and alcohols under microwave irradiation and solvent-free conditions in high yields within seconds.

**DOI:** 10.1134/S1070363214090333

Esterification is a widely used technological process [1]. Most procedures require acidic or basic conditions. Development of simple environmentally friendly and atom-efficient methods of direct esterification under mild conditions is of high demand [2]. Since the Pollution Prevention Act of 1990 was passed chemists made a significant enefort to develop more environmentally friendly methods for a variety of organic compounds. This approach often referred to as "Green Chemistry," has produced an array of improved methods including the use of clays as chemical catalysts [3]. Natural alumosilicates, such as zeolites and clays, are solid acids that could act as an efficient alternative to liquid acids. Natural and modified clays have attracted attention due to their extremely versatile properties and high potential in green chemistry [4]. Many clay based catalysts such as claycop, clayzinc, clayfen, envirocat, etc. are commercially available and two most common modified clays applied in organic synthesis are K-10 and KSF montmorillonites. Though the physicochemical properties of the clays are similar their BET surface areas differ. K-10 Has a higher surface area (about 250 $m^2 g^{-1}$) compared to that of KSF (10 $m^2 g^{-1}$). Microwave-assisted (MW-assisted) organic synthesis has become a rapidly developing method [5]. It provides a number of advantages over the conventional approaches such as environmentally clean reactions, higher yields, shorter reaction time, easy work-up, and solvent free reaction media.

In continuation of our efforts on the microwave-assisted reactions on solid surfaces under solvent free conditions [6], herein, we have presented a fast and simple method for reaction of esterification of benzoic acid with phenols and alcohols on montmorillonite KSF and montmorillonite K-10 clays.

$$R_1COOH + R_2OH \xrightarrow[\text{Microwave}]{\text{KSF or K10 montmorillonite}} R_1COOR_2.$$

A variety of esters was synthesized using the above procedure with no by-products detected (see the table). Yields of the products based on KSF clay were higher than those synthesized with K-10 clay and the reaction time with the latter catalyst was shorter due to more developed surface of K-10 and higher acidic character of KSF clay [7]. Enhanced selectivity and lamellar swelling structures of K-10 and KSF make these solid supports of certain potential in synthetic organic chemistry.

## EXPERIMENTAL

Melting points were measured by an Electro Thermal 9100 apparatus. $^1$H NMR spectra were recorded by a FTNMR BRUKER DRX 500 Avence spectrometer. Chemical shifts were measured in ppm with TMS internal standard in $CDCl_3$ solutions. The IR spectra were recorded by a Perkin Elmer FT-IR GX instrument in KBr tablets. Montmorillonite KSF clay, surface area 15±10 $m^2$/g, surface acidity: 0.75 meq. $H^+$/g (determined in our laboratory by temperature programmed desorption of ammonia gas ($NH_3$-TPD); chemical composition (average value): $SiO_2$ (54.0%), $Al_2O_3$ (17.0%), $Fe_2O_3$ (5.2%), CaO (1.5%), MgO

[1] The text was submitted by the authors in English.

Yields and reaction time for the solvent-free synthesis of esters on montmorillonite KSF and K-10 clays under MWI

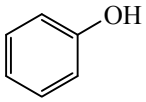
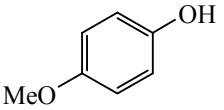
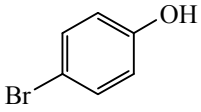
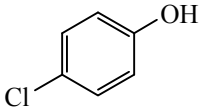
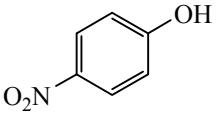
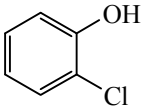
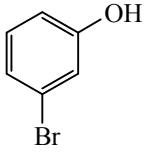
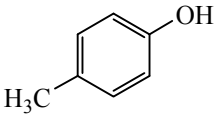
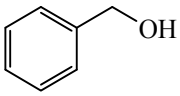
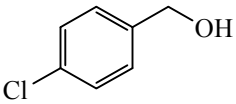
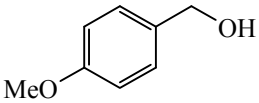
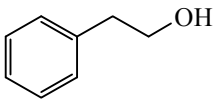
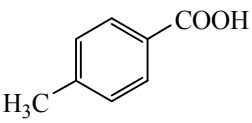
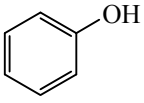
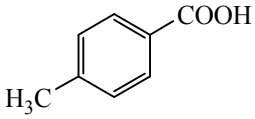
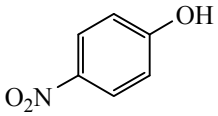
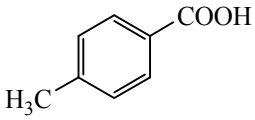
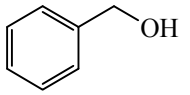
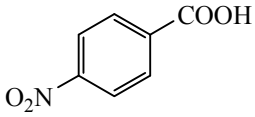
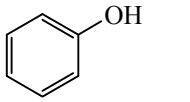
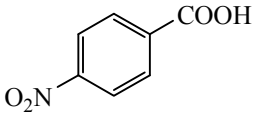
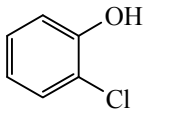
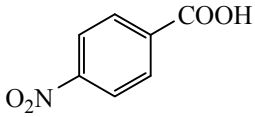
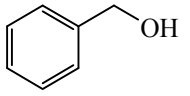
| Benzoic acid (BA) | Alcohol, phenol | Product[a] | Yield, % K10/KSF | Time, s K10/KSF |
|---|---|---|---|---|
| BA |  | Phenyl benzoate | 84/92 | 15/25 |
| BA |  | 4-Methoxyphenyl benzoate | 90/98 | 10/20 |
| BA |  | 4-Bromophenyl benzoate | 81/87 | 20/25 |
| BA |  | 4-Chlorophenyl benzoate | 79/85 | 20/30 |
| BA |  | 4-Nitrophenyl benzoate | 72/80 | 15/25 |
| BA |  | 2-Chlorophenyl benzoate | 77/82 | 15/25 |
| BA |  | 3-Bromophenyl benzoate | 75/81 | 15/30 |
| BA |  | 4-Methylphenyl benzoate | 80/89 | 15/25 |
| BA |  | Benzyl benzoate | 78/86 | 15/20 |
| BA |  | 4-Chlorobenzyl benzoate | 76/83 | 20/30 |
| BA |  | 4-Methoxybenzyl benzoate | 86/94 | 15/25 |
| BA |  | Phenethyl benzoate | 82/90 | 20/25 |
|  |  | Phenyl-4-methylbenzoate | 84/93 | 15/25 |

**Table** (Contd.)

| Benzoic acid (BA) | Alcohol, phenol | Product[a] | Yield, % K10/KSF | Time, s K10/KSF |
|---|---|---|---|---|
|  |  | 4-Nitrophenyl-4-methylbenzoate | 77/82 | 20/30 |
|  |  | Benzyl-4-methylbenzoate | 79/86 | 15/20 |
|  |  | Phenyl-4-nitrobenzoate | 90/97 | 25/35 |
|  |  | 2-Chlorophenyl-4-nitrobenzoate | 89/95 | 20/35 |
|  |  | Benzyl-4-nitrobenzoate | 91/96 | 20/30 |

[a] All products are well known compounds.

(2.5%), $Na_2O$ (0.4%), $K_2O$ (1.5%) and montmorillonite K10 clay, surface area: (200±10) $m^2/g$, surface acidity 0.65 meq. $H^+/g$ (determined in our laboratory by temperature programmed desorption of ammonia gas ($NH_3$-TPD); chemical composition (average value): $SiO_2$ (73.0%), $Al_2O_3$ (14.0%), $Fe_2O_3$ (2.7%), CaO (0.2%), MgO (1.1%), $Na_2O$ (0.6%), $K_2O$ (1.9%) were purchased from Fluka chemical company. Microwave irradiation was carried out with a Synthewave 402® (Prolabo, France) single mode focused microwave reactor [8]. The chemicals used in this work were purchased from Merck and Fluka chemical companies.

**General procedure for the synthesis of esters.** Phenol or alcohol (1 mmol) and acid (1 mmol), and montmorillonite K10 or KSF clay (1 g) were stirred in a 25 mL beaker for 1 min followed by irradiation in a microwave reactor with continuous rotation for the time listed in the table. Upon completion of the reaction monitored by TLC (*n*-hexane : ethyl acetate, 3 : 1), the products were extracted from the surface of K-10 or KSF clay with methylene chloride (30 mL) followed by filtration. The combined organic fractions were treated with aqueous NaOH, water, and dried by sodium sulphate. The solvent was removed under reduced pressure. The crude reaction mixture was analyzed and purified according to conventional methods. $^1$H NMR and IR spectra of the products were identical to the corresponding reference data.

The studied process that involved K-10 or KSF clays and MWI provided the general procedure for highly selective method of esterification. The most important advantages of this method are mild reaction conditions and high reaction rate. Montmorillonite K-10 and KSF catalysts make the process inexpensive, solvent free, non-toxic, and environmentally friendly.

## REFERENCES

1. *Esterification: Methods, Reactions, and Applications.* Otera, J., Weinheim: Wiley-VCH, 2003; Larock, R.C., *Comprehensive Organic Transformations*, 2nd ed., VCH: New York, 1999; Franklin, A.S., *J. Chem. Soc., Perkin Trans.,* 1999, vol. 1, p. 3537; Iranpoor, N., Firouzabadi, H., Khalili, D., and Motevalli, S., *J. Org. Chem.,* 2008, vol. 73, p. 4882; Soltani Rad, M.N., Behrouz, S., Faghihi, M.A., and Khalafi-Nezhad, A., *Tetrahedron Lett.,* 2008, vol. 49, p. 1115; Nowrouzi, N.,

Mehranpour, A.M., and Ameri Rad, J., *Tetrahedron*, 2010, vol. 66, p. 9596; Sarpong, R. and Heller, S.T., *Tetrahedron,* 2011, vol. 67, p. 8851.

2. Chen, C.-T. and Munot, Y. S., *J. Org. Chem*., 2005, vol. 70, p. 8625; Yang, C.- G. and He, C., *J. Am. Chem., Soc*. 2005, vol. 127, p. 6966; Nowrouzi, N. and Alizadeh, S.Z., *Tetrahedron Lett.,* 2013, vol. 54, p. 2412.
3. Nasreen, A., *Synlett*, 2001, p. 1341; Kaur, N. and Kishore, D*., J. Chem. Pharm. Res.,* 2012, vol. 4, no. 2, p. 991.
4. Lasszlo, P., *Science,* 1987, vol. 235, p. 1473; Baghernejad, B., *Lett. Org. Chem.* 2010, vol. 7, p. 255.
5. *Microwave-Assisted Organic Synthesis.,* Lidstrom, P. and Tierney, J.P., Eds., Oxford: Blackwell, 2005; *Microwave Methods in Organic Synthesis*, Larhed, M. and Olofsson, K., Eds., Berlin: Springer, 2006; Dallinger, D. and Kappe, C.O., *Chem. Rev.,* 2007, vol. 107, p. 2563; Belov, P., Campanella, V.L., Smith, A.W., and Priefer, R., *Tetrahedron Lett.,* 2011, vol. 52, p. 2776.
6. Habibi, D. and Marvi, O., *Chinese J. Chem*., 2008, vol. 26, p. 522; Marvi, O. and Giahi, M., *Bull. Korean Chem. Soc*., 2009, vol. 30, p. 2918. Marvi, O. and Nikpasand, M*., Lett. Org. Chem*. 2013, vol. 10, p. 353.
7. Woods, H.J., US Patent 4 042 633, August 16, 1977.
8. Prolabo, Fr., Patent 62241/D, 14669 FR, December 23th 1991; R. Commarmot, R. and Didenot, G., JF Rhône-Poulenc/Prolabo Patent number 84/03496, October 27, 1986.