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Full Paper

Catalytic Olefin Hydroalkoxylation by Nano Particles of Pollucite

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The catalytic hydroalkoxylation of α,β-unsaturated esters, nitriles, and ethers with aliphatic and aromatic alcohols over pollucite using thermal and microwave-assisted methods was investigated. To study the effect of the alcohol structures on the mechanism of the hydroalkoxylation reaction, different alcohols, such as methanol to butanol, cyclohexanol, phenol, and 2-ethylhexanol were used. The activities of pollucite, in contrast to other basic solids, were scarcely affected by the presence of air and moisture. The correlation between alcohol acidity and reaction activity is discussed. The prepared pollucite was characterized by X-ray diffraction, volumetric nitrogen adsorption surface area analysis, and CO_2 temperature-programmed desorption. Scanning electron microscopy analysis revealed that the size of the modified nano catalyst particles was under 40 nm.

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Introduction

The catalytic nucleophilic addition of alcohols to olefins, hydroalkoxylation, has been of interest to synthetic and medicinal chemists because of the formation of key compounds, which consist of C–O bonds, that have importance in biological research and industrial fields.[1–3]

The intermolecular hydroalkoxylation of unactivated olefins with different alcohols for the synthesis of different types of new ethers has been recognized and employed by several research groups to improve synthesis techniques.[4–6] One of the most important applications of these synthetic compounds is fuel ethers, which are added to gasoline as oxygen-bearing compounds. Direct addition of ethanol to gasoline increases the risk of corrosion and phase separation problems.[7] For this reason, it could be converted into value-added molecules such as ethers by reacting with alkenes.[8] On the other hand, addition of the oxygenated compounds to the gasoline can decrease harmful exhaust emissions and increase octane rating.[9] Classic catalysts that have been used in hydroalkoxylation reactions are strong acids[10–19] and bases such as phosphines and amines.[20,21] For example, vapour phase synthesis of ethyl *tert*-butyl ether from ethanol and isobutene over different acidic zeolites as heterogeneous catalysts has been reported by Collignon and Poncelet.[22] In the presence of acids, the stability of the carbocation intermediate controls the regioselectivity of the reaction products,[23,24] and the yields of reactions are ~50 %. In this situation, polymerization and rearrangement of alkenes could occur. On the other hand, a series of non-toxic industrial solvents, such as ethyl 3-ethoxypropanoate (EEP) and methyl 3-methoxypropanoate (MMP), can be obtained from the reaction of alcohols with methyl and ethylacrylate in the presence of a strong acidic catalyst.[25,26] Strong basic catalysts, such as alkali metal alkoxides and basic anionic resins, have been reported for preparing of EEP.[27] Likewise, low conversion and poor selectivity are the main problems in using such soluble catalysts. So, various hydroalkoxylation catalysts based on different metals such as Cu,[28–30] Ag,[31] Au,[32–36] Ru,[37,38] Rh,[39] Pd,[40–45] and Pt[46–49] have been developed to overcome the limitation of using acid base catalysts and to achieve the more selective products. There are several reports of hydroalkoxylation of olefins on heterogeneous catalysts such as anion exchange resins,[50–54] zeolites,[55–57] alumina-supported KF,[58] modified layered double hydroxides (LDHs),[59–64] and aluminium-exchanged montmorillonite clays.[65]

Strong basic catalysts are not suitable for hydroalkoxylation of sensitive unsaturated compounds, such as acrylate esters, so choosing a well-balanced base is essential for achieving the selective products. Published papers showed that caesium salts can provide this balance,[66] and for this reason they are very suitable for use in organic syntheses such as C–C, C–O, C–N, C–P, and C–S bond formation.[67–71] Pollucite is an ANA-type zeolite with distorted 8-ring pores. Pollucite, the most important caesium-bearing ore, is a caesium alumino silicate ($CsAlSi_2O_6$) zeolite. Pollucite, unlike the alkali metal alkoxide or anionic basic resins, is not sensitive to moisture and can be used as a basic catalyst several times without loss in activity.

In this paper, we prepared the above-mentioned ether compounds by the reaction of activated olefins with alcohols over nano-sized pollucite zeolite. In our previous work, we reported a simple method of the preparation of nano-sized pollucite,[72] and here we investigated its catalytic activity for hydroalkoxylation of ethyl acrylate (EA), methyl acrylate (MA), acrylonitrile (AN), and isobutylvinyl ether (IBVE). As mentioned above, methanol and ethanol are the most common alcohols that are used in industrial etherification. For expanding the application of this heterogeneous catalyst, other alcohols, such as propanol, cyclohexanol, phenol, and 2-ethylhexanol were used in hydroalkoxylation reactions.

Experimental

Materials

All the reagents were used without further purification. Pollucite was prepared as we reported in the previous work.[72] Before running the catalytic test, pollucite was dried overnight at 100°C and calcined at 600°C for 4 h.

Reaction Procedure

Alcohols (38 mmol, excess amount), olefin (9.5 mmol), and the catalyst (0.03 g) were reacted in a suitable vessel. No additional solvent was used except for the reaction of phenol.

For reactions performed under reflux conditions, a 10-mL two-neck round-bottom flask equipped with a reflux condenser and argon inlet and for reaction under autogenously pressure a 5 mL, a high pressure stainless steel reactor was used. Reactions with microwave irradiation were performed in a 15 mL polytetrafluoroethylene (PTFE) container at 900 W for 30 min. After the reaction, the solid catalyst was separated by centrifugation (5040 *g* for 5 min) and the products were analyzed by gas chromatography mass spectrometry (GC–MS). Conversions were determined by using *o*-xylene as an internal standard. In some cases, the used catalysts were washed with ethanol, dried at 100°C overnight, and calcined at 300°C for 4 h. Catalytic reactions were performed three times in the presence of the recovered catalysts that showed no loss in activity.

Characterization

The structure and phase purity of synthesized pollucite was monitored by powder X-ray diffraction (XRD). A Bruker D8 advance diffractometer using $\mathrm{Cu_{K\alpha}}$ radiation was used. The scanning range of 2θ was set between 5° and 50°. N_2 adsorption–desorption isotherms were performed at −196°C by a BELSORP mini-II surface area measurement equipment after degassing the samples under vacuum at 300°C overnight. The surface area of the pollucite sample was obtained using the BET (Brunauer–Emmett–Teller) methodology. The surface morphology of the catalysts was obtained on a Zeiss DSM 960 A scanning electron microscope, with an accelerating voltage of 15 kV.

Temperature-programmed desorption (TPD) of the synthesized catalyst was carried out using CO_2 as a probe for determining the number and strength of active basic sites. CO_2-TPD analysis was performed on a ChemBET-3000 Quantachrome instrument. The temperature-programmed desorption ramp of the chemically adsorbed CO_2 was as follows: from 50°C to 1000°C with a heating rate of 10°C $\mathrm{min^{-1}}$ using helium as carrier gas. The sample (0.103 g) with a particle size of 60–80 μm was located in a plug flow quartz reactor that was coupled with a thermal conductivity detector (TCD). The catalyst sample was degassed under a nitrogen flow (10 mL $\mathrm{min^{-1}}$) at constant heating rate (10°C $\mathrm{min^{-1}}$) to 500°C, and held at the final temperature for 1 h. Then, a stream of He/CO_2 with a 19 : 1 feed ratio was passed over the catalyst bed for 20 min at 50°C and finally flushed with helium flow for 1 h. To identify and determine the purity of products, a mass spectrometer (model 5975C) with a triple- axis detector and a gas chromatograph, Agilent 7890A, coupled with a HP-5 capillary column and a flame ionization detector (FID) was used.

The caesium content of the catalysts was determined using an inductively coupled plasma optical emission spectroscopy (ICP–OES; Varian Vista-MPX). This sample contained 40.2 % of caesium.

Microwave reactions were carried out using a Samsung domestic oven, operating at 2.45 GHz in a 15 mL PTFE closed container.

Results and Discussion

The XRD diffraction pattern of the as-synthesized pollucite is shown in Fig. 1. All peaks are well matched in position and relative intensity to a standard XRD pattern for crystalline pollucite (PDF No. 29–0407, International Center of Diffraction Data (ICDD), Newton Square, PA). The diffraction pattern showed that the sample was monophasic with no traces of other phases. No peaks at $\sim 2\theta = 27°$ were recorded in ICDD standard 29–0407. This peak is related to the excess of caesium ions that was shown in Fig. 1.

The surface area and pore volume of the synthesized pollucite were 194 $\mathrm{m^2\,g^{-1}}$ and 0.02 $\mathrm{cm^3\,g^{-1}}$, respectively. The basic character of pollucite in comparison with NaY zeolite was confirmed by CO_2 temperature-programmed desorption. This technique is a suitable tool for obtaining information about the activity and distribution of active sites in zeolites. In Fig. 2, the TPD profile for pollucite was shown and compared with that of zeolite NaY. The first maxima of pollucite appeared at 580°C,

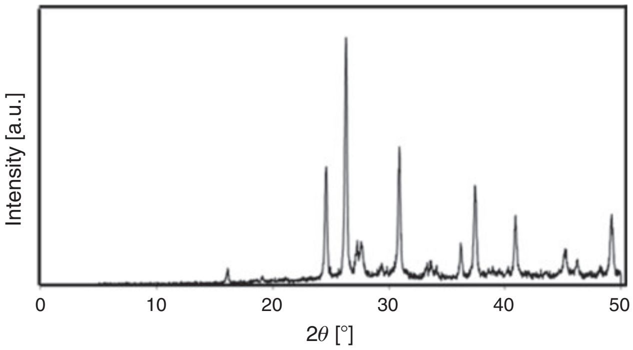


Fig. 1. Powder X-ray diffraction patterns of as-synthesized pollucite.

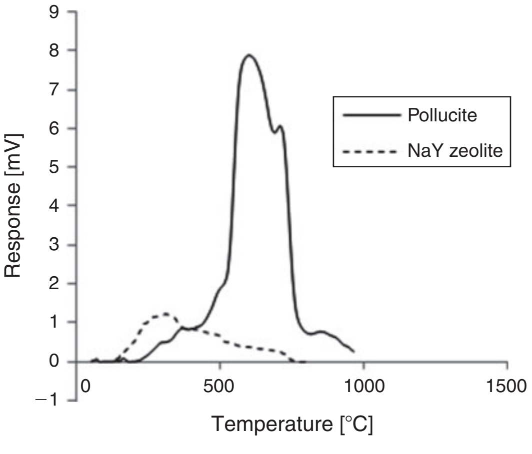


Fig. 2. Comparison of the temperature-programmed desorption profiles of adsorbed CO_2 onto the synthesized pollucite and NaY zeolite.

which is much higher than that of NaY zeolite (263°C). The higher maxima for the CO_2 desorption temperature and the peak area of pollucite catalyst confirm that the prepared zeolite has a higher basicity and a higher concentration of basic sites with respect to NaY zeolite.

The scanning electron microscopy (SEM) image of the prepared pollucite shows uniform particles with sizes below 50 nm, Fig. 3.

The prepared catalyst was tested in hydroalkoxylation reactions, Scheme 1. This catalyst has enough basicity to catalyze reactions of alcohols with ethyl acrylate, methyl acrylate, acrylonitrile, and isobutylvinyl ether.

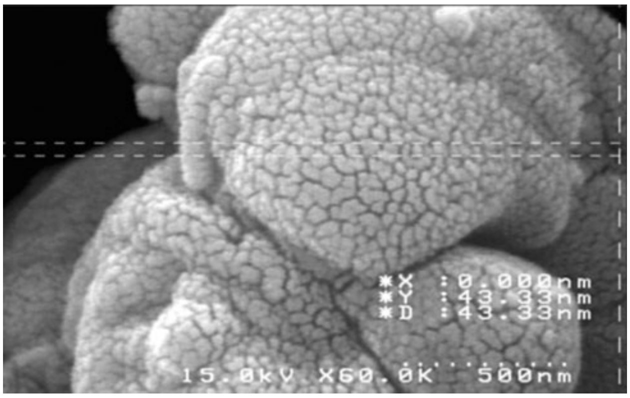
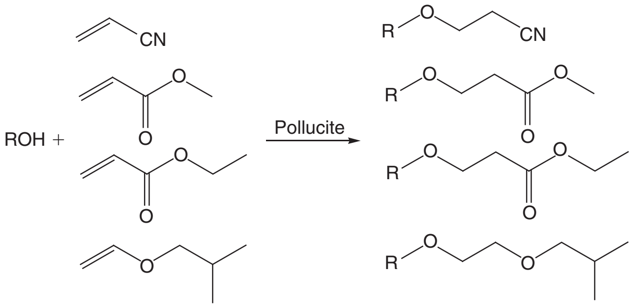


Fig. 3. Scanning electron microscopy image of synthesized pollucite.



R = CH_3, C_2H_5, C_3H_7, C_4H_9, Phenyl, Cyclohexyl, 2-Ethylhexyl

Scheme 1. Hydroalkoxylation reaction of activated alkenes with different alcohols.

The results of the hydroalkoxylation reactions are summarized in Table 1. Reactions were performed under reflux conditions and also under autogenous pressure in a high pressure stainless steel reactor.

The conversions of alkenes in hydroalkoxylation reaction with alcohols were influenced by the acidity of alcohols, the electron density on the C=C and the catalyst basicity. Alcohols were activated after deprotonation by surface of basic catalyst and converted into alkoxides. The resulting alkoxide was attacked to C=C of the surface-adsorbed alkene to produce the product. According to the mechanism, Scheme 2, the rate of the deprotonation step increased with acidity of alcohols. As it was shown in Table 1, the linear alcohols have reactivity in the order of methanol > ethanol > propanol > butanol, which is consistent with the acidity strength of the alcohols. This means that the more acidic alcohol show more activity in reaction with alkenes. The performance of basic catalysts in abstracting the hydrogen atom from the hydroxyl group of alcohol is the first step of the hydroalkoxyation reaction (step 1, Scheme 2). In step 2, the alkene was adsorbed onto the catalyst surface and affected by the high electrostatic field of the caesium ions in pollucite.

So, an electron-deficient centre at the β-carbon of the alkene was formed and the produced alkoxide was attacked to this positive centre. This new produced anion picks up the hydrogen atom from surface of catalyst that was adsorbed in the first step (step 3, Scheme 2), and finally the product was formed.

All the types of alkenes used in this study showed better reactivity in the presence of the prepared nano pollucite catalyst with respect to other basic or acidic catalysts such as alkali metal alkoxides, anionic resins, sulfonic acids, and phosphoric acids derivatives.[25–27] Low conversion and poor selectivity are the main problems associated with the use of these types of soluble catalysts. On the other hand, using expensive catalysts based on transition metals has no advantages from an economic point of view in comparison with pollucite.[31,32,37–40,46]

The adsorption of olefin onto the surface of basic catalysts is an important step for hydroalkoxyation reaction. Olefins with low polarity show lower affinity to adsorption onto the surface. Isobutylvinyl ether showed lower reactivity in comparison with acrylates in the reaction with linear alcohols that is probably related to its lower polarity and lower attraction for adsorption onto the surface. In this case, the lowest acidity of butanol leads to the production of the alkoxide anion with a more negative charge density. So the existence of repulsive forces between the alkene group and alkoxide anion leads to lower reactivity in this

Table 1. Conversion of different alkenes in the presence of pollucite in various reactions with alcohols

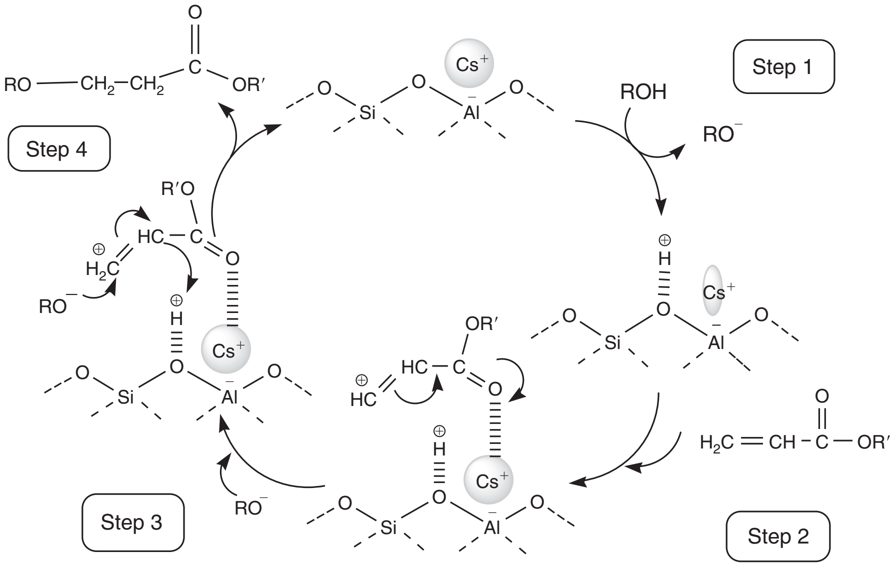
RF, reflux; AC, autoclave

Alcohol	Acrylonitrile		Methyl acrylate		Ethyl acrylate		Isobutylvinyl ether	
	RF[A] [%]	AC[B] [%]	RF[A] [%]	AC[B] [%]	RF[A] [%]	AC[B] [%]	RF[A] [%]	AC[B] [%]
Methanol	99.7	99.9	76.2	98.3	88.2	96	32	63
Ethanol	99.1	99.9	65.3	98.2	58.4	87	16	25
Propanol	99.5	99.9	53.5	87.4	47.6	81	30	57
Butanol	95.1	99.9	41.9	69.7	40.7	62	14	22
2-Ethylhexanol	3	5	8	14	6	11	54	86
Cyclohexanol	2	11	4	9	2	8	22	32
Phenol[C]	75	99.9	55	99	79	99	75	99

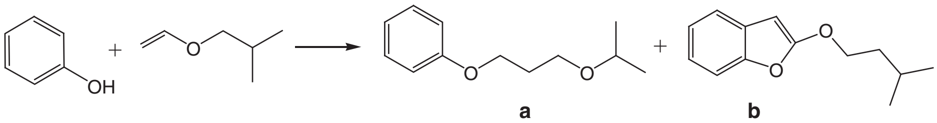
[A] Reaction conditions: alcohol (38 mmol), olefin (9.5 mmol), pollucite catalyst (0.03 g), reflux, 12 h.

[B] Reaction conditions: alcohol (38 mmol), olefin (9.5 mmol), pollucite catalyst (0.03 g), reaction in autoclave, 170°C, 12 h.

[C] Toluene was used as solvent.



Scheme 2. Plausible mechanism for hydroalkoxylation of acrylates with alcohols.



Scheme 3. Products of hydroalkoxyation reaction of isobutylvinyl ether with phenol.

reaction, even under high temperature conditions in an autoclave system.

Our prepared catalyst showed 100 % selectivity for producing phenyl ester as the main product in the reactions of phenol with acrylates, whereas in the reaction of IBVE with phenol, phenyl ether (**a** in Scheme 3) was produced with 88 % and 71 % selectivity under reflux conditions and in autoclave system, respectively. In this reaction, related benzofuran (**b** in Scheme 3) was produced as the minor product. There are some reports for the reaction of phenol with olefins for producing benzofurans and cumarines as the main products over transition metal catalysts under acidic conditions.[73–76] Also, there is a report for using alkali metal catalysts for producing phenol esters as the main products.[77]

Phenol showed better conversion than cyclohexanol as shown in Table 1. Phenol is more acidic and the phenoxide ion was stabilized by resonance effect. It seems that the basicity of pollucite is not enough to catalyze the reaction of cyclohexanol with acrylates. The more basic and acidic catalysts, such as sodium oxide or sulfuric acid derivatives, have been reported for the related cyclohexanol reaction.[78,79] Cyclohexanol showed only a moderate yield with IBVE. Probably reaction of cyclohexanol is very slow, then the heat-sensitive acrylates polymerized during the course of the reaction.

As we mentioned before, pollucite is an ANA-type zeolite with distorted 8-ring pores and classified as small pore zeolites. It seems that cyclohexanol and 2-ethyl hexanol cannot enter the pollucite small pores, and their activation was done only by surface basic sites. So, the reactivity of this catalyst is not enough to catalyze these two alcohols for reaction with the desired alkenes and low conversions were observed. On the other hand, the polymerization of acrylates occurred when we used 2-ethyl hexanol as the reactant. Polymerization of acrylates also occurred when the reaction was done at high temperature and pressure. Normally, using polymerization inhibitors, such as methyl hydroquinone, nitrophenol, phenothiazine, and ferrous ions can inhibit polymerization.[80] In this paper, we used $FeSO_4$ to inhibit free radical polymerization by trapping free radical intermediates. So, in the presence of ferrous ions we achieved low conversions for AN, MA, and EA. It is interesting to consider that the large alcohol, 2-ethylhexanol, is only successfully added to isobutylvinyl ether in the presence pollucite in an autogenously pressure system with 86 % conversion.

Table 2. Conversion [%] of different alkenes in the presence of pollucite in various reactions with alcohols using microwave irradiation

Alcohol	Acrylonitrile	Methyl acrylate	Ethyl acrylate	Isobutylvinyl ether
Methanol	98	52	47	0
Ethanol	77	38	33	0
Propanol	64	38	29	0
Butanol	0	0	0	0
Phenol	0	0	0	0

To improve the reactivity and reduce the reaction time, a microwave-assisted technique was employed for some hydroalkoxylation reactions. The use of a microwave oven is convenient and cleaner when compared with other experimental conditions. Results of the microwave-assisted hydroalkoxylation reactions are summarized in Table 2.

The higher dielectric constant of methanol ($\varepsilon = 32.7$) in comparison with that of ethanol ($\varepsilon = 24.3$), propanol ($\varepsilon = 20.1$), or butanol ($\varepsilon = 19.5$) leads to a higher reactivity under microwave irradiation. Isobutylvinyl ether has a lower dielectric

Table 3. Conversion of acrylonitrile in the reaction with phenol using microwave irradiation and in the presence of different solvents

Solvent	Time [min]	Conversion [%]
Toluene	15	0
	30	0
DMF	15	38
	30	72
DMSO	15	28
	30	50

constant ($\varepsilon < 4$) than MA ($\varepsilon = 7.03$), EA ($\varepsilon = 6.5$), and AN ($\varepsilon = 33.0$). According to the value of dielectric constants, we expected a higher conversion for the reaction of methanol with acrylonitrile as shown in Table 2. No products were found when alcohols were reacted with IBVE due to the very low dielectric constant of IBVE. Phenol was unreactive under our experimental conditions when toluene was used as the solvent.

To investigate the solvent effect on the reaction of phenol with acrylonitrile, we repeated this reaction in the presence of DMSO and DMF. As shown in Table 3, the higher dielectric constants of DMSO ($\varepsilon = 46.7$) and DMF ($\varepsilon = 36.7$) have a positive effect on the reaction reactivity. So, for the first time, we achieved the acceptable conversion for this reaction using a simple microwave method.

Conclusions

Pollucite is an active heterogeneous catalyst for hydroalkoxylation of activated alkenes such as AN, MA, EA, and IBVE with alcohols. The activity of this catalyst, unlike other basic solids, was scarcely affected by the presence of air or moisture. The reaction activity in addition to the catalyst basicity were affected by the alcohol acidity. So, the highest conversions were observed for the reaction of methanol with alkenes. On the other hand, acrylates show higher conversion in comparison with IBVE when linear alcohols were used, but the heavier alcohols, such as cyclohexanol, 2-ethylhexanol, and phenol, showed higher reactivity with IBVE with respect to the acrylates.

The SEM images of all the catalysts showed particles with sizes of <50 nm. Using microwave irradiation, the reaction times of chosen alkenes with different alcohols were reduced to 30 min with good yields in the presence of pollucite.

Supplementary Material

Mass spectra and a GC chromatogram are available on the Journal's website.

Acknowledgement

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