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Study on Application of Functionalized Ionic Liquid in Fine Organic Synthesis

Xuezhen Li, Wenjing Han, Shulan Yu, Fang Zou

Weifang Vocational College, Weifang 261041, China
xuezhenli6689@126.com

This study is to discuss the application of functionalized ionic liquid in fine organic synthesis. Functionalized ionic liquid oligomer is selected as the research object, and its application effect in styrene epoxy reaction is studied. It is found that the size of nanogold particles is in the range of 10nm, and temperature and oxidant dosage will affect the action of functionalized ionic liquid. The styrene conversion rate can reach 100% when the catalyst is under the most reactive conditions. The conclusion has been drawn that the thioether functionalized ionic liquid has the research and application value in the styrene oxidation reaction.

1. Introduction

Instructions:
Green chemistry is a kind of harmless chemistry based on green innovative technology, which hardly causes harm to environment and has certain application value in environmental pollution. In the process of green chemistry research, functionalized ionic liquid have gradually aroused people's attention and become one of the hot topics. Ionic liquid has certain stability, which is beneficial to the stability of air or water environment. Compared with other common organic solvents, many kinds of ionic liquid will decompose when they are raised to a certain temperature and have good thermal stability. In addition, functionalized ionic liquid can't be burned and has certain safety in the practical application process. Functionalized ionic liquid can play a great role in environmental pollution, so many scholars at home and abroad have explored the application of this ionic liquid. Based on this, this study mainly takes the oligomer functionalized ionic liquid as the research object, and uses the styrene reduction reaction to conduct research analysis on the reagent catalysis. This study first introduces the functionalization of ionic liquid, and then discusses the materials, equipment and methods used in the experiment. According to the experimental results, it analyzes the catalytic performance of functionalized ionic liquid, and investigates the catalytic action by fixing the characterization results of nanogold particles, the dosage of oxidant and the temperature so as to judge whether the catalyst has the research value.

2. Literature review

Ionic liquid is a room temperature molten salt. It is used as a green solvent in many organic synthesis reactions. Polyether is also used as a solvent for many reactions. Ionic liquids and polyether are two kinds of liquids that have similarities but have their own characteristics. They combine these two substances together to get polyether functionalized ionic liquids.
Binder and others report that the glass transition temperature of polyether functionalized ionic liquids is related to the length of polyether chain, the cation structure and the type of anionic groups. The size of lattice energy depends on the intermolecular interaction, intramolecular interaction and the degree of freedom of anions and cations. Cecchini and others pointed out that the length of polyether chain of polyether functionalized ionic liquids has an important influence on melting point (Cecchini et al., 2014). The melting point of polyether functionalized ionic liquid increases with the increase of polyether chain. The melting point is not observed in the polyether chain functional ionic liquids, because the high degree of freedom of polyether chains hinders

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crystallization. However, the melting point of polyether chain functional ionic liquids increases with the increase of ether alkyl groups.

Multi component organic synthesis has good atomic economy in the synthesis of heterocyclic and complex structural compounds. Godajdar and Soleimani synthesized other compounds by one pot method to synthesize indazole derivatives, which are synthesized in a solvent free condition with a polyethylene glycol double cation ionic liquid (PEG-MRTDIL) as a catalyst. Under the condition of 100 C, the yield of 20min can reach 90%. The method showed good environmental friendliness, high yield, simple working process and recyclable catalyst (Godajdar and Soleimani, 2015).

Wang and other reports have reported a new type of poly (ethylene glycol) that connects the N, N- two methyl amino pyridine with the functionalized double cation ionic liquid ([DMAP-PEG-1000-DIL] [BF4]). 3,4- two hydropyran and [3,2-c] benzo - pyran derivatives were synthesized by one pot reaction by three components of aromatic aldehyde, propylene two nitrile and 4- hydroxyl coumarin, with excellent yield. The system has mild reaction conditions, flexible application, simple operation and environmental friendliness. In addition, the catalyst can be reused several times without any obvious catalytic activity loss (Wang, et al., 2016).

Hu and others reported that the polyether functional ionic liquid (PEG600 - DAIL) series of ionic liquids and toluene were composed of a temperature-controlled phase system, and chloromethyl -4- benzoethers were hydrolyzed under the catalysis of CuSO4. The results show that the greater the molecular weight of the ionic liquid is, the more obvious the catalytic effect is, because the larger the molecular weight, the better the compatibility of the ionic liquid to the substrate, and the more binding sites for the catalyst, which can promote the reaction. After the reaction is completed, the catalyst and product are separated easily. The catalyst can be reused for 8 times and the loss rate is only 5.7%.

Lv and other polyether imidazole functional ionic liquid 1- butyl -3- polyethylene glycol imidazole four carbonyl cobalt containing carbonyl cobalt was synthesized by ion exchange reaction and was applied to the preparation of 2- (4- isobutylphenyl) methyl propionate by catalytic hydrogenation of 1- (4- isobutyl phenyl) ethanol (IBPE). The conversion of IBPE reached 100%, the catalyst could be reused for 5 times, and the catalytic activity did not decrease significantly (Lv et al., 2016).

Wang reports that polyether functionalized ionic liquids are used as ligands for palladium catalyzed Suzuki-Miyaura reactions. The experimental results show that the conversion rate is only 29% and the catalytic effect is not ideal without the participation of ionic liquids. With the participation of ionic liquids, the conversion rate increased significantly. When the ionic liquid is [salox-PEG1000-DIL] [PF6], the conversion rate is 90% and the ionic liquid is [salox-PEG1000-DIL] [BF4], the catalytic effect is best and the conversion rate can reach 94%. Under the optimum reaction conditions, the catalytic system can be recycled 5 times and the conversion rate is over 81%, which is also effective for other coupling reactions (Wang et al., 2013). By synthesizing polyether functionalized bimidazole ionic liquids, it was applied to the silylation reaction of olefins. The results show that the degree of polymerization of polyether chain is different from that of rhodium complex. When the reaction temperature is 90, the conversion and selectivity are the highest, and the recycling of the catalyst can reach more than 6 times.

Zeng and others used polyether ionic liquids which have the characteristics of temperature control. A temperature controlled organic biphasic catalytic system has been constructed. At room temperature, the two phases state is presented. At a high pressure, the homogeneous reaction system is formed after heating to a certain temperature. The reaction can be carried out quickly. The reaction becomes two phases after cooling and pressure relief. The catalyst remains in the polyether to function the ionic liquid phase, and the reaction product remains in the organic phase (Zeng et al., 2012).

Jin and others reported a class of polyether guanidine ionic liquids. The polyether functionalized ionic liquid, under the participation of TPPTS, forms an active species with RhCl3? 3H2O to catalyze hydroformylation of olefins. The experimental results show that under the polyether guanidine ionic liquid / organic two-phase catalytic system, the cycle utilization of the catalyst in the hydroformylation of 1- octyl catalyzed by rhodium can reach 35 times, showing the super long service life, the lowest rhodium loss 0.04%, and the cumulative TON value up to 30 thousand (Jin et al., 2012).

Liu and others reported that the polyether functionalized imidazolium salt ionic liquid and the transition metal ruthenium complex were used to catalyze the asymmetric hydrogen transfer reaction of ketones. The cation of ionic liquid can regulate the temperature control performance, while anion provides the catalytic active center of the hydrogen source of ketone body. [PEG-4000-C8MIM] [Ru-TsDPENDS] was used as catalyst and ethyl acetate as solvent to build a temperature-controlled phase separation catalyst system. The catalytic system has a good catalytic effect on aromatic ketones, with acetophenone as the substrate, the conversion rate can reach 97%, and the corresponding selectivity is up to 96%. The reaction system showed good application prospects in the separation and recovery of catalysts (Liu et al., 2015).

To sum up, the above research work is mainly about the study of the recovery and utilization of the catalyst in the ionic liquid two phase catalytic system. However, in the two-phase catalytic system, a great number of ionic liquids are needed as the carrier of the catalyst, and the dissolution or diffusion of olefin into the ionic liquid will meet with the catalysis of the active species. Resistance to mass transfer leads to a decrease in catalytic activity and selectivity. Therefore, based on the above research status, this paper mainly aims at the need to add a great number of other ionic liquids as a carrier. A new type of phosphine reactive power polyether ionic liquid is synthesized by a simple ion exchange reaction with the sulfonic Water-soluble Phosphine Ligands and polyether functionalized ionic liquids. The amount of ionic liquid is reduced to the minimum, thus solving the problem of low catalytic activity of two-phase system.

3. Methods

3.1 Functionalization of ionic liquid

Ionic liquid is a kind of special liquid molten salt that has excellent physical and chemical properties, and modified and modulated structure of anion and cation, and can be recycled. Ionic liquid is referred to as “designer’s solvent”. Ionic liquid designed to meet specific requirements is functionalized ionic liquid, including functionalization for physical properties and chemical properties (polarity, acidity, chirality, coordination capability). In recent years, the functionalized ionic liquid with modified chemical properties has been paid more and more attention. The introduction of different functional groups has realized the specific functional requirements of ionic liquid. In 2002, some scholars synthesized a kind of functionalized ionic liquid containing hydroxyl so that the capability of ionic liquid to dissolve LiCl, HgCl2, LaCl3 is greatly improved. The ionic liquid containing phosphoric acid acetate group in the alkyl chain has a very good lubricating function. Bronsted acidic ionic liquid can be easily obtained by using halogenated carboxylic acid. The acidic ionic liquid of carboxylic acid has been used to carry out some acidic catalytic reactions in place of the traditional Bronsted acid. The sulfonic ionic liquid is now the most acidic Bronsted acidic ionic liquid [34]. The ionic liquid with alkenyl, alkynyl, and benzene ring and cyan at the chain end has been reported. These kinds of functionalized ionic liquid form complexes with different metals respectively and have good catalytic properties. Ionic liquid can replace traditional inorganic base to catalyze Michael addition reaction. Based on the property that mercapto group and disulfide bonds are easy to form unique Au-S bonds with gold atoms, ionic liquid containing mercapto group and disulfide bonds synthesizes Au and Pt nanoparticles with a certain size.
Functionalized ionic liquid is ionic liquid that is synthesized according to specific needs and its chemical properties are generally modified. In recent years, more and more attention has been paid to functionalized ionic liquid. The introduction of different functional groups has realized the specific functionalized needs of ionic liquid. Ionic liquid containing chiral centers, protonic acid, and hydroxyl radicals, as well as ionic liquid with ligand properties has been reported. Most kinds of ionic liquid are obtained by functionalization of cationic alkyl chains mainly because the synthesis process is mature, the commonly used alkylation reaction effect is good, and the kinds of functional groups that can be introduced are relatively wide, including hydroxyl, ether group, mercapto group, carboxylic acid group, sulfonic acid group, cool group and acid amine. The anionic part of ionic liquid is usually a relatively small -1-valent inorganic or organic anion. The range of anionic structural modulation is relatively small and the structure of organic anions is more easily changed. However, the types of functional groups that can be introduced are relatively limited due to the relatively complex synthesis process. Anionic functionalized ionic liquid is usually obtained by anion substitution reaction mainly by reaction of corresponding monovalent salts, such as potassium, sodium and silver with ionic liquid precursors in which anions are halogen. And the reaction is promoted by low dissolution of halides in organic solvents such as acetone or acetonitrile. The flexibility of structural modulation of ionic liquid makes it possible to introduce two or more functional groups into the same ionic liquid. Several functional groups make ionic liquid have different properties, which raises higher requirements for adjusting functional groups of different properties so that they don’t interfere with each other and show their own advantages.

3.2 Preparation of functionalized ionic liquid

Ionic liquid, especially Misi ionic liquid, has the properties of no vapor pressure, low toxicity, high chemical stability and thermal stability. It is functionalized ionic liquid with special properties can be easily obtained by modulating the structure. Due to the Ostwald maturation effect, the low interfacial tension of ionic liquid accelerates the nucleation rate and yields small-sized nano particles. Thus, ionic liquid is suitable for the developing efficient and environmentally friendly metal nano particle catalytic systems. (Main reagents and instruments for the experiment are listed in Table 1 and Table 2)

Table 1: Main reagent of the experiment

The reagent	The purity	source
[bmim]PF_6		homemade
M-CPBA	Analysis of pure	ACROS
acetone	Analysis of pure	Reagent factory of hunan normal university
B eyes	Analysis of pure	Reagent factory of hunan normal university
styrene	Analysis of pure	China pharmaceutical group chemical reagent co. LTD
n-hexane	Analysis of pure	Reagent factory of hunan normal university
Methylene chloride	Analysis of pure	Tianjin da MAO chemical reagent factory
methanol	Analysis of pure	Shanghai chemical reagent co. LTD
Gold acid	Analysis of pure	China pharmaceutical group Shanghai chemical reagent co. LTD
Sodium borohydride	Analysis of pure	Tianjin fuchen chemical reagent factory
styrene	Analysis of pure	China pharmaceutical group Shanghai chemical reagent co. LTD

Table 2: Main instruments and equipment

The name of the instrument	model	manufacturer
Gas chromatograph	Agilent-6890N	AgilentTeehnologie
Vacuum drying oven	DZF-6020	Gongyi yinyu to China instrument factory
Electronic scale	DL30	Mederle tolido instrument (Shanghai) co. LTD
	DF-10IB	Zhejiang yueqing electric appliance factory
Magnetic stirrer	DF-101	Gongyi yinyu to China instrument factory
	85-2	Shanghai si le instrument co. LTD
Rotary evaporator	RE-300	Shanghai arong biochemical instrument factory
	R201D-11	Zhengzhou Great Wall science and trade co. LTD

3.3 Characterization methods

Uv-vis characterization: UV spectrogram of 400-700 nm is taken on an Agilent 8453 UV spectrometer. TEM characterization is carried out on a JEOL JEM1230 type transmission electron microscope. Before testing, the samples are dispersed with ethanol by ultrasonic wave, and are directly photographed after drying on a copper wire mesh. The accelerating voltage is 100KV. Gaseous phase detection is carried out on an Agilent Technofogies 6890 gas chromatograph. The detection conditions are: HP-5 capillary column (30mx0.32mmxo.25μm), FID detector, air carrying gas, flow rate of 30mL/min, sample injector temperature, vaporizing chamber temperature and column temperature are maintained at 250^{0}C, 250^{0}C and 100^{0}C respectively.

4. Results and Discussion

4.1 Characterization rwsults of nanogold particles immobilized in oligomer ionic liquid

Figure 1 is an ultraviolet spectrum of GNPs-TFIL prepared in [bm] PF_6. It can be seen from the figure that the surface plasmon absorption peak of the nanogold particles obtained in the ratio m] PF6 is 526 nm (Figure 1), indicating that the diameter of the nanogold particles prepared in the ratio m] PF6 doesn’t exceed 10n.

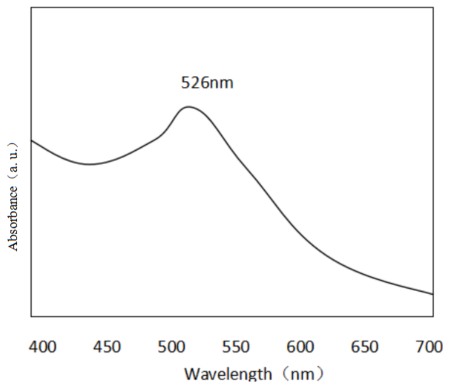

Figure 1: UV-viss Pectrum 0f the GN[Ps-TFIL PrePared in [bmimlPF6

In the absence of the catalyst nanogold, the conversion rate of epoxidation of styrene is 36% and the selectivity is 32% (Table 3, cntry 1) because the oxidant m-CPBA also induces the epoxidation of styrene in the absence of the catalyst. After adding the nanogold particles to the reaction system, the conversion rate and selectivity significantly change (Table 3, entry 2). Moreover, increasing the dosage of catalyst can increase the conversion rate of styrene. When the catalyst is increased to 48x10^{-3}mmol, the conversion rate reaches 1000% (Table 3, entry 6). It is worth noting that there is no significant change in selectivity of epoxide after increasing the dosage of catalyst nanogold (Table 3, entries 2-6). (Table 3 shows the effect of catalyst dosage on the epoxidation of styrene)

Table 3: Effect of catalyst dosage on the epoxidation of styrene

Entry	n(Au)(10^{-2}mmol)	eonversion^{c}(%)	seleetivity^{d}(%)
1^{b}	0	36	32
2	1.0	71	88
3	1.9	85	88
4	2.9	88	89
5	3.9	92	89
6	4.8	100	90

4.2 Effect of oxidant dosage

In the reaction system containing GNPs, the conversion rate of styrene and the selectivity of styrene oxide significantly improve (entries 2-7), indicating that GNPs have very good catalytic activity and styrene epoxide selectivity. As the molar ratio of oxidant m-CPBA to styrene increases from 1: 1 to 3: 1, the conversion rate of styrene increases to 100% while the selectivity of styrene oxide increases first and then decreases. When m-CPBA increases to 100%, the selectivity of styrene oxide reaches a maximum of 90% (entry4). The increase of the oxidant dosage contributes to the mutual contact between the catalyst and the reactants and the increased contact can promote the epoxidation reaction of styrene, so the conversion rate of styrene reaches 100% with the increase of the oxidant. However, the addition of excessive oxidant will lead to the deep oxidation of styrene epoxide, resulting in the decrease of selectivity of styrene oxide. (Table 4 shows the effect of oxidant dosage on the epoxidation reaction of styrene)

Table 4: The effect of oxidant dosage on the epoxidation of styrene

Entry	m-CPBA (mmol)	conversion^{b} (%)	seleetivity^{c} (%)
1	5	43	87
2	10	71	88
3	15	100	90
4	20	100	91
5	25	100	78
6	30	100	78

4.3 Effect of temperature on the epoxidation of styrene

Nanogold is taken as the catalyst. With the increase of the reaction temperature, the conversion rate of styrene increases while the selectivity of styrene epoxide first increases and then decreases. The styrene epoxide formed at higher temperatures is easy to produce phenylacetaldehyde or the oxidability of the oxidant is enhanced at high temperature, so styrene is directly oxidized to benzaldehyde. With the increase of reaction temperature, the conversion rate of styrene increases but the selectivity of styrene oxide has different trend. When the reaction time is 4h and reaction temperature increases from 0^{0}C to 45^{0}C, the selectivity of styrene oxide increases from 75% to 90% and then decreases to 79%. The reason may be that increasing the reaction temperature will cause the further oxidation or rearrangement of styrene oxide to produce corresponding benzaldehyde or phenylacetaldehyde, which will lead to the decrease of the selectivity of styrene oxide. (Table 5 shows the effect of temperature on the epoxidation reaction of styrene)

Table 5: effect of temperature on the epoxidation of styrene

Entry	Temperature(^{0}C)	conversion^{b}(%)	seleetivity^{c}(%)
1	0	59	75
2	15	100	90
3	30	100	81
4	45	100	79

5. Conclusions

This study deals with the catalytic effect of nanogold particles in fine organic synthesis by taking thioether functionalized ionic liquid as an example. It has been found that the catalyst used in this study has certain catalytic activity, the conversion rate of styrene can reach 100% under the best reaction conditions, and 90% has selected styrene oxide. The catalyst can be reused and has certain application research value. Nowadays, as green environmental protection has attracted more and more attention, green chemistry has gradually become the focus of many scholars. Through the analysis of the catalysis of functionalized ionic liquid in fine organic synthesis, it is found that the chemical material thioether can be made into green solvent, which has little harm to the environment and can play a certain role in the future environmental pollution improvement and prevention. Therefore, relevant researchers shall pay attention to this. This study mainly judges whether the selected material has catalysis through analyzing related data of the experiment research, so the experiment research results still need the practice testing to verify the correctness.

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