Heck reaction using nickel/TPPTS catalyst and inorganic base on supported ethylene glycol phase

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The vinylation of butyl acrylate and halobenzene was studied using the Ni/TPPTS (TPPTS: triphenylphosphine trisulfonate, sodium salt) catalyst immobilized on silica. Inorganic base such as potassium acetate was found to be effective. The catalyst stability and recycle ability have been studied in the temperature range of 130–150 °C.

Keywords: supported liquid film catalyst, Ni/TPPTS catalyst, Heck reaction, biphasic catalysis

1. Introduction

The Heck reaction is a versatile method for generating new C–C bonds by coupling of alkenes with aromatic halides [1,2]. It finds several applications such as synthesis of taxol, antitumor antibiotic CC-1065, drug intermediates, UV absorbers and antioxidants [1]. Hoechst AG is about to commercialize the two-phase catalyzed Suzuki coupling reaction [3]. The reaction is normally carried out using a palladium catalyst, phosphine ligand and a base in homogeneous medium. There is a need for development of a suitable catalyst/product separation method. Tonk et al. [4] have demonstrated Pd/TPPTS (TPPTS: triphenylphosphine trisulfonate, sodium salt) catalyzed Heck reaction using freeze-dry ethylene glycol film coated on glass beads. The major drawbacks of this system are the presence of triethylamine (one of the important catalyst components) in the organic phase and leaching of Pd metal in the organic phase. Li et al. [5] developed a new heterogeneous catalyst using Pd on porous glass. The reactions can be performed in air, without the need for solubilizing and activating ligands. Kihiaho et al. [6] have shown heterogeneous catalysts for the Heck reaction using Pd supported on modified silica supports such as polyalumazane, polytitanazane and polystanane. The catalysts were stable and could be used several times in normal atmosphere without suffering appreciable loss in catalytic activity. Most of these attempts to heterogenize the catalyst system were based on Pd catalysts, not focussing on inexpensive Ni catalysts. Although Pd catalysts are active, they are prone to precipitate Pd metal. Nickel is known to be active for Heck vinylation and 500 times cheaper than Pd [3]. Heck vinylation using a homogeneous Ni catalyst is reported earlier by several researchers. $NiCl_2(PPh_3)_2$ is known to catalyze the reaction of aryl halides with olefins in the presence of Zn dust to give mixtures of addition and substitution products [7,8] resulting in poor selectivity to the vinylation. Kelkar et al. [9] have reported the vinylation of bromobiphenyls using $NiCl_2{\cdot}H_2O/PPh_3$ in the presence of inorganic base. The key feature of this work is that it does not need any reducing agent such as Zn dust. Iyer et al. [10] have also reported $Ni[P(OPh)_3]_4$ and $Ni[P(OEt)_3]_4$ catalyzed reactions of aryl and vinyl halides with olefins and alkynes. In this paper we report a new heterogeneous catalyst system using Ni-TPPTS catalyst immobilized on ethylene glycol film on silica support and an inorganic base such as potassium acetate (see scheme 1). This gives many advantages such that the organic phase contains only reactants and products without any catalyst component, they can be separated from the catalyst by simple filtration and the catalyst can be recycled several times without any deactivation. A new method for regeneration of supported catalyst has also been developed.

2. Experimental

All chemicals and solvents were purchased from Wako Pure Chem. Inc., Japan, and used without any purification. Ligand TPPTS was prepared by sulfonation of triphenyl phosphine. Solvents were distilled and degassed before use. $Ni(OAc)_2$ (0.1 mmol) and TPPTS (0.2 mmol) were dissolved in 350 mg ethylene glycol under argon atmosphere in a 100 cm^3 round bottom flask agitated with teflon needle. To this solution 1.5 g silica gel (Davisil grade 646, 35–60 mesh, 300 m^2/g) and 50 cm^3 toluene were added. This mixture was stirred for 24 h to ensure uniform mixing. After filtration, the catalyst supported on silica was vacuum dried for 2 h. In a mechanical agitated 100 cm^3 autoclave, the prepared catalyst, iodobenzene (10 mmol), butyl acrylate (12.5 mmol), KOAc (10 mmol) and toluene (10 cm^3) were added. The reaction was continued for 20 h at 150 °C. The reaction mixture was filtered and analyzed using GC (Yanaco G3800, Silicone OV-1, 6 m). The GC analysis

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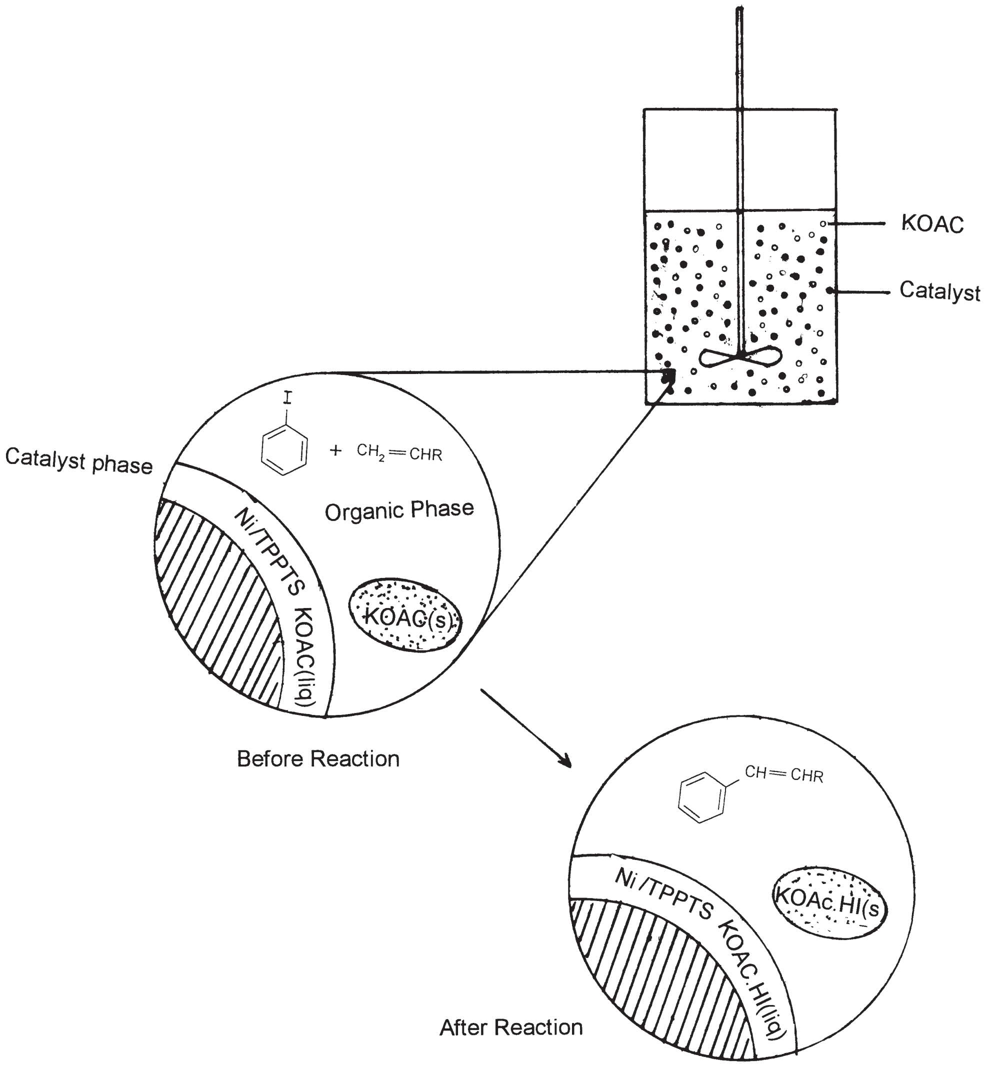
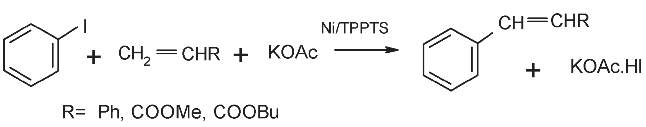


Scheme 1. Heterogenized Ni/TPPTS/KOAc catalyst in ethylene glycol supported on silica.

indicated 80% conversion based on iodobenzene consumed and 100% selectivity towards *trans*-butylcinnamate. Leaching of the Ni metal catalyst was measured using atomic absorption spectroscopic method (AAS) [4]. For recycle studies, the residue containing catalyst and base adduct were added instead of the fresh catalyst in the above reaction. Regeneration of catalyst is also possible after several recycles. The catalyst containing base adduct was refluxed with 5–10 times excess ethyl acetate. The catalyst transfers into ethyl acetate due to marginal solubility of ethylene glycol in ethyl acetate. Ethyl acetate was evaporated, fresh ethylene glycol and silica were added to the residue and the mixture was stirred for 4 h in toluene solvent. The resulting catalyst sample was filtered and used for further recycles.

3. Results and discussion

We have carried out some preliminary experiments regarding selection of solvent, inorganic base, catalyst supporting phase, catalyst precursor and optimization of reaction conditions for the following reaction:



The results are presented in table 1. It is observed that the nature of a Ni catalyst precursor such as $NiCl_2$ or $Ni(OAc)_2$ has no significant effect on catalyst performance and, therefore, $Ni(OAc)_2$ was selected for further studies mainly due to its high solubility in ethylene glycol. The performance of the Ni/TPPTS catalyst is comparable with that of homogeneous $NiCl_2(PPh_3)_2$. The effect of silica concentration shows significant improvement in conversion from 46 to 88%, mainly due to increase in catalyst surface area. The turnover number (TON) is defined as mol product formed/mol of catalyst. The TON given in table 1 may be larger as bulk nickel atoms are not exposed to the reactants as indicated by the effect of silica concentration. Several inorganic bases are screened. KOAc and NaOAc were found to be suitable due to their high solubility in the catalyst containing ethylene glycol film. K_2CO_3 and Na_2CO_3 are not effective due to poor solubility in the catalyst contain-

Table 1
Heck vinylation of butyl acrylate (BA) with iodobenzene using nickel supported film catalyst.[a]

PhI (mmol)	BA (mmol)	KOAc (mmol)	SiO_2 (g)	Temp. (°C)	Conversion[b] (%)	Selectivity *trans* (%)	TON	Remark
Comparison with homogeneous catalyst								
10	12.5	12.5	–	150	100	100	>100	Homo. NMP solvent
10	12.5	12.5	1.5	150	80	100	80	
Effect of silica concentration								
10	12.5	12.5	1	140	46	100	46	
10	12.5	12.5	1.5	140	55	100	55	
10	12.5	12.5	4	140	88	100	88	
Effect of catalyst precursor								
10	12.5	12.5	1.5	140	55	100	55	$Ni(OAc)_2$ cat.
10	12.5	12.5	1.5	140	54	100	54	$NiCl_2 \cdot H_2O$
Effect of reactant concentration								
10	12.5	12.5	1.5	140	55	100	55	
20	25	25	1.5	140	35	95	70	
30	37.5	37.5	1.5	140	44	85	132	
Effect of temperature								
10	12.5	12.5	1.5	130	25	100	25	
10	12.5	12.5	1.5	140	55	100	55	
10	12.5	12.5	1.5	150	80	100	80	

[a] $Ni(OAc)_2$: 0.1 mmol; TPPTS: 0.2 mmol; catalyst phase (ethylene glycol): 350 mg; toluene (solvent): 15 cm^3; time: 22 h; TON: mol product/mol catalyst.

[b] Conversion was calculated based on aryl halide consumed.

ing ethylene glycol film. We confirmed no leaching of Ni metal up to 1 ppm level. Use of organic bases like triethylamine and pyridine has two major drawbacks such as very high leaching of Ni in the organic phase and its miscibility with the reactants and products. It has been reported that inorganic base such as sodium acetate gives acetic acid and sodium bromide in the case of aryl bromide and butyl acrylate vinylation [11] in N,N′-dimethylacetamide solvent. We observed the formation of base adduct (KOAc·HI) [12] instead of acetic acid and sodium iodide. This is useful in the present catalyst system, since formation of acetic acid will leach out catalyst in the organic phase. KOAc is essentially dissolved in the catalyst phase and reaction occurs only in the catalyst film. The product is delivered to toluene due to its high solubility in toluene whereas the base adduct is not soluble in toluene and separated as solid in the reaction mixture. The effect of catalyst film was also screened and it has been observed that ethylene glycol was more active than water film. Water film has another disadvantage as it deteriorates at temperatures as high as 120–140 °C. The effect of reactant concentration has also been studied and it has been observed that TON increases with increase in reactant concentration. This can be explained on the basis of increase in concentration of reactant for liquid–liquid mass transfer and at liquid–liquid interface.

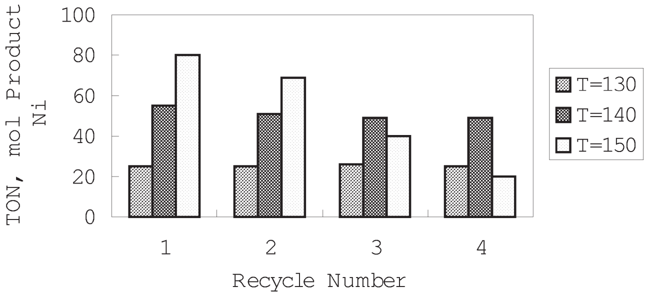


Figure 1. Recycle data at various temperatures.

For effective utilization of a catalyst it is necessary that it should be recycled several times. Results on catalyst recycling are presented in figure 1. It can be seen that the catalyst retains its activity and selectivity performance up to three recycles at 130 and 140 °C, while it loses its activity performance at higher temperatures such as 150 °C due to catalyst deactivation. In this case the catalyst is not leached into the organic phase, confirmed by AAS analysis and at such high temperatures phosphine ligand is prone to degrade, hence causing catalyst deactivation observed. Therefore the present catalyst can indicate stable activities at temperatures below 150 °C. In obtaining recycle data the catalyst was filtered along with base adduct and recycled for a next reaction with freshly added KOAc, butyl acrylate and iodobenzene. We stopped the recycle experiments after three recycles. After several recycles the catalyst, containing base adduct, can be separated by extraction in ethyl acetate (see experimental procedure). This catalyst is also active for Heck vinylation and can be further recycled several times. We have concentrated our focus to improve the performance of this catalyst at lower temperatures with reasonable reaction rates and work is in progress in this direction.

In conclusion, the catalyst system consisting of Ni/TPPTS catalyst in ethylene glycol film supported on high surface area silica along with an inorganic base such as potassium acetate is effective for heterogenizing the Heck reaction. The organic phase contains only reactants and product. The catalyst recycle efficiency is also very high.

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