Solid base and their performance in synthesis of dipropylene glycol

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Introduction

In recent years, there has been increasing interest in the using and designing of environmental friendly heterogeneous catalysts in order to reduce the amount of toxic waste arising from the chemical process [1]. The attempt to heterogenize homogeneous catalyst as alternatives to more traditional reagents and catalysts has been one area of research that has seen increasing interest. The modification process was generally operated by stirring, heating, refluxing, etc. [2-4]. Most of these catalysts took silica gel as the carriers. Few studied have done about activated carbon as the carriers.

O-alkylation is an important kind of reaction leading to C-O bond formation that is widely employed in organic synthesis. For example, dipropylene glycol (DPG) can be synthesized through the reaction of propylene oxide with 1, 2-Propanediol via acid or basic catalyst. The catalysts used in this process include earlier homogenous base or acid (NaOH, alcoholic sodium and BF_3), later solid acid and base. However, few studied have reported the use of amine modified activated carbon as catalyst.

In the present work, an alternative prepared route for the formation of amine modified activated carbon was developed by using refluxing. An organic triallyl-amine (NEA) was selected as the active component to prepare the supported catalyst and the catalytic activity was evaluated by the DPG yield and selectivity.

Experimental

Materials and Apparatus

1, 2-Propanediol, Propylene Oxide and organic amine, analytical grade pure, purchased from Shanghai chemical regents company in china, were dried by magnesium sulfate before use. Commercial coconut shell activated carbon was supplied by HAYCARB Limited (PHO. 12/40).

The apparatus consisted of a flask equipped with a reflux condenser was used in the catalyst prepared process and high pressure kettle as well as temperature controller were used in the DPG synthesis process. The qualitative analysis and quantitative analysis were carried out by Agilent 6820 gas chromatograph.

Preparation of catalyst

The amine modified carbon catalyst could be achieved as the followings: 12.0 g shell carbon was preheated for 12 h at 473K in vacuum to remove all adsorbed moisture and ash content and then cool down to ambient temperature in vacuum. The shell activated carbon was divided into three and transferred into a 50ml conical flask, respectively. After mixed the 10ml organic amine, the mixture in conical flask was heated to reflux for 2h, 4h and 7h, respectively. The catalysts were then obtained by air-pumpfiltration over a period of 30 min and named NEA-2/AC, NEA-4/AC, NEA-7/AC, respectively.

Characterization

The support catalyst NEA-7/AC was measured by FT-IR in room temperature. The FT-IR spectra of the support catalyst were recorded in a Nicolet (AVATAR) spectrometer in absorbance mode using KBr pellet technique.

Catalytic test

The catalytic properties were measured in a 300 ml bath reactor with mol ratio of 1, 2-propanediol and propylene oxide being 1:1. After running at 473K for 90 min under magnetic stirring, the reactor was cooled down to ambient temperature. The product was then filtered and analyzed by a gas chromatograph with a flame ionization detector after centrifugal separation with solvent and used for recycling test.

Results and Discussion

FT-IR

The adsorbed FT-IR spectra of the solid base and activated carbon are shown in Fig.1. Compared to the carrier, a peak appeared shifting around 3347 cm^{-1} on the solid base catalyst indicating the presence of NEA.

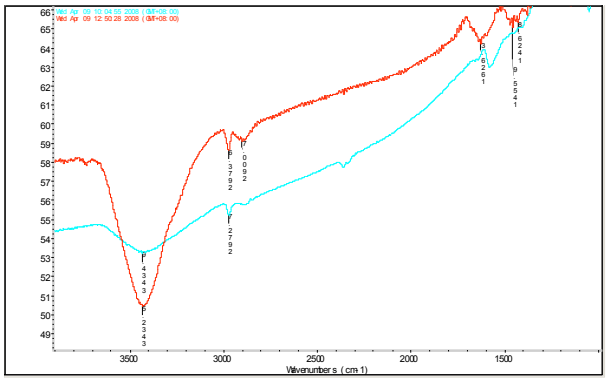

Figure 1. Changes of catalyst in FT-IR during adsorption

Basicity of the catalyst

The potentiometric titration curves for the free base and the modified base catalyst were shown in Fig. 2. The free base showed typical titration curve with a pronounced step at the equivalence point. However, the titration curve of the modified catalyst showed a continuous drop in PH with the added volume of HCl. The organic-inorganic hybrid materials are less strongly basic than the corresponding free organic molecules and possess a wide distribution of base sites by an H-bonding interaction of the amine with the activated carbon [5-7].

From Fig. 2, `the distinct change in the slope about the titration curve can be seen.

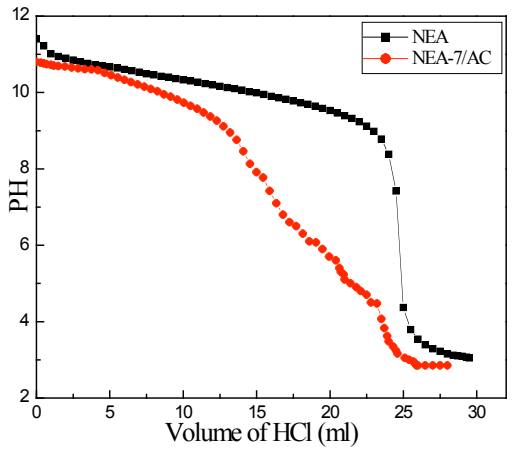

Figure 2. Potentiometric titration curves of (a) free base and (b) modified catalyst

Amount adsorbed

The amount of organic material adsorbed on the support was determined from the weight increase by analytical balance in room temperature. The three kinds of catalyst were tested, respectively. From the Fig. 3, the effect of refluxing hour on the amount adsorbed can be seen. The amount of active component adsorbed decreased with increasing refluxing hour. This phenomenon may be due to the following reason that when the mixture was heated to refluxed, the molecule thermal motion was accelerated and lead to the amount of active component decreasing.

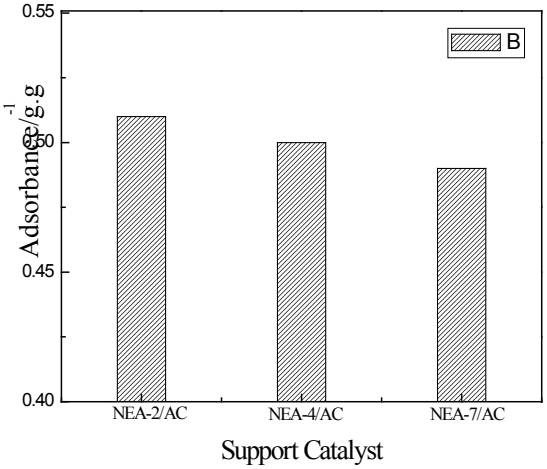

Figure 3. The catalyst adsorbance

Catalytic performance

The yield and selectivity of the DPG for the different catalyst were shown in Table 1.

Date in Table 1 illustrate the catalytic performance of NEA-2/AC, NEA-4/AC, NEA-7/AC in synthesis of DPG from propylene oxide and 1, 2-Propanediol. NEA-7/AC showed the highest DPG yield and selectivity, which may be due to the reason that with the refluxing hour increasing, the active component in carrier channels turned to more and more homogeneous.

Table 1. Yield and selectivity of DPG over different catalyst

Name	DPG yield / %	DPG selectivity / %
NEA-2/AC	32.05	82.57
NEA-4/AC	38.75	85.61
NEA-7/AC	40.14	85.87

Conclusion

Solid basic catalysts have considerable advantages, especially in reactions in non-aqueous solvents. The results presented above led to the following conclusions:

1. the organic-inorganic hybrid catalyst prepared by refluxing show good activity.
2. the characterization indicated that the amine groups were grafted onto the carriers by H-bond.
3. the nature of the support leads to a very high surface area and loading of base in the order of 0.49g.g-1.

Reference

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