Mesoporous polymeric carbon nitride and its composites as metal-free catalysts for the selective hydrogenation of phenylacetylene to styrene

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Abstract: Hydrogenation of carbon–carbon multiple bonds is one of the most important processes widely used in chemical industry. We have demonstrated for the first time that graphite-like carbon nitrides are capable of activating hydrogen molecules in the absence of any metals in the gas phase. In the present study, efficient catalysts prepared on the base of mesoporous polymeric carbon nitride and its composites with different additives, such as graphite oxide, S, NaOH, KOH and Al_2O_3, have been developed for the selective hydrogenation of phenylacetylene to styrene. The hydrogenation of phenylacetylene to styrene on prepared carbon nitrides takes place with remarkable selectivity.

Keywords: *carbon nitrides, metal-free catalyst, phenylacetylene, hydrogenation.*

1.Introduction

Metal-free heterogeneous catalysis using carbon compounds is a potentially alternative to a number of metal-containing catalysts used for the realization of chemical reactions. Recently it has been demonstrated that polymeric carbon nitrides are capable of catalyzing many practically important processes, such as oxidation, alkylation, oligomerization, etc. without the participation of metals[1].Due to special semiconductor properties, they can also act as a heterogeneous photo-catalyst in water decomposition reactions and activate carbon dioxide in the absence of any metal. We first established that hydrogen molecules can also be activated on the surface of carbon nitrides, which is capable to replace metal-containing catalysts for the selective hydrogenation of phenylacetylene (PhA) to styrene in the gas phase[2].

The selective hydrogenation of PhA to styrene has a fundamental importance in the production of polystyrene. It is well-known that PhA acts as a brake on chain growth and as a cross-linker. Hence the amount of phenylacetylene PhA in styrene is strongly restricted and normally, specifications are at a level of 10 ppm. The most widely used application for the removal of PhA was the method used to catalyze its partial hydrogenation into styrene on palladium-based catalysts [3].However, in addition to excessive hydrogenation, these catalysts initiate some other side reactions.

In this paper, the experimental results on synthesis of polymer carbon nitride of mesoporous morphology and its composites with different additives, such as graphite oxide, S, NaOH, KOH, Al_2O_3, and their application as selective hydrogenation of PhA are discussed.

2. Experimental

Mesoporous carbon nitride was synthesized by using 1:1 hydrogen-bonded melamine - cyanuric acid complex[4]. A white powder of this complex was graduallyheated up to 550°C under nitrogen yielding polymeric carbon nitride of mesoporous morphology (meso-g-C_3N_4). The composites ofgraphite-like carbon nitrides were synthesized by thermal condensation of melamine and S, NaOH,KOH, Al_2O_3 at 490-550°C. Graphite oxide (GO) was obtained by oxidation of natural graphite according to the improved Hammers method [5]. For the synthesis of the hybrid composites,meso-g-C_3N_4 and GO powders were dispersed in water and continuously stirred for 7- 8 hours. The solid phase separated from mixture was dried at 60°C, then placed in a quartz tube and heated to 250°C with a gradual increase in temperature during 3 hours under a nitrogen atmosphere.The synthesized catalyst samples were characterized by X-ray diffraction (Bruker-D2 Phaser, Germany) and Fourier transform infrared spectroscopy (Nicolet-iS10, USA). The specific surface areas were determined by Sorbi-MS, (Russia).The X-ray diffraction patterns of the fresh and used samples were almost identical.

3. Results and discussion

Our study revealed that polymeric carbon nitrides are capable to provide selective hydrogenation of PhA to styrene and slightly directly to ethylbenzene. And at the same time, they, unlike the metal-containing catalysts, cannot convert styrene (Figure 1).

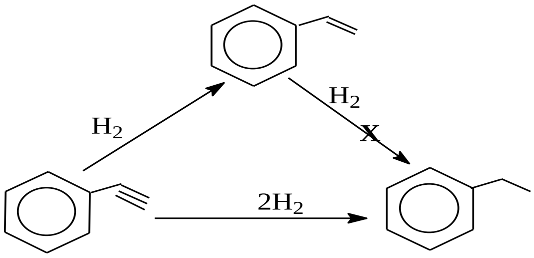

Figure 1. The scheme of phenylacetylene hydrogenation on polymeric carbon nitride

The prepared samples exhibit prolonged catalytic activity in partial hydrogenation of FA with high selectivity (up to 94%) avoiding any metal (Table 1). Compared with known Pd-based catalysts [3],the developed method is more advantageous for the selective hydrogenation of FA due to effective catalyst recyclability. Feature of polymeric carbon nitrides makes it a promising platform for the construction of the metal free green catalytic systems.

Table1: Hydrogenation of fenylasetilene onmeso-porous polymeric carbon nitride composites

Precursor → Catalyst	**S_{BET},** m^{2}g^{-1}	**S_{St},** %	**S_{Eb}, %**	**K_{FA},** %
Melamin/sianurik turşusu → *mezo*-g-C_3N_4	60.0	98.8	1.2	70.7
Melamin → g-C_3N_4	5.3	94.1	5.9	67.7
Catalyst				
meso-g-C_3N_4 / GO	-	85.5	14.5	93.4
meso-g-C_3N_4 / S	-	94.1	5.9	67.7
meso-g-C_3N_4 / Al_2O_3	-	93.4	6.6	56.2
meso-g-C_3N_4 / NaOH	-	90.2	9.8	44.9
meso-g-C_3N_4 / KOH	-	92.6	7.4	47.4

Temperature - 150 °C; FA-flow rate - 0.018 mol/h, H_2-flow rate - 0.04 mol/h.
K_{FA} – FA- conversion; S_{St}, - selectivity to styrene, S_{Eb} – selectivity to ethyl benzene.

Graphite-like carbon nitrides exhibit an appropriate microstructure as graphene with surface defects at a distance and contains additionally nitrogen atoms for electron localization or for anchoring the active sites [1]. Presumably, the reaction mechanism should involve the uptake of H_2 on the defects of carbon nitrides surface that subsequently would transfer to the compounds with unsaturated bonds.

4. Conclusions

This paper presents an advance for designing and developing the efficient heterogeneous organic catalysts based on polymeric carbon nitrides, which can replace metals for selective hydrogenation of phenylacetylene to styrene. The carbon nitrides possessing the functions of Bronsted and Lewis bases, rich in electronic centers and easily forming the hydrogen bonds, tolerating the functional groups in the reaction medium and therefore, can be considered as an environmentally friendly multifunctional green catalyst for the implementation of many important chemical synthesis.

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