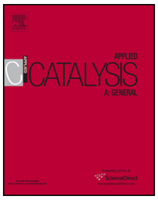
Applied Catalysis A: General 520 (2016) 7–12

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Ammoxidation of acrolein to acrylonitrile over bismuth molybdate catalysts

Nguyen Thanh-Binh [a], Jean-Luc Dubois [b], Serge Kaliaguine [a,*]

[a] Department of Chemical Engineering, Laval University, 1065, avenue de la Médecine, G1V 0A6 Québec, Canada
[b] ARKEMA, 420 Rue d'Estienne d'Orves, F-92705 Colombes, France

ARTICLE INFO

Article history:
Received 21 January 2016
Received in revised form 11 March 2016
Accepted 26 March 2016
Available online 1 April 2016

Keywords:
Ammoxidation
Acrolein
Acrylonitrile
Mesostructure
Bismuth-molybdate catalysts

ABSTRACT

The present work deals with the potentially significant process converting acrolein of green origin to acrylonitrile using mesoporous bismuth molybdate catalysts. The ammoxidation catalysts were characterized by N_2 physisorption, X-ray diffraction, and catalytic tests under various conditions at different temperatures, contact times, and reactant molar ratios. The results indicated a catalytic activity proportional to specific surface area, which depends on bismuth molybdate phases, and concentration of oxygen in the gas feed. The selectivity of the catalysts only depends on reaction temperature. ACN selectivity obtained at 350–400 °C was 100% and reduced to 97% at 450 °C.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Acrylonitrile (ACN) is a key monomer of the polymer industry. Therefore, the global market of ACN is about 6 Mt in 2015 and expected to reach 8 Mt in 2020 [1–3]. However, the major source of ACN is propylene or propane from fossil origin [4]. Current research trends for a greener chemical industry is based on using platform molecules of biological origin such as glycerol. This tricarbon trialcohol is a 10 wt% by-product of biodiesel production. As reported in [5] the annual production of biodiesel increases steadily and reached 27 Mt in 2015. A process was developed by Dubois [6,7] and Takaaki and Minoru [8] to convert glycerol to ACN using direct or indirect processes. For the indirect process, the first step is dehydration of glycerol to acrolein (AC) over acidic catalysts such as WO_3/TiO_2 or $FePO_4$ [7,9]. The second one is the ammoxidation of acrolein to acrylonitrile using mixed metal oxides such as bismuth molybdate or antimonate catalysts. For the direct process, both above steps were combined by using catalysts comprising Sb, Nb, and V [9]. This direct process was also previously examined by Guerrero-Pérez et al. both in gas [10–12] and liquid phases [13]. Most importantly the indirect process allows controlling the water content in the acrolein ammoxidation reactor. This is done by using a condenser between the two reactors. A strict control of high water to ammonia ratio is suppressing the risk of acrylonitrile hydrolysis to acrylic acid. The indirect method yields an easier control of temperature and higher ACN yields. Therefore, the indirect process seems preferable for the synthesis of ACN from renewable glycerol.

Only a few references discussed ammoxidation of acrolein to acrylonitrile [14–21]. Mixed metal oxides based on molybdates, antimonates, tin oxide were used as catalysts for ammoxidation of acrolein. The results showed that the ammoxidation of acrolein is faster than ammoxidation of propylene over the same catalysts. The reaction was carried out at temperatures around 300–500 °C under gas feeds including AC, ammonia, oxygen, and nitrogen. The results showed that molybdate catalysts are better catalysts than antimonate ones. The catalysts have however really low specific surface area of about 1–4 m^2/g. Recently, Hoelderich's group researched on this reaction [9,20]. SbVO, SbFeO, and MoO_3 were investigated for ammoxidation of AC to ACN. The highest ACN yield was however only 40%. This study was conducted in the presence of water vapor and at low AC partial pressure. They demonstrated that higher specific surface area catalysts yield higher activity. Hence, in the present work simple catalysts with high specific surface area were studied.

The bismuth molybdate catalysts are the simplest and most promising candidates for ammoxidation of acrolein. In general, the two major factors to achieve a good heterogeneous catalyst for ammoxidation of acrolein are a large active surface area and the right composition yielding not only high activity but also high selectivity [4,22,23]. High surface area oxidation catalysts

---

* Corresponding author.
E-mail address: serge.kaliaguine@gch.ulaval.ca (S. Kaliaguine).

http://dx.doi.org/10.1016/j.apcata.2016.03.030
0926-860X/© 2016 Elsevier B.V. All rights reserved.

are prone to overheating and require special reactor design to enhance local heat transfer. In 1972, Batist et al. reported several ways for synthesis of Bi-Mo-O based on $Bi(NO_3)_3 \cdot 5H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and H_2MoO_4 and the method to avoid precipitation of the two precursors by using strong acid HNO_3 [24]. Recently, the bismuth molybdates were obtained by several methods such as combining complexation and spray drying [25,26], surfactant assisted hydrothermal treatment [27], hydrothermal treatment [28], reflux and solid state [29], and hard-templating [30]. However, the specific surface area of the bismuth molybdate catalysts are still low (most specific surface areas are around 2–4 m^2/g). Therefore, preparing bismuth molybdate with high surface area requires attention. On the other hand, the different phases of bismuth molybdate also show different effects on catalytic performance [4,31]. Bismuth molybdates have three phases including α ($Bi_2Mo_3O_{12}$), β ($Bi_2Mo_2O_9$), and γ (Bi_2MoO_6). For ammoxidation of propylene, the α phase shows good NH_3 activation and α-H abstraction. The γ phase is good for the reoxidation process. Finally, the β phase combines α and γ structures, so this phase is the most effective for ammoxidation of propylene. No report has however described the effect of the phase on the ammoxidation of acrolein to acrylonitrile yet.

Metal oxides supported on mesostructured silica are widely applied in the catalysis field because of their large specific surface area, high pore volume, large pore size, and high stability [32,33]. The bismuth and molybdate precursors precipitate from their solutions upon mixing, so that a suitable method should be considered. Several reports indicated that in a strong acid, or base, or in glycerol, the mixture remains homogeneous [24,34,35]. However, strong acids or bases will change silica surface properties. In addition, glycerol has high viscosity, making it difficult for the precursors to diffuse into the pores of the mesoporous silica. Yen et al. synthesized mesostructured metal oxides using a hard-templating technique based on a dual-solvent and solid–liquid impregnation method [36]. A non-polar solvent (heptane in our work) was used for pre-wetting, so as to reduce surface tension (surface tensions of solid–gas are larger than surface tensions of solid–liquid) [36,37]. Therefore, metal salts can be easily transported inside the pores of the mesoporous silica. In addition, using this method in absence of water will reduce precipitation of precursors.

Hence, the effect of surface area and the phases of the bismuth molybdate catalysts could be studied for ammoxidation of acrolein to acrylonitrile by using Yen et al. one-step impregnation catalyst preparation method. The catalysts including supported on mesoporous 3D KIT-6 and non-supported bismuth molybdate will be investigated in this work.

2. Experimental

2.1. Synthesis of bismuth molybdate catalysts

Ordered mesoporous silica KIT-6 with large specific surface area, large pore size (8.1 nm), and 3D mesopore connectivity structure, synthesized, at 100 °C aging temperature, according to a previous report [38] was used as support. The catalysts designed as different mixtures between Bi_2O_3 and MoO_3 were synthesized based on the method developed by Yen et al. [36]. Specifically, the mixtures $Bi_2O_3.nMoO_3$ with $n = 1$, 2, and 3 supported on KIT-6 were designated as n1, n2, and n3, respectively. First, 1.25 g evacuated KIT-6 was pre-wetted by *n*-heptane, and then pre-mixed with 0.94 g of the precursors including calculated weights of bismuth nitrate $Bi(NO_3)_3 \cdot 5H_2O$ and ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. The mixture was transferred to a round bottom flask and heated at 85 °C overnight. The solids were filtered and dried at 50 °C, and then calcined at 550 °C for 3 h in air. In order to compare supports, catalyst C3 was synthesized using commercial porasil silica (Milipore Corporation, 34 Maple Street, Milford, MA 01757) as support and same elemental composition as catalyst n3 active phase.

In preparing the non-supported catalyst a similar impregnated silica was prepared and the KIT-6 silica support was then removed by digestion in 2M NaOH solution at room temperature (three times over one day). A total amount of 4.5 g of the mixed precursors was impregnated on 1.25 g of KIT-6. The resulting solids were filtered and calcined at 500 °C for 3 h before silica removal. The final bismuth molybdate mixed oxide was then washed for several times in water and aqueous ethanol and dried at 100 °C.

2.2. Characterization

N_2 physisorption isotherms at 77 K were measured using a Quantachrome Nova 2000 series instrument. The samples were preliminarily degassed in vacuumn at 150 °C for 6 h. Specific surface area of the catalysts was calculated using the linear part of the BET plot (0.05–0.2 in relative pressure). The pore size distribution is calculated from the adsorption branch following the NLDFT (nonlocal density functional theory) method for cylinder shape. The pore volume is taken as the adsorbed nitrogen volume at 0.99 relative pressure. Wide-angle X-ray diffraction (XRD) analysis was performed with a Siemens 80 Model D5000 diffractometer using CuKα radiation ($\lambda = 0.15496$ nm). In addition, the catalysts phases were monitored by Raman spectroscopy LABRAM HR800 (Horiba Jobin Yvon, Villeneuve d'Ascq, France) coupled with an Olympus BX30 fixed stage microscope using Ar+ laser (514.5 nm) as an excitation light source (Coherent, INNOCA 70C Series Ion Laser, Santa Clara, CA). The chemical composition of the samples was established by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) using a Perkin Elmer Optima 4300DV spectrometer.

2.3. Catalysts test

50 mg of the catalysts was loaded in a fixed-bed quartz reactor (inner diameter and length 8 mm and 420 mm, respectively) at atmospheric pressure, on-line connected with a gas chromatograph (GC, HP 5890). The low catalyst mass allows avoiding hot spots. The reactants and products were analyzed using a TCD detector and Haysep P and molecular sieve 13X columns. The reactor system is shown in Fig. 1. Gas feeds including acrolein, air, ammonia, and nitrogen enter the quartz reactor through two separate inlets in order to avoid polymerization at the contact between ammonia and acrolein. One feed comprises air, ammonia (0.47 cc/min), and nitrogen diluent. Acrolein is vaporized from a 95% aqueous solution at 0 °C. The acrolein vapor diluted in 25 cc/min nitrogen is fed separately. In order to investigate the effect of total flow rate (contact time) on catalytic reaction, reactant molar ratio ($AC/NH_3/O_2$) was fixed whereas the diluent nitrogen flow rate was varied. All inlet gas compositions were selected outside of the flammability region (see Figs. S1 and S2 in supporting information). On the other hand, studying the effect of reactant molar ratio on catalytic performance, the flow rates of air and diluent nitrogen were changed to keep total flow rate constant (detail information in Table S1). In order to avoid condensation of polyacrolein and polyacrylonitrile, the system lines are heated (red-lines) to 180 °C and several three way valves (V1, V3, V4, V5) were used. After each catalytic test, methanol is flown through part of the system for cleaning. In order to protect the GC sampling loop, the reactor exhaust is send to the vent using valves V3 and V4 between samplings.

A carbon balance was calculated based on all detected products including carbon dioxide, acrolein, acetonitrile (ACE), and acrylonitrile (carbon monoxide was never detected). The reported

Download English Version:

https://daneshyari.com/en/article/38913

Download Persian Version:

https://daneshyari.com/article/38913

Daneshyari.com