Direct Synthesis of *o*-Bromobenzonitrile by Catalytic and Gas-Phase Ammoxidation of *o*-Bromotoluene[1]

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Abstract—The VCrPO/SiO$_2$ catalyst was obtained by doping a Cr element into VPO/SiO$_2$. Using this catalyst for the ammoxidation of o-bromotoluene (OBT) to o-bromobenzonitrile (OBBN), we studied the influence and effect of each single factor such as reaction temperature, the molar ratio air/OBT (air ratio), the molar ratio NH$_3$/OBT (NH$_3$ ratio), and the molar ratio H$_2$O/OBT (H$_2$O ratio) in the feed and feed load on the reaction. As the results show, the most appropriate reaction conditions of the catalyst are a temperature of 360°C, an air ratio of 30, a NH$_3$ ratio of 8, an H$_2$O ratio of 0.6, and a feed load of 57 g/(l Cat h). With these parameters the conversion of OBT is 99.4 mol% and the mole productivity of OBBN is 77.9%. The function of the doped Cr element is mainly to increase the lattice defects in the catalyst and improve the quantity and activity of lattice oxygen [O^{2-}], which contributes to increasing the activity of the catalyst and to reducing the most appropriate reaction temperature.

1. INTRODUCTION

Bromobenzonitriles are important organic intermediates; we can make use of them to synthesize many complex organic compounds [1, 2]. As one of the bromobenzonitriles, o-bromobenzonitrile (OBBN) could serve as an intermediate of many medicines and pesticides. For example, OBBN can react with substituted bromobenzenes to synthesize new antihypertension agents [3] and serve as a midbody of many tetrazole medications [4].

Traditionally, four different pathways were used for the synthesis of OBBN: (1) By simultaneously passing cyanogen and the vaporized *o*-bromotoluene (OBT) through the plasma generated by a 13.6 MHz radio frequency discharge, OBT was converted to OBBN [5]. (2) Using trichloromethyl carbonochloridate as a dehydrating agent, *o*-bromobenzaldoxime was converted to OBBN [6]. (3) *o*-Bromobenzaldoxime was converted to OBBN in a microwave in the presence of the modified zeolite ersorb-4 under solvent-free conditions [7]. (4) OBBN was obtained through the electrophilic substitution reaction of bromobenzene and BrF without using catalysts [8]. However, all of these methods have some significant drawbacks: For method (1), the conversion of OBT, the selectivity of OBBN, and the purity of the product are too low. For method (2), the dehydrating agent is extremely toxic and can be decomposed into phosgene in the reaction. Furthermore, it is hard to obtain *o*-bromobenzaldoxime. For method (3),

o-bromobenzaldoxime as the initial material is not a common industrial product and is hard to obtain. For method (4), the selectivity and productivity of OBBN are very low and it is a very dangerous process for the preparation of BrF by F$_2$ reacting with Br$_2$ in the CFCl$_3$ suspending liquid.

The ammoxidation pathway to synthesis of aromatic nitriles can be traced back to the 1960s [9]. OBT can be directly ammoxidated into OBBN using only very common raw materials, with a high productivity and product purity. The critical factor in the ammoxidation is the choice of catalyst. In addition, it is also very important to select suitable reaction conditions to match the performance of the catalyst. In 1978, Hiroshi Hayami et al. [10, 11] invented a kind of multicomponent catalyst composed of V-oxide and P-oxide. Using this catalyst in the ammoxidation of OBT to OBBN at 395°C, 4.8 s for contact time, the mole productivity of OBBN is 77.5 [10] or 83.3% [11]. However, a relative high reaction temperature has to be employed in such a process.

In the present work, a series of Cr-doped VCrPO/SiO$_2$ catalysts have been prepared. Applying the obtained VCrPO/SiO$_2$ catalyst to catalysis ammoxidation of OBT to OBBN, the optimized temperature is 360°C and the mole productivity of OBBN is 77.9%. This paper will put an emphasis on investigating the activity of the resultant VCrPO/SiO$_2$ catalyst and the influence of reaction conditions on the ammoxidation of OBT.

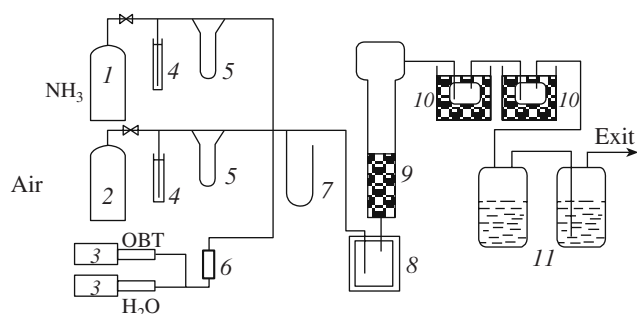[1] This article was submitted by the authors in English.

Fig. 1. Apparatus for investigation of ammoxidation of OBT. Note: *1*—ammonia cylinder; *2*—air cylinder; *3*—microinfusion pump; *4*—bleed-off tube; *5*—flowmeter; *6*—evaporator; *7*—manometer; *8*—preheater; *9*—reactor; *10*—condenser; *11*—offgas absorber.

Fig. 2. Conversion and selectivity as a function of temperature air ratio = 30, NH_3 ratio = 9, H_2O ratio = 0.6, feed load = 57 g/(l Cat h).

2. EXPERIMENTAL

2.1. Raw Materials and Reagents

OBT: technical grade, purity ≥99.8%, Wuxi Suburb Southward Chemical Auxiliary Co., Ltd.; V_2O_5: technical grade, purity ≥98%; H_3PO_4: Analytic reagent, Whuhan Chemical Reagent Plant; CrO_3: Analytic reagent, Henan Jiaozuo Third Chemical Plant; SiO_2: ~125–425 μm, Branch of Qingdao Haiyang Chemical Plant; NH_3: technical grade, provided by Huangpi Ammonia Supply Station; AIR: technical grade.

2.2. Catalyst Preparation

The $VCrPO/SiO_2$ catalyst was prepared by impregnating SiO_2 (specific surface = 250 m²/g) into an oxalic acid solution containing V, Cr, and P elements. After impregnation, the catalyst was dried at 85°C for 24 h and subsequently calcined in air at 580°C for 6 h.

2.3. Research on Reaction Conditions

The reaction was carried out under atmospheric pressure in a GG-17 glass tube with an inside diameter of 26 mm in a fixed bed reactor. Ammonia and air were first mixed with vaporized OBT and water vapor, and then passed to the catalyst bed. The reactor outlet flow was condensed by ice and then collected (Fig. 1).

2.4. Characterization of the Product

The composition and purity of the product were analyzed by gas chromatography (GC 102M, Shanghai, China) equipped with a thermal conductivity cell using a SE-30 chromatographic column. Fourier transfer infrared spectroscopy (FTIR) was recorded on a Nicolet Avatar 370 (United States) using the KBr disk method.
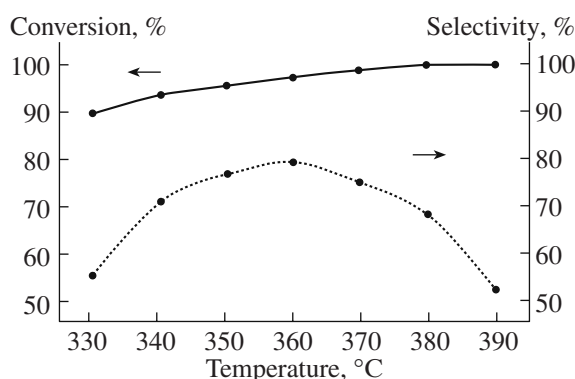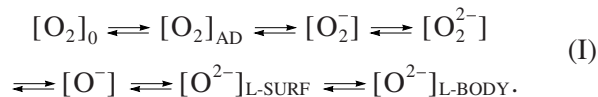
3. RESULTS AND DISCUSSION

3.1. Effect of Temperature on the Reaction

The effect of temperature on the reaction is shown in Fig. 2. With temperature rising, the percent conversion of OBT increases until 100% and the selectivity of the product passes through a maximum of 79.0% at 360°C. When the temperature is over 360°C, the selectivity of OBBN decreases. In the process of ammoxidation, O_2 is converted into lattice oxygen $[O^{2-}]$, which is the active ingredient by adsorption, bonding, and electron transfer. In the reaction, the nucleophilic lattice oxygen $[O^{2-}]$, which owns two units of negative charge, can make the catalyst have more selectivity [12]; the transition of gas O_2 in the reaction system can be shown simply following [13].

$$[O_2]_0 \rightleftharpoons [O_2]_{AD} \rightleftharpoons [O_2^-] \rightleftharpoons [O_2^{2-}]$$
$$\rightleftharpoons [O^-] \rightleftharpoons [O^{2-}]_{L\text{-}SURF} \rightleftharpoons [O^{2-}]_{L\text{-}BODY}. \tag{I}$$

As the system's temperature rises, the quantity of lattice oxygen participating in the reaction increases, the migration rate of lattice oxygens become faster, the activity of the catalyst increases, and conversion of OBT rises. However, an excessive number of lattice oxygens will excessively oxidate OBT and make the selectivity of OBBN worse. For that reason, the catalyst should have a preferable temperature. The lattice defects of the catalyst on the surface and in the body are increased by adding transition metal Cr^{3+} ions, which result in higher activity of lattice oxygens and the preferable temperature of catalyst decreasing. As the reaction temperature is at 360°C, and under the reaction condition given by Fig. 2, the mole productivity of OBBN reaches 77.0%.

3.2. Effect of the Molar Ratio Air/OBT

The influence of the molar ratio air/OBT (air ratio) is shown in Fig. 3. As can be seen, the conversion is increasing slowly until 100% and the selectivity passes

through a maximum of 79.0% at an air ratio of 30, while the best productivity of OBBN is 77.0%.

The phenomenon mentioned above can be explained by the theory about the adsorbed reaction of O_2 molecules on the surface of the catalyst. When the air ratio increases, the adsorbed oxygen on the surface of the catalyst increases and formula (1) shifts to the right, which increases the amount of lattice oxygen on the surface and in the body of the catalyst, as well as the activity of the catalyst until the conversion of OBT reaches 100%. But an excessively high air ratio can reduce adsorption of ammonia and OBT on the surface of the catalyst and deeply oxidate OBT, which results in byproducts (H_2O and CO_2) increasing and the selectivity of OBBN decreasing dramatically.

3.3. Effect of the Molar Ratio NH₃/OBT

From Fig. 4 it follows that when the molar ratio NH_3/OBT (NH_3 ratio) exceeds 8, the conversion of OBT decreases slightly, while the selectivity of OBBN begins to decrease over a transient platform. According to the research of Centi [14], when the surface of the $(VO)_2P_2O_7$ was completely covered by NH_3, the selectivity for the product nitrile would decrease quickly. In this case, the adsorbed oxygen and OBT on the surface of the catalyst are not enough, so the conversion of OBT decreases. On the other hand, OBT is more strongly oxidated by O_2 gas, which decreases the selectivity of OBBN. Centi [14] have shown that when the adsorbed NH_3 and O_2 each covered half of the surface of the catalyst, the selectivity of the nitrile was the highest. In our experiments, the best NH_3 ratio is 8–9. While the NH_3 ratio is 8, the mole productivity of OBBN is 77.9%.

3.4. Effect of Feed Load

From Fig. 5 we can draw the conclusion that, when the feed load of the catalyst is 57 g/(l Cat h), OBBN can reach the highest productivity of 77.9%. For a lower feed load, OBT will be oxidized excessively; for a higher feed load, the OBT adsorbed on the surface of the catalyst decreases, the reaction between OBT and gas O_2 becomes stronger, the conversion of OBT decreases, and the selectivity of OBBN also decreases quickly.

3.5. Effect of the Molar Ratio H₂O/OBT

Figure 6 shows the effect of water vapor added to the reactant stream on the reaction. Adding a little water in the reaction system can increase the number of Bransted acidic centers and accelerate adsorption of raw material on the surface of the catalyst [15]. On the other hand, by adding water, the feed material can be diluted and the reaction temperature can be effectively controlled [16], thus improving the conversion and the selectivity. As shown in Fig. 6, the conversion and
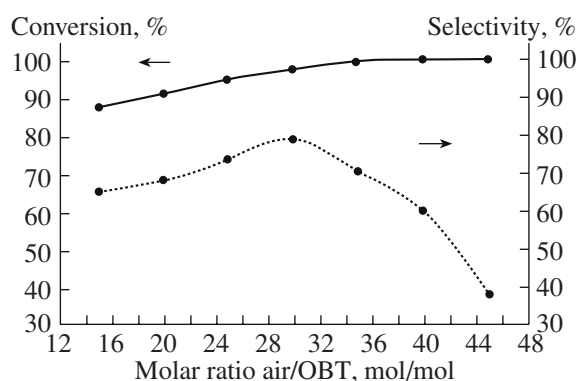
Fig. 3. Conversion and selectivity as a function of air ratio. $T = 360°C$, NH_3 ratio = 9, H_2O ratio = 0.6, feed load = 57 g/(l Cat h).
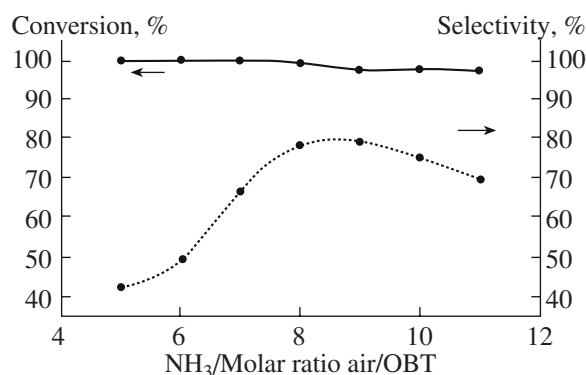

Fig. 4. Conversion and selectivity as a function of the NH_3 ratio. $T = 360°C$, air ratio = 30, H_2O ratio = 0.6, feed load = 57 g/(l Cat h).
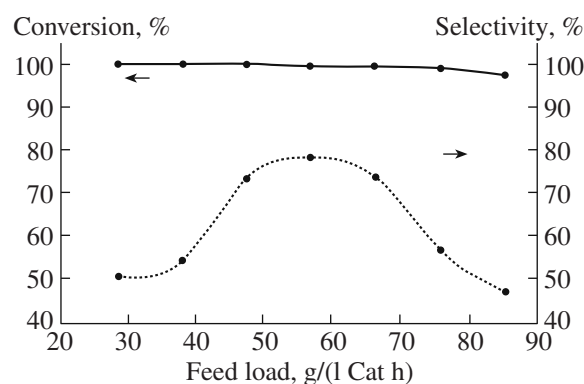

Fig. 5. Conversion and selectivity as a function of feed load. $T = 360°C$, air ratio = 30, NH_3 ratio = 8, H_2O ratio = 0.6.

selectivity synchronously increase before 0.6 of the H_2O ratio. After 0.6 of the H_2O ratio, the conversion basically keeps constant (~100%) while selectivity decreases dramatically. From the discussion above, we can see that the acidic property of the catalyst is so strong that the product is oxidized deeply due to diffi-
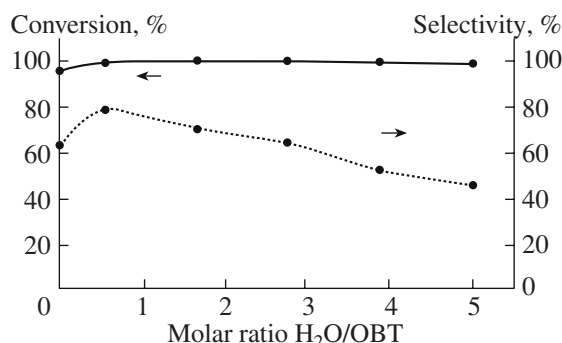
Conversion, %   Selectivity, %

Fig. 6. Conversion and selectivity as a function of the H$_2$O ratio. Note: $T = 360°C$, air ratio = 30, NH$_3$ ratio = 8, feed load = 57 g/(l Cat h).
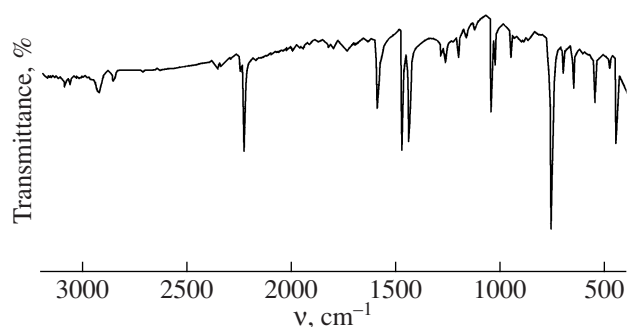

Fig. 7. The FTIR spectrum of the product.

cult desorption of the reaction intermediate after 0.6 of the H$_2$O ratio. At the point of 0.6 of the H$_2$O ratio, the mole productivity of OBBN can reach 77.9%.

3.6. The Characteristic of the Reaction and the Characterization of OBBN

The dissociation energy of the C–Br bond in the OBT molecular is about 280 kJ/mol, which is much weaker than that in the C–X bond (X = F, Cl; the dissociation energy of the C–Cl bond is about 340 kJ/mol and that of the C–F bond is about 480 kJ/mol). On the other hand, the Br atom is more easily polarized and fractured than CI or F from the benzene ring due to its longer radius. Both these reasons result in the ammoxidation of bromotulene being more difficult than fluorotulene or chlorotulene and having higher conversion and lower selectivity. From our discussion above, we can see that the conversions of OBT are all close to 100% while the productivities of OBBN are all under 80%.

The purity of obtained OBBN is measured by GC, and the result shows that the purity is above 99%. The FTIR spectrum (Fig. 7) of the product showed the adsorption band at 2225 cm^{-1} assigned to the C≡N stretching vibration, the adsorption band at 555 cm^{-1} assigned to the C≡N out-of-plane linear bending vibration, and the adsorption

band at 1045 cm^{-1} assigned to the C–Br stretching vibration. Other bands are assigned to the characteristic bands of ortho-benzene derivatives [17].

4. CONCLUSIONS

(1) The investigation of the influence of the reaction parameters on the conversion of OBT and selectivity of OBBN leads to the conclusion that the following conditions are suitable for synthesis OBBN on a VCrPO/SiO$_2$ catalyst that was obtained by doping the Cr element into VPO/SiO$_2$:

temperature: 360°C,

molar ratio air/OBT: 30,

molar ratio NH$_3$/OBT: 8,

feed load: 57g/(l Cat h),

molar ratio H$_2$O/OBT: 0.6.

With these parameters the conversion of OBT is 99.4% and the mole yield of OBBN is 77.9%.

(2) By doping the Cr element, more lattice defects in the catalyst are formed and the number and activity of lattice oxygen [O$_2$] become greater, which results in the activity of the catalyst increasing and the optimum temperature of the reaction decreasing obviously.

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