Catalytic synthesis of propionitrile from methanol and acetonitrile over activated carbon-supported sodium catalysts

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Catalytic synthesis of propionitrile from methanol and acetonitrile was achieved by using activated-carbon-supported sodium catalysts. The activity of catalysts is determined by the precursor of the sodium; the catalysts prepared from sodium hydrogen carbonate show the highest activity. At high conversion of acetonitrile (70%), a propionitrile yield selectively exceeding 80% is achieved with a minor amount of methacrylonitrile as a secondary product. The order of catalytic activity of catalysts correlates well with the adsorption capacities for methanol and acetonitrile measured by the TPD method.

KEY WORDS: propionitrile; acetonitrile; methanol; activated-carbon-supported sodium catalysts; TPD

1. Introduction

In recent years, many attempts have been made to develop synthesis methods for fine chemicals based on the utilization of C_1 chemicals such as CO, CH_4, and methanol, instead of olefins [1–4]. Some of the methanol-based processes have been already industrialized; other processes are technologically ready for commercialization [5–8]. An interesting example is the alkylation of compounds, such as aromatics, ketones, and esters of carboxylic acids by addition of methanol as a carbon source [9–12].

Acetonitrile is produced as a by-product of the ammoxidation of propane or propene for the synthesis of acrylonitrile. Acetonitrile can be used as a solvent, but the world demand is much lower than the availability. Hence, the use of acetonitrile for production of more valuable products would be a very important technological achievement. The selective transformation of acetonitrile to propionitrile is a promising route by the addition of a carbon atom at the α position of the acetonitrile. Methane and methanol were considered as methylating agents. Reports in the Russian literature claim that in the presence of oxygen, acetonitrile can be transformed to propionitrile with methane over K-, Ba-, and Mg-halides supported on quartz in a wide range of temperatures (700–850 °C) [13]. However, methane is very stable and therefore higher temperature or the presence of oxygen is required for its activation. Other researchers used methanol as methylation agent for the selective transformation of acetonitrile to propionitrile over magnesia-based catalysts [14], but the yield of propionitrile is still low.

Recently, we have found that an activated-carbon-supported sodium catalyst is a good catalyst for the formation of propionitrile from acetonitrile and methanol. This catalyst is better than magnesia-based catalysts in the yield of propionitrile.

2. Experimental

All chemicals used were of reagent grade quality and were commercially available. Commercial activated carbon (AC, Yijing Activated Carbon, Ltd., PD-3) made from wood and metal oxides was used as support without further treatment. The characterization data of the activated carbon are shown in table 1. Supported catalysts were prepared by a simple impregnation method. Catalysts containing 5% sodium by weight were prepared as follows. To 1 l of deionized water containing 1.83 g sodium hydrogen carbonate ($NaHCO_3$), 10 g of the activated carbon was added. Impregnation took place on a water bath with stirring at 100 °C to evaporate excess water, and the cake was dried at 110 °C in an oven overnight. It was finally calcined by slow heating to 500 °C in a stream of nitrogen and holding for 6 h at the final temperature. Other catalysts were prepared in a similar manner. The main catalysts used in this study were the activated-carbon-supported sodium hydrogen carbonate catalysts.

The reactions of acetonitrile and methanol were carried out in a continuous down flow fixed-bed reactor. The reactor

Table 1
Characterization data for the activated carbon used in this study.

Mesh size (ASTM mesh)	200–325
Bulky density (g/ml)	0.45–0.5
MB (mg/g)	165
Iodine No. (mg/g)	900
Surface area BET-N_2 (m^2/g)	850
Pore volume (cm^3/g)	0.9
Ash (%)	3

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was a vertical quartz tube with an inside diameter of 1.8 cm. It was heated by an electrical tubular furnace, and the temperature was controlled with a PID temperature controller with a sensor in the center of the catalyst bed. The catalyst (1 g) was packed in the reactor and pretreated at 500 °C in a stream of nitrogen (30 ml/min) for 2 h. After pretreatment, the catalytic reactions were carried out at 350–520 °C and 1 atm. The reactant mixture (acetonitrile/methanol = 1/10) was fed by a syringe pump and vaporized in an evaporator. The vapor was adjusted to a constant rate of 15 ml/min and then diluted with nitrogen. The total flow rate was controlled at 45 ml/min. The products were identified by gas chromatography–mass spectrometry and analyzed quantitatively with a gas chromatograph attached to the reaction system through a gas-sampling valve. The columns used in the gas chromatography were a Porapak-Q column (3 m) at 110–200 °C (25 °C/min ramp) and a Chromsieve II column at room temperature for H_2, CO, and CO_2 analysis.

TPD experiments were carried out using a Micromeritics series 2900 spectrometer. A 20 mg sample was placed in a quartz TPD tube and pretreated at 400 °C in helium flow of 50 ml/min for 1 h. After cooling to 100 °C, methanol or acetonitrile was adsorbed on the catalysts. The TPD measurement was effected by heating to 880 °C at a rate 20 °C/min in a He stream of 30 ml/min. The desorption was continuously monitored by a TCD detector. The desorbed gases were identified by mass-spectroscopic analysis attached to the TPD system through a gas-sampling valve to be only methanol or acetonitrile.

Table 2
Reaction of acetonitrile and methanol with methanol : acetonitrile = 10 : 1 at 1 atm and 400 °C catalyzed by various catalysts.

Run	Catalyst	Conversion (%)	Selectivity (%)		
			PN	MAN	Others
1	$LiNO_3$/C	2.8	0	0	0
2	$NaNO_3$/C	30.2	91	7.7	1.4
3	KNO_3/C	22.1	90.2	7.9	2
4	$CsNO_3$/C	1.2	0	0	100
5	$Mg(NO_3)_2$/C	0.6	0	0	0
6	$Ca(NO_3)_2$/C	0.5	100	0	0
7	$Ba(NO_3)_2$/C	0.8	100	0	0
8	Na_2SO_4/C	0.4	100	0	0
9	CH_3COONa/C	25.7	91.5	6.2	2.3
10	$NaHCO_3$/C	30.3	94.5	5.1	0.5
11	$NaAlO_2$/C	14.5	93.6	6.4	0
12	$Na_2C_2O_4$/C	17.2	95.5	4.5	0
13	Na_2HPO_4/C	0	0	0	0
14	NaCl/C	0.6	100	0	0
15	$NaHCO_3$/CaO	0	0	0	0
16	$NaHCO_3$/graphite	1.4	0	0	100
17	$NaHCO_3/TiO_2$	3.7	38.7	0	61.3
18	$NaHCO_3/SiO_2$	1.1	0	0	100
19	$NaHCO_3/Al_2O_3$	0	0	0	0
20	$NaHCO_3$/MgO	1.8	28.9	0	71.1

3. Activity of activated-carbon-supported catalysts

Although activated carbon (AC) does not show any effective catalysis, a significant synergism in catalytic activity and selectivity is observed on the binary metal and activated carbon (M/AC). We have found that, except for alkali and alkali earth metals, any other transition metals loaded on activated carbon cannot enhance the characteristic activity for the formation of propionitrile from the reaction of methanol and acetonitrile. Table 2 summarizes the results of activity tests on the various activated-carbon-supported alkali and alkali earth metal ion catalysts after the reaction for 5 h. The reaction of acetonitrile and methanol yields propionitrile, methacrylonitrile, and some compounds indicated as “others” including acetic acid and oligomers of acetonitrile. All of the excess methanol is recovered, together with a small amount of methane, after the reaction. All catalysts deactivate gradually over the initial reaction period and then show steady activities over a few hours. As seen in table 2, the activated-carbon-supported sodium catalyst exhibits the most promising characteristic in the catalytic synthesis of propionitrile (PN) (run 2). Replacement of sodium by potassium results in a similar effect on the catalytic activity, while the activity is slightly lower (run 3). A less active catalyst is obtained with lithium because of a remarkable decay of activity in a short reaction time, a behavior that is associated with the gradual loss of lithium from the catalyst (run 1). Characteristically, cesium and alkali earth metals are not effective for the formation of PN (runs 4–7). Probably, the corresponding salts added to activated carbon are not easily decomposed during the pretreatment. This conclusion is validated also with catalysts containing various sodium salts (runs 8–14). Catalysts containing Na_2SO_4, Na_2HPO_4, and NaCl having a higher decomposition temperature show poor activities (runs 12–14). Consequently, $NaHCO_3$ is found to be the best starting material of sodium in preparing catalysts for high PN yields (run 10). In addition, we have also found that $NaHCO_3$ loaded on some conventional supports, i.e., acidic, basic, or amphoteric oxides, cannot enhance the characteristic activity for the formation of PN (runs 15–20). So far, the best combination for the reaction is $NaHCO_3$ and activated carbon.

Figure 1 shows the acetonitrile conversion and the selectivities of products as a function of time in the reaction of acetonitrile and methanol (mole ratio acetonitrile : methanol = 1 : 10) over Na (5 wt%)/C catalyst (1 g) at 480 °C. The reaction yields a high selectivity to propionitrile (PN) with small amounts of methacrylonitrile (MAN) and oligomers (others). Excess methanol is recovered after the reaction in addition to a trace amount of methane. As seen in figure 1, an initial decrease in the conversion of acetonitrile is observed, but a stable activity is obtained within a few hours. Other Na (x wt%)/C catalysts behave similarly at different reaction conditions.

The activity of Na/AC catalysts strongly depends on the concentration of sodium. The dependence of acetonitrile conversion and selectivities on the sodium content is shown in figure 2. Only small amounts of sodium result in catalysts of high performance. Excess addition results in a de-

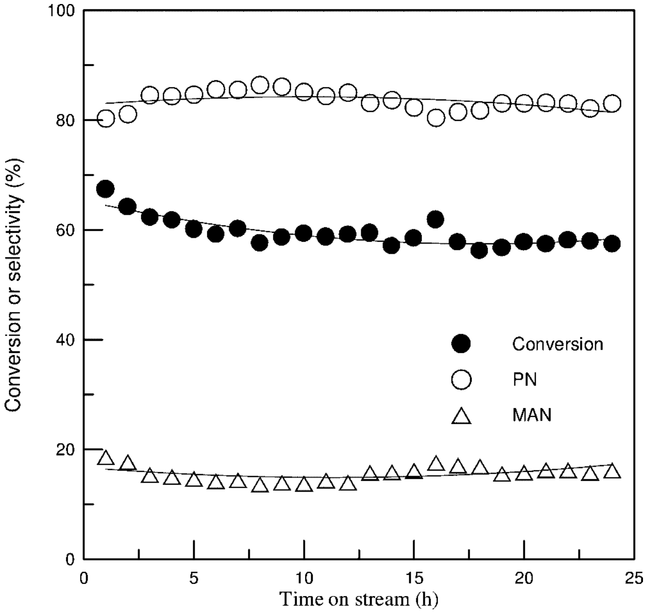

Figure 1. Acetonitrile conversion and selectivities to propionitrile and methacrylonitrile versus time on stream over Na (5 wt%)/AC at 480 °C in the reaction of acetonitrile with methanol (1 : 10).

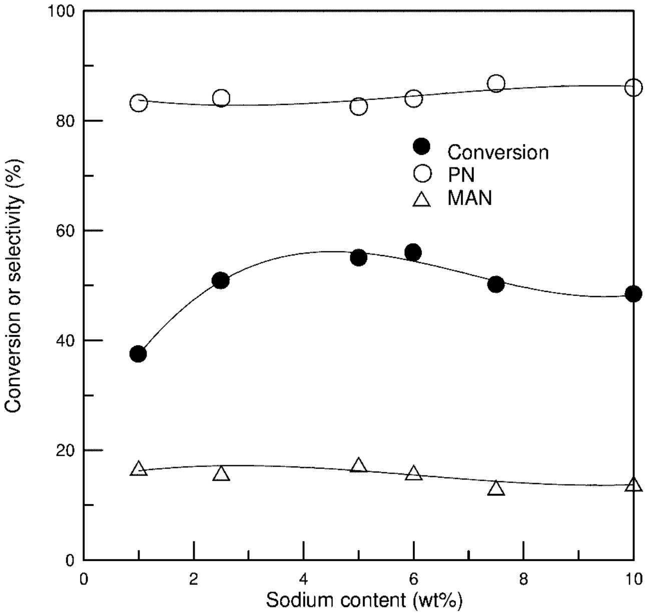

Figure 2. Addition effect of Na ions to activated carbon on the reaction of acetonitrile with methanol (1 : 10) at 480 °C.

crease in activity. Optimum results of acetonitrile conversion and selectivity of propionitrile are obtained by using Na (5 wt%)/AC as catalyst.

For the Na (5 wt%)/C catalyst, the dependencies of acetonitrile conversion and selectivity on reaction temperature are shown in figure 3. The conversion of acetonitrile increases with reaction temperature, passes through a maximum, and then decreases. In contrast, the selectivity to propionitrile decreases, passes through a minimum, and then increases. The catalyst used at higher temperatures (>500 °C) transforms into a powder. This indicates that the catalysts

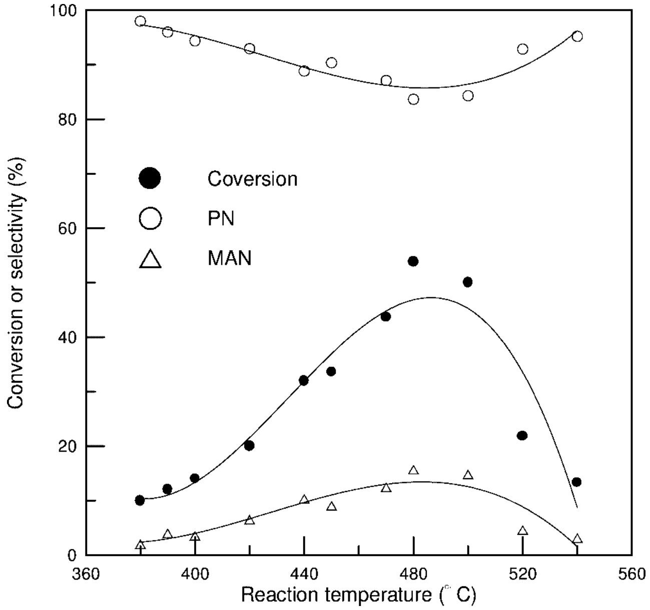

Figure 3. Effect of reaction temperature on the reaction of acetonitrile and methanol (1 : 10) over Na (5 wt%)/AC.

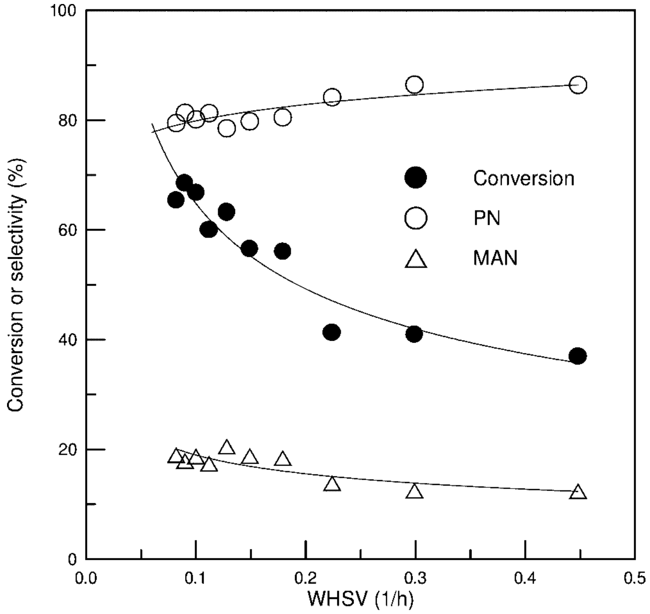

Figure 4. Effect of WHSV on the reaction of acetonitrile and methanol (1 : 10) over Na (5 wt%)/AC at 480 °C.

are deformed and this may be the reason why Na/AC catalysts lose their catalytic activity, when they are used at higher temperatures.

The variations in acetonitrile conversion and selectivity as a function of space velocity are shown in figure 4. The selectivity to propionitrile increases with increasing space velocity. For the highest space velocity used, the selectivity acquires its highest value, namely about 85%. While, the selectivity for methacrylonitrile decreases with the increase of the space velocity, which indicates that methacrylonitrile is a secondary product and results from the methylation of propionitrile. As expected, the decrease of space velocity increases the conversion of acetonitrile. Evidently, one can maximize the production of the desired propionitrile and simultaneously suppress the production of methacrylonitrile, by operating at relatively high space velocities.

4. Temperature-programmed desorption

The methanol TPD profiles of various metal ions containing activated carbon catalysts are shown in figure 5. A comparison of the area under the curve for each catalyst reveals that alkali metal ions have a larger effect than alkali earth metal ions in increasing the amount of methanol adsorbed. Instead of methanol, acetonitrile was used as adsorbate in some experiment; the acetonitrile TPD profiles of various metal ions containing activated carbon catalysts are shown in figure 6. A similar relation has been found by comparing figures 5 and 6. It is noteworthy that the adsorption capacities for both methanol and acetonitrile are more appreciable for Na-containing activated carbon.

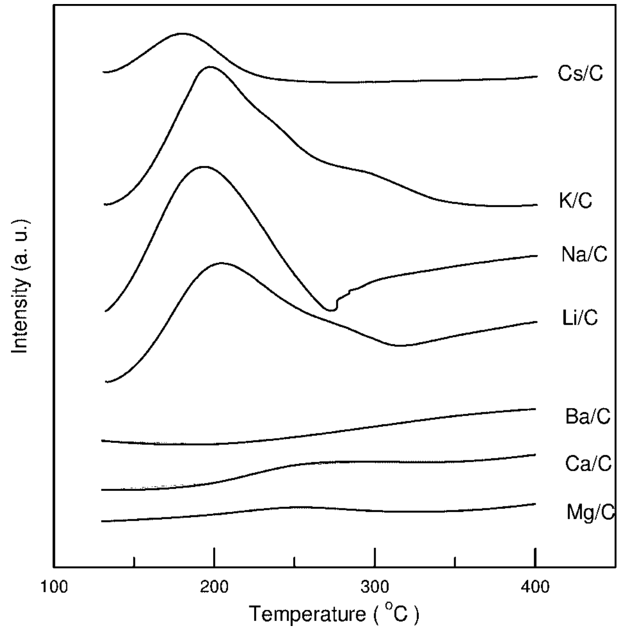

Figure 5. Methanol TPD profiles of various activated carbon catalysts containing different metal ions.

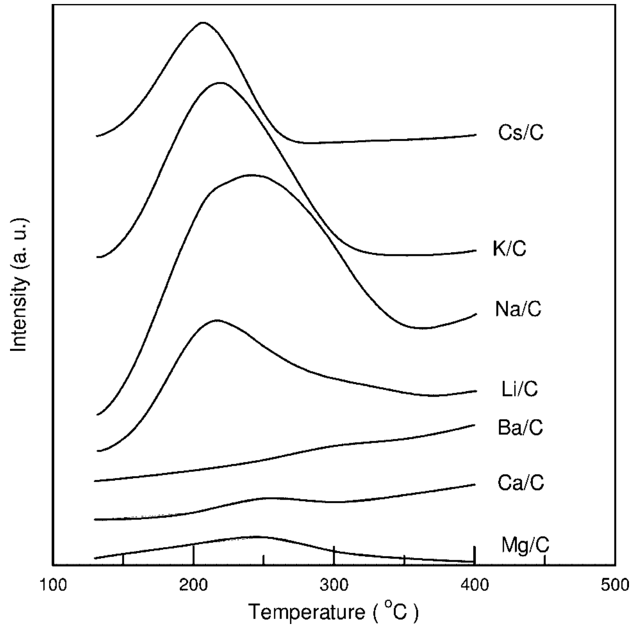

Figure 6. Acetonitrile TPD profiles of various activated carbon catalysts containing different metal ions.

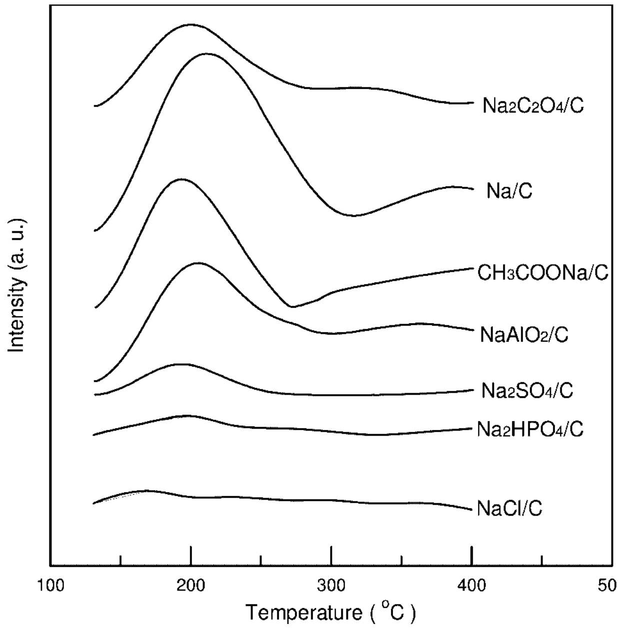

Figure 7. Methanol TPD profiles of various activated carbon catalysts prepared from different sodium salts.

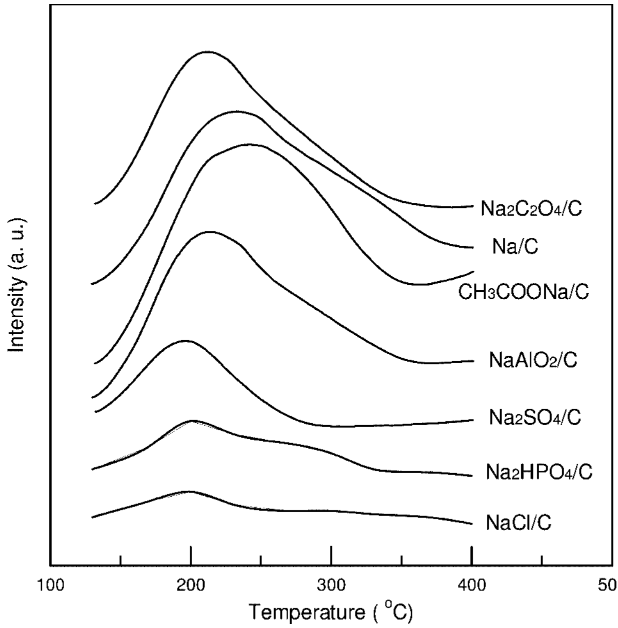

Figure 8. Acetonitrile TPD profiles of various activated carbon catalysts prepared from different sodium salts.

The methanol TPD profiles of various Na/AC catalysts with different sources of sodium are shown in figure 7, while the acetonitrile TPD profiles are shown in figure 8. The catalysts prepared by using $NaHCO_3$, $NaCH_3COO$ as sodium sources show higher capacities for adsorbing both methanol and acetonitrile. With Na/AC catalysts prepared from $Na_2C_2O_4$ and $NaAlO_2$ the desorbed amounts of acetonitrile and methanol are smaller than those with the catalysts described previously. As Na_2SO_4 is used as starting material, the formed catalyst shows a behavior of small capacity for the adsorption of methanol or acetonitrile. For Na_2HPO_3 and NaCl, their adsorption capacities are surprisingly poor.

Instead of activated carbon, some conventional metal oxides (TiO_2, SiO_2: J.T. Baker; MgO: Merck; graphite Flake: Showa Chemical Co., Ltd.) are used as supports for preparing $NaHCO_3$-containing catalysts. No methanol or acetonitrile desorption peak is observed at all with Na/TiO_2, Na/MgO, etc. The results indicate that loading Na ions on these materials generates no considerable amount of adsorption sites.

5. Conclusions

The work presented in this paper shows that the best combination for the catalytic synthesis of propionitrile from methanol and acetonitrile is $NaHCO_3$ and activated carbon. Among the alkali metal and alkali earth metal salts used as additives for preparing the supported catalysts, the catalytic activity for synthesis of propionitrile is markedly correlated with both methanol and acetonitrile adsorption capacity, as examined by TPD, which is indicative of the adsorption of reactants playing an important role in the synthesis reaction.

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