

## Selective synthesis of acetonitrile by reaction of ethanol with ammonia over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst

Ye-Seul Jeong, Sang Hee An, and Chae-Ho Shin<sup>†</sup>

Department of Chemical Engineering, Chungbuk National University, Cheongju, Chungbuk 28644, Korea

(Received 28 March 2019 • accepted 7 May 2019)

**Abstract**—A highly selective synthesis of acetonitrile was carried out by the reaction of ethanol with ammonia on a 10 wt% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. The conversion of ethanol and selectivity to acetonitrile, ethylene, and monoethylamine were examined by varying experimental parameters such as ammonia partial pressure, reaction temperature, and space time. The increase in the ammonia partial pressure led to a considerable decrease in the conversion and small increase in the acetonitrile selectivity up to a molar ratio of NH<sub>3</sub>/ethanol of 3, followed by almost constant values. The partial reaction order of ethanol obtained by controlling the space time was one, while that of ammonia was negative, −0.4. The deactivation behavior of the catalyst after 100 h on stream reaction at 230 °C was analyzed by X-ray photoelectron spectroscopy and temperature programmed oxidation of the catalyst used. The catalyst deactivation was attributed to the gradual formation of nickel carbonitride on the catalyst surface.

**Keywords:** Acetonitrile, Nickel Catalyst, Ethanol, Carbonitride, Deactivation

### INTRODUCTION

Acetonitrile is used mainly as a solvent of extractive distillation, isolation of butadiene from C4 hydrocarbons, in battery applications owing to its relatively high dielectric constant and ability to dissolve electrolytes. In addition, it can be used as a solvent for syntheses of various pharmaceutical intermediates and pesticides. It can be used as a raw material for synthesis of acrylonitrile by reaction of acetonitrile and methanol and as a raw material for acetonitrile hydrogenation for synthesis of ethylamine [1-3]. Acetonitrile is a byproduct of the manufacture of acrylonitrile by ammoxidation of propylene and can also be produced by many other methods, including dehydration of acetamide and hydrogenation of mixtures of carbon monoxide and ammonia [4-7].

Various catalysts and reactants have been reported for the synthesis of acetonitrile [8-15]. Reductive amination of ethanol over Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, direct synthesis of acetonitrile by reaction of ethanol with ammonia over Ni-doped Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [9], bimetallic Ni-Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [10,11], ammoxidation of ethanol, acetaldehyde, or acetic acid over Sb-V-P-O/Al<sub>2</sub>O<sub>3</sub> catalyst [12], ammoxidation of ethanol over molecular sieves such as silicoaluminophosphate (SAPO), V-SAPO, NaY, and V-NaY [13], ammoxidation of ethane over niobia-supported bulk-NiO catalysts [14], and aerobic dehydrogenation of ethylamine over supported ruthenium catalysts [15] have been used for the synthesis of acetonitrile.

In the reaction of ethanol and ammonia on a metal catalyst, the main product in the presence of hydrogen are ethylamines, while that in the absence of hydrogen is acetonitrile [16]. However, in the absence of hydrogen, it is challenging to maintain the catalyst sur-

face in a metallic state, so that a gradual deactivation is observed. The development of a highly selective acetonitrile synthesis catalyst by controlling these simple experimental parameters is important to guide the development of novel catalysts in the future.

In this study, the reaction of ethanol with ammonia for the highly selective acetonitrile synthesis on a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was investigated by changing the reaction temperature, ammonia partial pressure, and weight hourly space velocity (WHSV). The temperature programmed technique was used to observe the desorption behavior of ethanol and ammonia on the catalyst surface. The causes of deactivation affecting the catalyst stability are discussed.

### EXPERIMENTAL

#### 1. Catalyst Preparation

The Ni-loaded (10 wt%) Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by the impregnation method using Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (>98%, Samchun) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Procatalyse). Nickel nitrate was dissolved in distilled water and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was dispersed into the aqueous solution under vigorous stirring for 1 h. The solution was then evaporated to dryness at 80 °C using a rotary evaporator. The obtained powder was dried at 100 °C for 12 h and calcined at 500 °C for 2 h under air flow.

#### 2. Characterization

X-ray diffraction (XRD) patterns of the prepared 10 wt% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst after the calcination and H<sub>2</sub> reduction treatment and H<sub>2</sub> temperature programmed reduction (H<sub>2</sub>-TPR) profile are shown in Figs. S1 and S2, respectively. The Brunauer-Emmett-Teller (BET) surface area of the support  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was 194 m<sup>2</sup> g<sup>−1</sup>, while that of the calcined 10 wt% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was 157 m<sup>2</sup> g<sup>−1</sup>. Table S1 shows the results of H<sub>2</sub> chemisorption, reduction degree obtained from an O<sub>2</sub> titration method, and TPR behavior [16].

A temperature programmed desorption of ethanol (EtOH-TPD) was carried out to confirm the desorption behaviors of ethanol as

<sup>†</sup>To whom correspondence should be addressed.

E-mail: chshin@chungbuk.ac.kr

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a reactant using a quadrupole mass spectrometer (QMS, Balzers QMS 200). Prior to the experiment, the sample (0.2 g) was reduced at 600 °C for 3 h under H<sub>2</sub> flow (50 cm<sup>3</sup> min<sup>-1</sup>). After cooling to room temperature, the reduced sample was exposed to ethanol vapor (3 kPa) with an Ar gas stream for 2 h and purged in the Ar stream to remove the physisorbed ethanol at the same temperature. The sample was heated at a rate of 10 °C min<sup>-1</sup> from room temperature to 700 °C. The effluent gases were detected using a QMS. QMS fragments with *m/z*=44, 31, 29, 28, 27, 18, 15, and 2 were set for CO<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>CHO, CO, C<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>O, CH<sub>4</sub>, and H<sub>2</sub>, respectively.

A temperature programmed surface reaction (TPSR) experiment of pre-adsorbed ethanol with NH<sub>3</sub> was carried out over the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. After the H<sub>2</sub>-treated catalyst at 600 °C was cooled to room temperature, it was exposed to ethanol (3 kPa) with Ar gas (30 cm<sup>3</sup> min<sup>-1</sup>) for 0.5 h. The reactor was then purged with Ar gas for 0.5 h. Subsequently, the sample was heated from 50 to 700 °C under a flow of 9 vol% NH<sub>3</sub>/Ar (30 cm<sup>3</sup> min<sup>-1</sup>). The effluent gases were analyzed continuously using the QMS instrument. The mass signals of *m/z*=29 (-CHO) from CH<sub>3</sub>CHO, 31 (-CH<sub>2</sub>OH) from C<sub>2</sub>H<sub>5</sub>OH, 41 (-CH<sub>3</sub>CN) from CH<sub>3</sub>CN, and 30 (-CH<sub>2</sub>NH<sub>2</sub>) from CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> were detected using a QMS detector.

To investigate the catalytic deactivation behavior, X-ray photoelectron spectroscopy (XPS) and temperature programmed oxidation (TPO) were performed. The XPS was carried out with a PHI Quantera-II instrument using an Al K<sub>α</sub> X-ray source. In the TPO experiment, the used catalyst was exposed to a 5% O<sub>2</sub>/Ar mixed gas (30 cm<sup>3</sup> min<sup>-1</sup>) and heated to 600 °C at a rate of 10 °C min<sup>-1</sup>. The effluent gases were analyzed continuously with the QMS. The mass signals of *m/z*=46, 44, 32, and 14 were referenced to NO<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, and N, respectively.

### 3. Catalytic Activity Test

The selective synthesis of acetonitrile was performed in a fixed-bed reactor at atmospheric pressure. Prior to the reaction, 0.2 g of catalyst was reduced at 600 °C for 3 h under H<sub>2</sub> flow (50 cm<sup>3</sup> min<sup>-1</sup>). The reaction parameters such as the partial pressure of ammonia (1.5–21 kPa), reaction temperature (180–240 °C), and WHSV (0.55–1.64 h<sup>-1</sup>) controlled by variations in total flow rate (25–100 cm<sup>3</sup> min<sup>-1</sup>) and catalyst quantity (0.1 and 0.2 g) were varied. The partial pressure of ethanol was fixed at 3 kPa. The products were analyzed using a gas chromatograph (CP9001) equipped with a CP-Volamine capillary column (60 m×0.32 mm) and a flame ionization detector. The conversion of ethanol, selectivity, WHSV, and deactivation rate were defined as:

$$\text{Conversion (\%)} = \frac{F_{\text{EtOH reacted}}}{F_{\text{EtOH fed}}} \times 100\%$$

$$i \text{ Component selectivity (\%)} = \frac{F_i C_i}{\sum F_i C_i} \times 100\%$$

$$\text{WHSV (h}^{-1}\text{)} = \frac{F_{\text{EtOH}}(\text{mol h}^{-1}) \times \text{MW}_{\text{EtOH}}(\text{g mol}^{-1})}{\text{Quantity of catalyst (g)}}$$

$$\begin{aligned} \text{Deactivation rate (\%)} \\ = \frac{\text{Initial conv. of EtOH} - \text{Conv. at 13 h on stream}}{\text{Initial conversion of EtOH}} \times 100\% \end{aligned}$$

where  $F_{\text{EtOH}}$  and  $F_i$  are molar flow rates of EtOH and *i* products

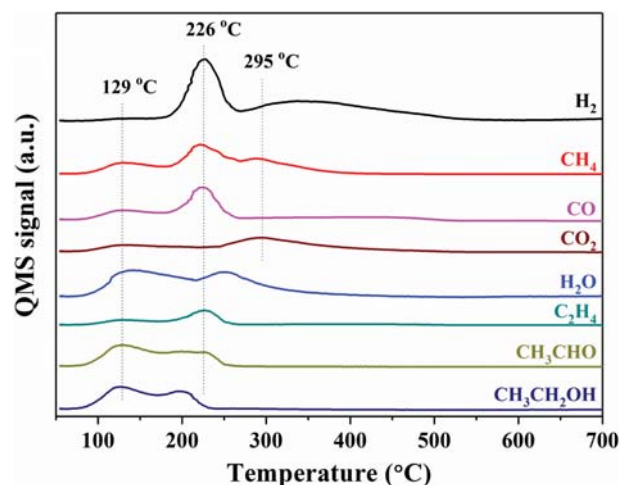


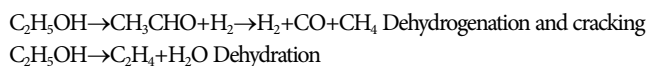
Fig. 1. EtOH-TPD profiles of 10 wt% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst reduced at 600 °C for 3 h under the flow of H<sub>2</sub> (50 cm<sup>3</sup> min<sup>-1</sup>). Ethanol was pre-adsorbed at room temperature.

(C<sub>2</sub>H<sub>4</sub>, monoethylamine, and acetonitrile), respectively.  $\text{MW}_{\text{EtOH}}$  is the molecular weight of ethanol, and  $C_i$  is the carbon number of *i* component.

## RESULTS AND DISCUSSION

### 1. EtOH-TPD and TPSR

EtOH-TPD profiles of the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst are shown in Fig. 1. The desorption of ethanol as a reactant exhibits two main peaks, corresponding to the physisorption of ethanol at a lower temperature (130 °C) and chemisorption of ethanol at approximately 200 °C. With the increase in the desorption temperature, various fragments formed by the interaction between the catalyst surface and adsorbed ethanol are observed. Fragments including CH<sub>3</sub>CHO, H<sub>2</sub>O, CO, C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>, and H<sub>2</sub> are detected at approximately 130 and 226 °C, obtained by [17]:



The desorption peak of CO<sub>2</sub> is generated by oxidizing the adsorbed CO on the surface with lattice oxygen of the catalyst. The peaks of CH<sub>3</sub>CHO and C<sub>2</sub>H<sub>4</sub> at 226 °C are attributed to the dehydrogenation and dehydration of ethanol. Moreover, C<sub>2</sub>H<sub>4</sub> generated in the dehydration of EtOH was easily desorbed, while the strongly adsorbed H<sub>2</sub>O was desorbed at a higher temperature than that for C<sub>2</sub>H<sub>4</sub>. At a high temperature of approximately 300 °C, the peaks of CO<sub>2</sub> and H<sub>2</sub> increased, while the CO and H<sub>2</sub>O peaks decreased. This implies that the water-gas shift reaction is possible in the presence of CO and H<sub>2</sub>O over 250 °C [17].

Fig. 2 shows the TPSR profiles of the Ni/Al<sub>2</sub>O<sub>3</sub>-catalyst-pre-adsorbed ethanol under the flow of 9 vol% NH<sub>3</sub>/Ar. The main mass signals of *m/z*=29 (-CHO) from CH<sub>3</sub>CHO, 31 (-CH<sub>2</sub>OH) from C<sub>2</sub>H<sub>5</sub>OH, 41 (-CH<sub>3</sub>CN) from CH<sub>3</sub>CN, and 30 (-CH<sub>2</sub>NH<sub>2</sub>) from CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> were detected using a QMS detector. The fragments (*m/z*=29 and 31) of physisorbed ethanol were observed at approximately 100 °C. Above this temperature, adsorbed ethanol was not

detected owing to the reaction with the ammonia reactant. Acetaldehyde peak was not observed except the broad peak at approximately 500 °C. Ethylamine-derived fragment ( $m/z=30$  ( $\cdot\text{CH}_2\text{NH}_2$ )) peaks were observed at 350 and 500 °C. These two peaks imply that different dual adsorption sites are present. In addition, two peaks of acetonitrile, which could be formed by monoethylamine dehydrogenation, were observed at 201 and 325 °C. The acetonitrile peak observed at a lower temperature than that for ethylamine indicates that the acetonitrile synthesis is easier than the ethylamine production.

## 2. Effects of Reaction Parameters

Fig. 3 shows the effect of the partial pressure of ammonia on the selective synthesis of acetonitrile on the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Acetoni-

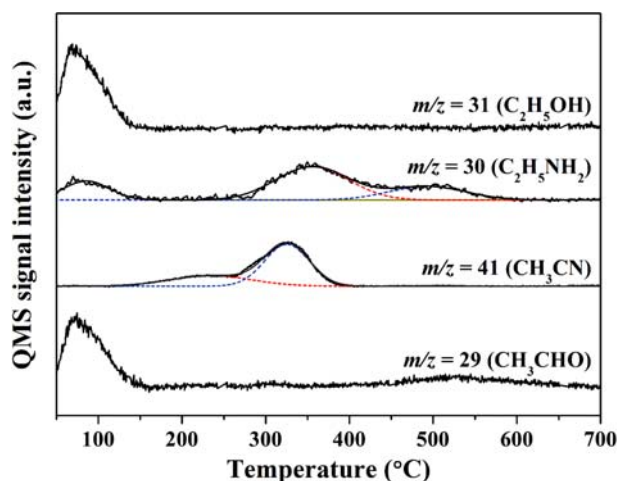


Fig. 2. TPSR profiles of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst in NH<sub>3</sub>/Ar flowing with pre-adsorbed ethanol. The mass signals of  $m/z=29$  ( $\cdot\text{CHO}$ ) from CH<sub>3</sub>CHO, 31 ( $\cdot\text{CH}_2\text{OH}$ ) from C<sub>2</sub>H<sub>5</sub>OH, 41 ( $\cdot\text{CH}_3\text{CN}$ ) from CH<sub>3</sub>CN and 30 ( $\cdot\text{CH}_2\text{NH}_2$ ) from CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> were detected using a QMS detector.

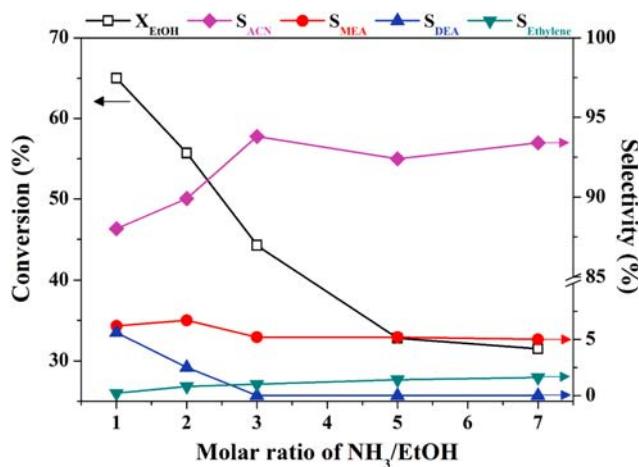


Fig. 3. Evolution of conversion and selectivities as a function of molar ratio of NH<sub>3</sub>/ethanol in the selective synthesis of acetonitrile over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Reaction conditions: 0.2 g of catalyst, T=190 °C, total flow rate=50 cm<sup>3</sup> min<sup>-1</sup>, and partial pressure of ethanol=3 kPa.

trile was observed as the main product; monoethylamine and C<sub>2</sub>H<sub>4</sub> were observed in minor quantities. The initial conversion continuously decreased with the increase in the partial pressure of ammonia, while the acetonitrile selectivity tended to slightly increase (Table S2 and Fig. S4). The synthesis of acetonitrile, which can be produced by the direct reaction of ethanol and ammonia, is possible at a molar ratio of NH<sub>3</sub>/EtOH of 1; however, under this reaction condition, continuous deactivation was observed with the time on stream. However, when the molar ratio exceeded 1, the conversion rate continuously increased with the time on stream; the acetonitrile selectivity in the conversion range of 31.5–65.0% was larger than 83%, up to 93%. The decrease in conversion with the increase in the ammonia partial pressure can be attributed to a decrease in the number of ethanol adsorption sites by competitive adsorption in the same active adsorption sites of ethanol and ammonia, which are reactants in the synthesis of the compound of amine and nitrile [16,18,19].

The initial conversion and selectivity in the reaction temperature range of 180–240 °C are shown in Fig. 4. At NH<sub>3</sub>/EtOH=2, the initial conversion increased from 24 to 94% in the range of

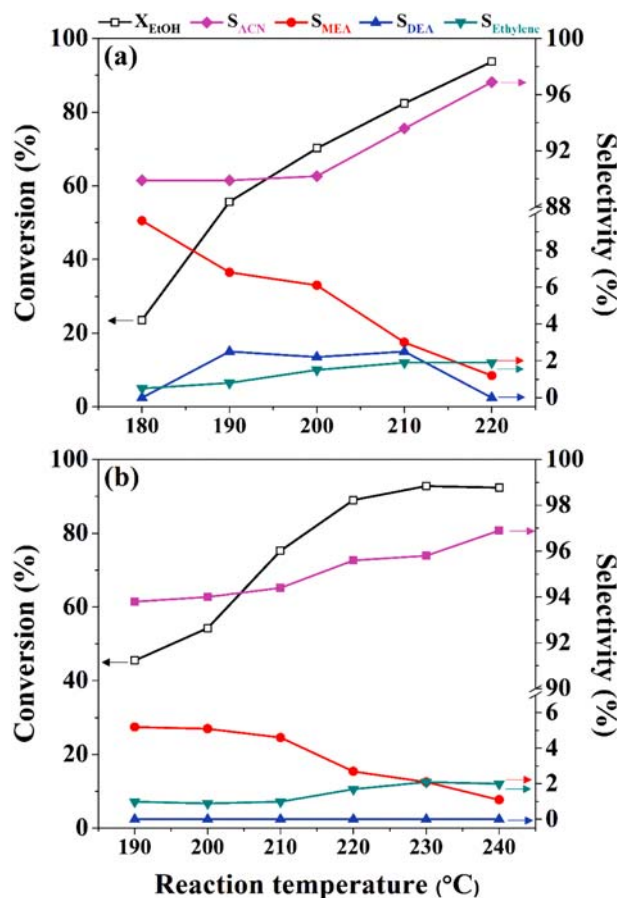


Fig. 4. Evolution of conversion and selectivities as a function of reaction temperature with NH<sub>3</sub>/ethanol (molar ratio) of (a) 2 and (b) 3 in the selective synthesis of acetonitrile over the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Reaction conditions: 0.2 g of catalyst, partial pressure of ethanol=3 kPa, T=180–240 °C, and total flow rate=50 cm<sup>3</sup> min<sup>-1</sup>.

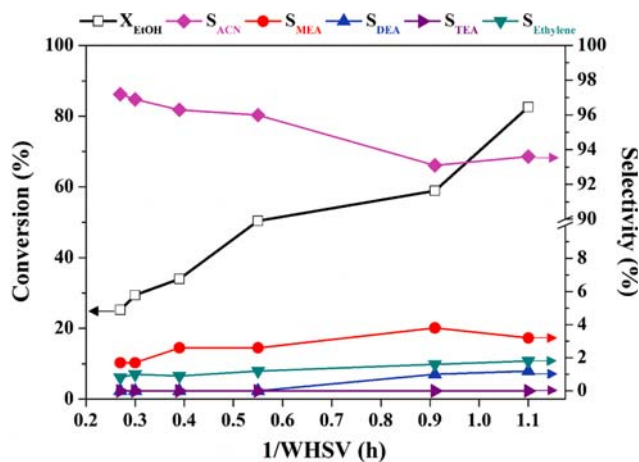


Fig. 5. Evolution of conversion and selectivities as a function of 1/WHHSV in the selective synthesis of acetonitrile over the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Reaction conditions: 0.1–0.2 g of catalyst, T=210 °C, and total flow rate=25–100 cm<sup>3</sup> min<sup>-1</sup>.

108–220 °C, while the acetonitrile selectivity increased from 90 to 97% with the increase in the conversion. The increase in the acetonitrile selectivity shows that the primary mono and diethylamine were converted to acetonitrile (Fig. S4(a) and Table S3). Under this reaction condition, the catalyst deactivation was negligible until 13 h on stream. At NH<sub>3</sub>/EtOH=3, the initial conversion increased from 44 to 97% in the range of 190–240 °C, while the acetonitrile selectivity increased from 90 to 97% as the conversion increased (Fig. S4(b) and Table S4). At NH<sub>3</sub>/EtOH=3, the conversion was decreased compared to that at NH<sub>3</sub>/EtOH=2, the deactivation rate was slightly increased with the NH<sub>3</sub> content, while the acetonitrile selectivity remained above 90%. The initial conversion and selectivity were compared in the 1/WHHSV (h) range of 0.27–1.10 (Fig. 5). With the increase in the space time, the initial conversion increased. The selectivity of mono- and diethylamine, and C<sub>2</sub>H<sub>4</sub> steadily increased with the time on stream with the decrease in the acetonitrile selectivity (Fig. S5 and Table S5).

The synthesis of acetonitrile by the reaction of ethanol and ammo-

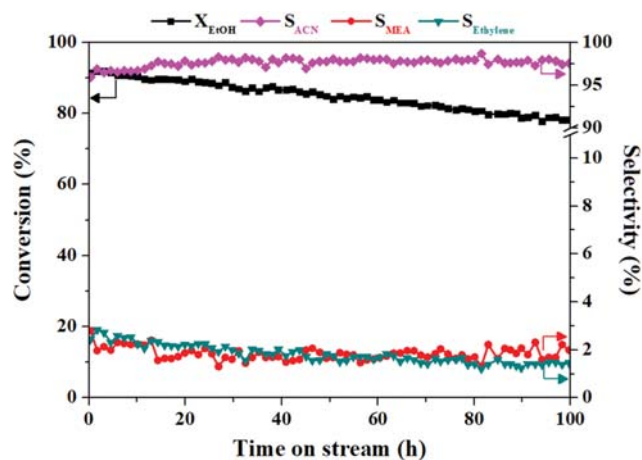
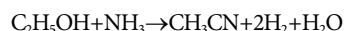


Fig. 7. Long-term stability of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst in the selective synthesis of acetonitrile. Reaction conditions: 0.2 g of catalyst, total flow rate=50 cm<sup>3</sup> min<sup>-1</sup>, T=230 °C, partial pressure of ethanol=3 kPa, and NH<sub>3</sub>/ethanol (molar ratio)=3/1.

nia is possible by simultaneous dehydration and dehydrogenation:



The partial reaction orders of ethanol and ammonia were obtained using the power-law rate equation by the integration method (Fig. 6). Assuming the reaction order of ethanol is one at a reaction temperature of 210 °C, the integration method shows that the first-order assumption is plausible. The partial reaction order of ammonia has a negative value of -0.4. The rate equation of the acetonitrile synthesis by ethanol consumption could be expressed as  $-r_{EtOH} = k P_{EtOH}^{1.0} P_{NH_3}^{-0.4}$  [11].

### 3. Deactivation Behavior of the Ni/Al<sub>2</sub>O<sub>3</sub> Catalyst

In the synthesis of amine and nitrile compounds, the chemical transformation converting the catalyst surface into an inactive nitride formation is a key factor affecting the catalyst deactivation [20–22]. Fig. 7 shows the evolution of the conversion and selectivity to acetonitrile, MEA, and C<sub>2</sub>H<sub>4</sub> in the time on stream up to 100 h. The catalytic deactivation behavior was investigated through character-

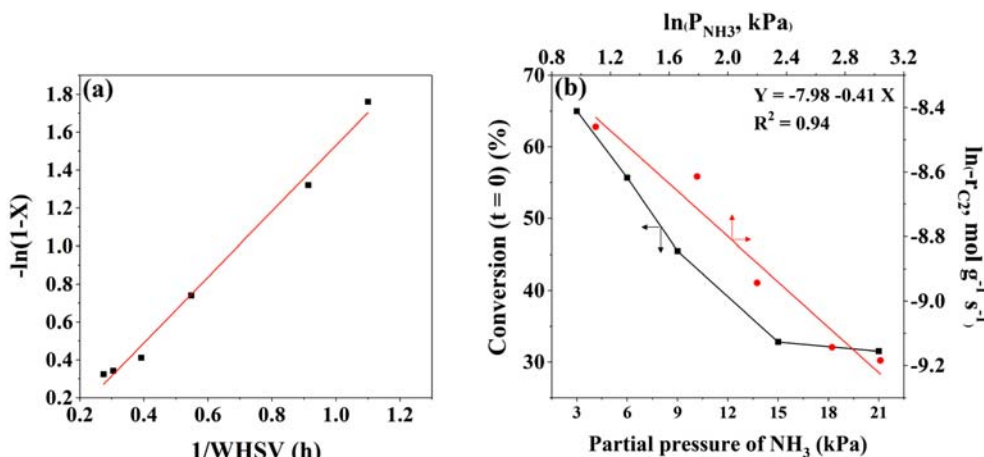


Fig. 6. (a) Pseudo-first-order reaction of ethanol amination and (b) negative order of ammonia in the selective synthesis of acetonitrile over the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. The reaction parameters were obtained from Figs. 3 and 5.



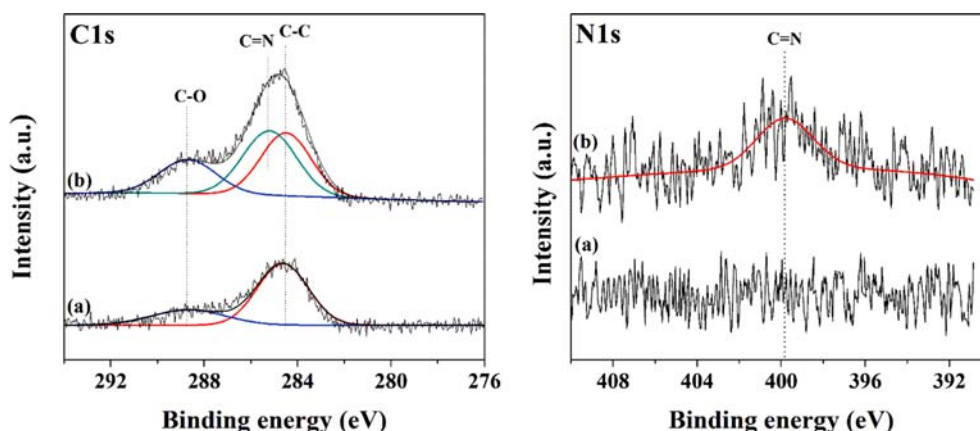
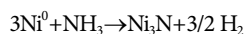


Fig. 8. XPS of the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst; C1s and N1s. (a) Catalyst pretreated at 600 °C for 3 h under H<sub>2</sub> flow and (b) catalyst after the amination reaction of ethanol at 230 °C for 100 h on stream.

ization by comparing the reduced fresh catalysts. Under this reaction condition, the initial conversion was 93.2%, while the conversion at a 100 h on stream was 78.1%, corresponding to a deactivation rate of 16.2% after 100 h. The acetonitrile selectivity always remained above 95%, while those of the byproducts (C<sub>2</sub>H<sub>4</sub> and monoethylamine) remained below 5%.

XPS of C 1s and N 1s of Ni/Al<sub>2</sub>O<sub>3</sub> for the fresh reduced catalyst and after 100 h on stream are shown in Fig. 8. During the amination reaction, nickel nitride can be formed by the reduced Ni metal and ammonia reactant [21-25]:



The metal nitride formation can also occur for the metallic Cu and Co [21]. However, the catalyst surface formed after the amination reaction has carbonitride derived from the ethanol as the carbon source as well as the nitride formation [23-25]. The peaks of C-O (288.6 eV) and C-C (284.5 eV) observed for the fresh reduced catalyst are attributed to adventitious carbon. However, in the case of the amination of ethanol with ammonia for 100 h, a new peak

attributed to C=N (285.2 eV) is observed. The deposition of carbon and nitrogen elements on the catalyst surface could be confirmed by a TPO analysis (Fig. 9). The TPO analysis of the deactivated catalyst showed two types of nitrogen source at approximately 274 and 445 °C. In addition, signals with  $m/z=44$  (·CO<sub>2</sub>), obtained by reacting with the carbon source in proportion to the O<sub>2</sub> consumption, and  $m/z=14$  (·N), which is a possible fragment of NO or NO<sub>2</sub>, are detected at almost equal temperatures. The simultaneous detection of CO<sub>2</sub> and NO<sub>2</sub> reflects the oxidation of the carbonitride compound. The peaks of the nitrogen compounds at 274 and 445 °C are attributed to the oxidation of surface and bulk nitrides, respectively. Surface carbonitride, which acts as a catalyst poisoning structure, can be regenerated by an oxidation reaction at a temperature of 450 °C (or higher).

## CONCLUSIONS

A high selectivity of acetonitrile over 90% was achieved in the entire conversion range over the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst by the reaction of ethanol and ammonia. In the expression of the rate equation with the consumption of ethanol, the partial reaction orders of ethanol and ammonia were 1 and -0.4, respectively. In the presence of excess ammonia, the reactivity was reduced, but the catalyst stability partially prevented catalyst deactivation. The catalytic deactivation was significant owing to the formation of nickel carbonitride. The surface carbonitride, which acted as a catalyst poisoning, could be regenerated by a simple oxidation reaction at a temperature of 450 °C (or higher).

## ACKNOWLEDGEMENT

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea, funded by the Ministry of Science, ICT, and Future Planning (2017R1A2 B3011316).

## SUPPORTING INFORMATION

Additional information as noted in the text. This information is

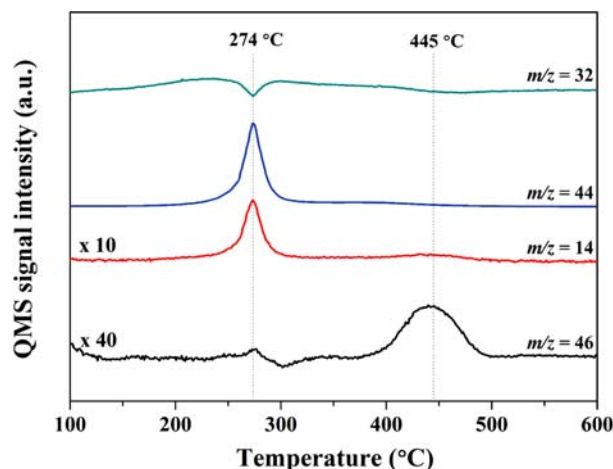


Fig. 9. TPO profiles of the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst obtained after the amination reaction of ethanol at 230 °C for 100 h. The mass signals of  $m/z=32$  (·O<sub>2</sub>), 44 (·CO<sub>2</sub>), 14 (·N), and 46 (·NO<sub>2</sub>) were detected by using a QMS detector.

available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

## REFERENCES

1. S. I. Galanov, O. Sidorova, M. A. Gavrilenko, O. Frants, V. Nekhoroshev, Y. D. Korolev and A. Egoshina, *Procedia Chemistry*, **15**, 14 (2015).
2. J. M. Hur, B. Y. Coh, L. Lu, H. H. Kwon and H. I. Lee, *Catal. Lett.*, **69**, 237 (2000).
3. Y.-L. Xie, M.-F. Luo and J.-J. Zhao, *React. Kinet. Catal. Lett.*, **89**, 29 (2006).
4. S. P. Naik and J. B. Fernandes, *Indian J. Chem. Technol.*, **5**, 405 (1998).
5. K. N. Kim and A. M. Lane, *J. Catal.*, **137**, 127 (1992).
6. T. Tatsumi, S. Kunitomi, J. Yoshiwara, A. Muramatsu and H.-o. Tominaga, *Catal. Lett.*, **3**, 223 (1989).
7. M. V. Badani and W. N. Delgass, *J. Catal.*, **187**, 506 (1999).
8. Y. Hu, J. Cao, J. Deng, B. Cui, M. Tan, J. Li and H. Zhang, *React. Kinet. Mech. Cat.*, **106**, 127 (2012).
9. Y. Zhang, Y. Zhang, C. Feng, C. Qiu, Y. Wen and J. Zhao, *Catal. Commun.*, **10**, 1454 (2009).
10. C. Feng, Y. Zhang, Y. Zhang, Y. Wen and J. Zhao, *Catal. Lett.*, **141**, 168 (2011).
11. D. Zhang, Y. Zhang, Y. Wen, K. Hou and J. Zhao, *Chem. Eng. Res. Des.*, **89**, 2147 (2011).
12. B. M. Reddy and B. Manohar, *J. Chem. Soc., Chem. Commun.*, 234 (1993).
13. S. Kulkarni, R. R. Rao, M. Subrahmanyam and A. R. Rao, *J. Chem. Soc., Chem. Commun.*, 273 (1994).
14. E. Rojas, M. O. Guerrero-Pérez and M. A. Bñares, *Catal. Lett.*, **143**, 31 (2013).
15. E. C. Corker, U. V. Mentzel, J. Mielby, A. Riisager and R. Fehrmann, *Green Chem.*, **15**, 928 (2013).
16. J.-H. Park, E. Hong, S. H. An, D.-H. Lim and C.-H. Shin, *Korean J. Chem. Eng.*, **34**, 2610 (2017).
17. L. Chen, C. K. S. Choong, Z. Zhong, L. Huang, Z. Wang and J. Lin, *Int. J. Hydrogen Energy*, **37**, 16321 (2012).
18. E. Hong, S. Bang, J. H. Cho, K. D. Jung and C.-H. Shin, *Appl. Catal. A-Gen.*, **542**, 146 (2017).
19. J. H. Cho, S. H. An, T.-S. Chang and C.-H. Shin, *Catal. Lett.*, **146**, 811 (2016).
20. C. H. Bartholomew, *Appl. Catal. A-Gen.*, **212**, 17 (2001).
21. A. Baiker, D. Monti and Y. S. Fan, *J. Catal.*, **88**, 81 (1984).
22. J. H. Cho, J. H. Park, T.-S. Chang, G. Seo and C.-H. Shin, *Appl. Catal. A-Gen.*, **417**, 313 (2012).
23. P. Papakonstantinou, D. Zeze, A. Klini and J. McLaughlin, *Diamond Relat. Mater.*, **10**, 1109 (2001).
24. C. Ronning, H. Feldermann, R. Merk, H. Hofsäss, P. Reinke and J.-U. Thiele, *Phys. Rev. B*, **58**, 2207 (1998).
25. X. Li, J. Zhang, L. Shen, Y. Ma, W. Lei, Q. Cui and G. Zou, *Appl. Phys. A*, **94**, 387 (2009).

## Supporting Information

### Selective synthesis of acetonitrile by reaction of ethanol with ammonia over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst

Ye-Seul Jeong, Sang Hee An, and Chae-Ho Shin<sup>†</sup>

Department of Chemical Engineering, Chungbuk National University, Cheongju, Chungbuk 28644, Korea

(Received 28 March 2019 • accepted 7 May 2019)

#### Catalyst characterization

Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku diffractometer equipped with Cu K $\alpha$  x-ray source operating at 40 kV and 50 mA. The crystalline phases were identified by matching the experimental patterns to the JCPDS powder diffraction files, and the particle sizes of NiO and Ni were calculated by the Scherrer's equation. The surface area and total pore volume of the Ni(x)/Al<sub>2</sub>O<sub>3</sub> catalysts were determined by N<sub>2</sub> physisorption at -196 °C on a Micromeritics ASAP2020 apparatus. Prior to the analysis, the samples were degassed at 250 °C for 4 h. Specific sur-

tion files, and the particle sizes of NiO and Ni were calculated by the Scherrer's equation. The surface area and total pore volume of the Ni(x)/Al<sub>2</sub>O<sub>3</sub> catalysts were determined by N<sub>2</sub> physisorption at -196 °C on a Micromeritics ASAP2020 apparatus. Prior to the analysis, the samples were degassed at 250 °C for 4 h. Specific sur-

Table S1. Physico-chemical properties of support and the calcined and reduced 10 wt% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst

| Sample                                   | XRD (NiO or Ni particle size, nm) |                             | N <sub>2</sub> sorption                            |   | O <sub>2</sub> titration          | H <sub>2</sub> chemisorption |                                 |   | H <sub>2</sub> -TPR        |          |         |
|--|-----------------------------------|-----------------------------|--|---|-----------------------------------|------------------------------|---------------------------------|---|----------------------------|----------|---------|
|  | Calcined sample <sup>a</sup>      | Reduced sample <sup>b</sup> | S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> ) | V <sub>p</sub> (cm <sup>3</sup> g <sup>-1</sup> ) | Reduction degree (%) <sup>c</sup> | D (%) <sup>d</sup>           | Particle size (nm) <sup>e</sup> | S <sub>Ni</sub> (m <sup>2</sup> g <sub>Ni</sub> <sup>-1</sup> ) | Reduction temperature (°C) |          |         |
|  |                                   |                             |  |   |                                   |                              |                                 |   | α                          | β        | γ       |
|  |                                   |                             |  |   |                                   |                              |                                 |   |                            |          |         |
| γ-Al <sub>2</sub> O <sub>3</sub>         | -                                 | -                           | 194  | 0.661   | -                                 | -                            | -                               | -   | -                          | -        |         |
| 10 wt% Ni/Al <sub>2</sub> O <sub>3</sub> | 8.2                               | 8.1                         | 157  | 0.561   | 48.8                              | 12.0                         | 8.1                             | 31.4  | 430 (8) <sup>f</sup>       | 620 (87) | 776 (5) |

<sup>a</sup>Calcined at 500 °C for 2 h

<sup>b</sup>Reduced at 600 °C for 3 h

<sup>c</sup>Calculated from O<sub>2</sub> uptake: [the amount of O<sub>2</sub> consumption]/[the theoretical amount of H<sub>2</sub> consumption with the assumption of fully reduced NiO (mmol H<sub>2</sub>; NiO+H<sub>2</sub>→Ni+2H<sup>+</sup>)]×100

<sup>d</sup>Corrected dispersion=surface Ni<sup>0</sup> atom/total reduced Ni<sup>0</sup> atom×100=surface Ni<sup>0</sup> atom/(total Ni atom×reduced fraction)×100

<sup>e</sup>Corrected Ni diameter=uncorrected Ni diameter×reduced Ni fraction

<sup>f</sup>Values in parentheses correspond to the relative distribution of NiO species of each reduction peak

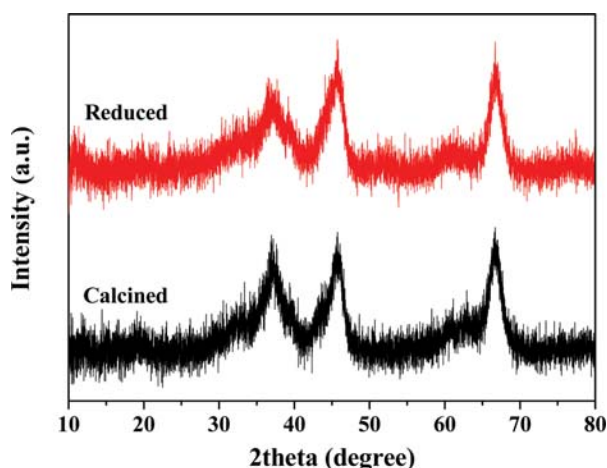


Fig. S1. XRD patterns of 10 wt% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 500 °C for 2 h and reduced at 600 °C for 2 h in flowing of H<sub>2</sub> (50 cm<sup>3</sup> min<sup>-1</sup>).

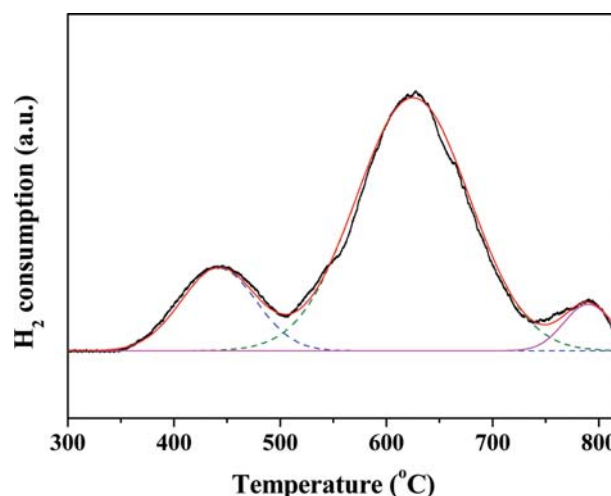


Fig. S2. H<sub>2</sub>-TPR profile of 10 wt% Ni/Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 500 °C for 2 h.

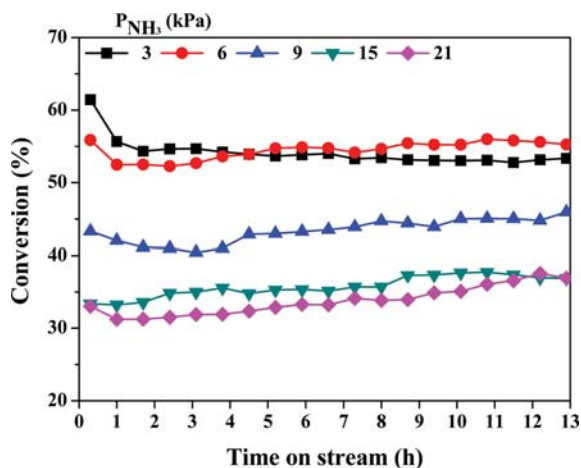


Fig. S3. Evolution of conversion as a function of partial pressure of  $\text{NH}_3$  vs. time on stream in the selective synthesis of acetonitrile over  $\text{Ni}/\text{Al}_2\text{O}_3$  catalyst. Reaction conditions: 0.2 g catalyst,  $T=190^\circ\text{C}$ , total flow rate= $50\text{ cm}^3\text{ min}^{-1}$ , partial pressure of  $\text{EtOH}=3\text{ kPa}$ .

face area was calculated by the Brunauer-Emmet-Teller (BET) equation in the relative pressure range 0.05-0.2, assuming a cross-sectional area of  $0.162\text{ nm}^2$  for the  $\text{N}_2$  molecules. The total pore volume was obtained from the quantity of volume adsorbed at  $P/P_0=0.995$  and the pore size distribution was calculated from desorption branch through the Barrett-Joyner-Hallenda (BJH) equation.

Temperature programmed reduction was performed using a quadrupole mass spectroscopy (Balzer QMS 200) as a detector. The samples (0.1 g) were loaded in a quartz reactor (I.D. 12 mm) and pretreated at  $400^\circ\text{C}$  for 1 h under Ar flowing ( $50\text{ cm}^3\text{ min}^{-1}$ ). After cooling to  $50^\circ\text{C}$ , a flow of 5%  $\text{H}_2/\text{Ar}$  mixed gas ( $50\text{ cm}^3\text{ min}^{-1}$ ) was introduced the catalyst bed and the temperature was increased to  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$ . The variation of  $\text{H}_2$  ( $m/z=2$ ) mass signal was collected by MS.

The metal dispersion, particle size and metallic surface area of the  $\text{Ni}(x)/\text{Al}_2\text{O}_3$  catalysts were determined by  $\text{H}_2$ -chemisorption using a Micromeritics ASAP2020. Prior to the analysis, the samples (0.3 g) were reduced at  $600^\circ\text{C}$  for 3 h under  $\text{H}_2$  flowing. The sample was cooled under vacuum to the adsorption temperature, and the chemisorption measurements were performed at  $50^\circ\text{C}$ . The chemisorption isotherm was obtained from the difference between the first adsorption isotherm, which is the sum of chemisorption and physisorption and the second adsorption isotherm, which is from the physisorption. The amount of chemisorbed  $\text{H}_2$  on the Ni was obtained by plotting the amounts of adsorbed  $\text{H}_2$  as a function of the partial pressure of  $\text{H}_2$  and back extrapolating to zero. The metal dispersion was calculated assuming a  $\text{H}_2/\text{Ni}$  stoichiometry of 1.0. The reduction degree of the  $\text{Ni}(x)/\text{Al}_2\text{O}_3$  catalysts was determined by the  $\text{O}_2$  titration method and calculated by the following equation:  $[\text{the amount of } \text{O}_2 \text{ consumption}]/[\text{the theoretical amount of } \text{H}_2 \text{ consumption with the assumption of fully reduced nickel oxides } (\text{mmol } \text{H}_2; \text{NiO} + \text{H}_2 \rightarrow \text{Ni}^0 + 2\text{H}^+)] \times 100$ .

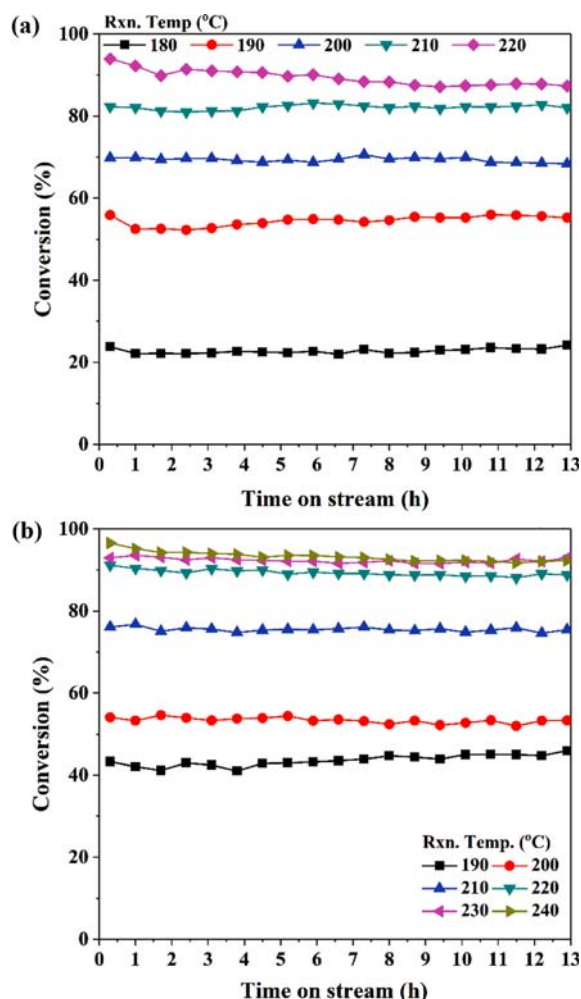


Fig. S4. Evolution of conversion as a function of reaction temperature with (a)  $\text{EtOH}/\text{NH}_3$  (molar ratio)=1/2 and (b) 1/3 vs. time on stream in the selective synthesis of acetonitrile over  $\text{Ni}/\text{Al}_2\text{O}_3$  catalyst. Reaction conditions: 0.2 g catalyst, partial pressure of  $\text{EtOH}=3\text{ kPa}$ ,  $T=180\text{--}240^\circ\text{C}$ , and total flow rate= $50\text{ cm}^3\text{ min}^{-1}$ .

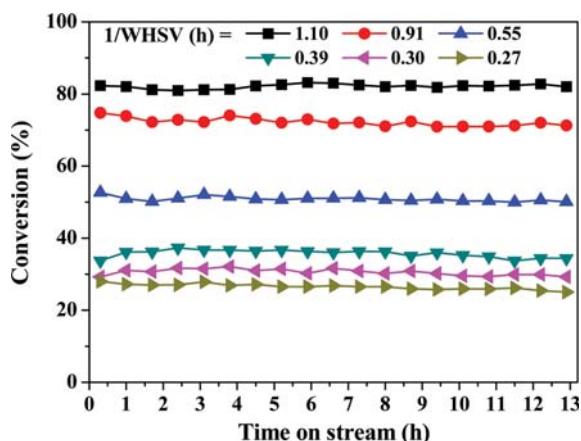


Fig. S5. Evolution of conversion as a function of  $1/\text{WHHSV}$  vs. time on stream in the selective synthesis of acetonitrile over  $\text{Ni}/\text{Al}_2\text{O}_3$  catalyst. Reaction conditions:  $T=210^\circ\text{C}$ , partial pressure of  $\text{EtOH}=3\text{ kPa}$ , and  $\text{NH}_3/\text{EtOH}$  (molar ratio)=2.



**Table S2. Conversion, selectivities and deactivation rate in the selective synthesis of acetonitrile over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst as a function of partial pressure of NH<sub>3</sub> at initial and 13 h on stream**

| P <sub>NH3</sub><br>(kPa) | Conv. (%) |        | Selectivity (%) |     |                               |      |        |     |                               |      | Deactivation<br>rate (%) |
|---------------------------|-----------|--------|-----------------|-----|-------------------------------|------|--------|-----|-------------------------------|------|--------------------------|
|                           | Initial   | t=13 h | Initial         |     |                               |      | t=13 h |     |                               |      |                          |
|                           |           |        | MEA             | DEA | C <sub>2</sub> H <sub>4</sub> | AcN  | MEA    | DEA | C <sub>2</sub> H <sub>4</sub> | AcN  |                          |
| 3                         | 65.0      | 55.6   | 6.2             | 5.6 | 0.2                           | 88.0 | 6.8    | 8.4 | 1.7                           | 83.1 | 14.5                     |
| 6                         | 55.7      | 55.8   | 6.8             | 2.5 | 0.8                           | 89.9 | 6.9    | 2.7 | 1.1                           | 89.2 | −0.2                     |
| 9                         | 45.5      | 45.9   | 5.2             | -   | 1.0                           | 93.8 | 8.0    | -   | 1.5                           | 90.5 | −0.9                     |
| 15                        | 32.8      | 37.6   | 5.2             | -   | 1.2                           | 93.6 | 5.5    | -   | 3.5                           | 91.0 | −14.6                    |
| 21                        | 31.5      | 37.1   | 5.0             | -   | 1.6                           | 93.4 | 5.2    | -   | 4.0                           | 90.8 | −17.8                    |

Reaction conditions: 0.2 g catalyst, T=190 °C, partial pressure of EtOH=3 kPa, total flow rate=50 cm<sup>3</sup> min<sup>-1</sup>

**Table S3. Conversion, selectivities and deactivation rate in the selective synthesis of acetonitrile over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst as a function of reaction temperature at initial and 13 h on stream**

| Temp.<br>(°C) | Conv. (%) |        | Selectivity (%) |     |                               |      |        |     |                               |      | Deactivation<br>rate (%) |
|---------------|-----------|--------|-----------------|-----|-------------------------------|------|--------|-----|-------------------------------|------|--------------------------|
|               | Initial   | t=13 h | Initial         |     |                               |      | t=13 h |     |                               |      |                          |
|               |           |        | MEA             | DEA | C <sub>2</sub> H <sub>4</sub> | AcN  | MEA    | DEA | C <sub>2</sub> H <sub>4</sub> | AcN  |                          |
| 180           | 23.6      | 24.1   | 9.6             | -   | 0.5                           | 89.9 | 13.7   | -   | 0.5                           | 85.8 | -2.1                     |
| 190           | 55.7      | 55.8   | 6.8             | 2.5 | 0.8                           | 89.9 | 6.9    | 2.7 | 1.2                           | 89.2 | -0.2                     |
| 200           | 70.2      | 69.1   | 6.1             | 2.2 | 1.5                           | 90.2 | 5.5    | 2.2 | 1.6                           | 90.7 | 1.6                      |
| 210           | 82.4      | 82.2   | 3.0             | 2.5 | 1.9                           | 92.6 | 3.2    | 1.2 | 2.0                           | 93.6 | 0.2                      |
| 220           | 93.7      | 88.0   | 1.2             | 0.0 | 1.9                           | 96.9 | 1.5    | -   | 2.9                           | 95.6 | 6.1                      |

Reaction conditions: NH<sub>3</sub>/EtOH=2, partial pressure of EtOH=3 kPa, 0.2 g catalyst, and total flow rate=50 cm<sup>3</sup> min<sup>-1</sup>

**Table S4. Conversion, selectivities and deactivation rate in the selective synthesis of acetonitrile over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst as a function of reaction temperature at initial and 13 h on stream**

| Temp.<br>(°C) | Conv. (%) |        | Selectivity (%) |                               |      |        |                               |      | Deactivation<br>rate (%) |
|---------------|-----------|--------|-----------------|-------------------------------|------|--------|-------------------------------|------|--------------------------|
|               | Initial   | t=13 h | Initial         |                               |      | t=13 h |                               |      |                          |
|               |           |        | MEA             | C <sub>2</sub> H <sub>4</sub> | AcN  | MEA    | C <sub>2</sub> H <sub>4</sub> | AcN  |                          |
| 190           | 45.5      | 45.9   | 5.2             | 1.0                           | 93.8 | 8.0    | 1.5                           | 90.5 | −0.9                     |
| 200           | 54.3      | 53.4   | 5.1             | 0.9                           | 94.0 | 5.3    | 0.9                           | 93.8 | 1.7                      |
| 210           | 76.7      | 75.3   | 4.6             | 1.0                           | 94.4 | 5.1    | 1.1                           | 93.8 | 1.8                      |
| 220           | 91.3      | 89.0   | 2.7             | 1.7                           | 95.6 | 3.0    | 1.5                           | 95.5 | 2.5                      |
| 230           | 93.1      | 90.9   | 2.1             | 2.1                           | 95.8 | 2.5    | 2.1                           | 95.4 | 2.4                      |
| 240           | 96.9      | 92.4   | 1.1             | 2.0                           | 96.9 | 1.4    | 1.6                           | 97.0 | 4.6                      |

Reaction conditions: NH<sub>3</sub>/EtOH=3, partial pressure of EtOH=3 kPa, 0.2 g catalyst, and total flow rate=50 cm<sup>3</sup> min<sup>-1</sup>

**Table S5. Conversions, selectivities and deactivation rate in the selective synthesis of acetonitrile over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst as a function of 1/WHSV at initial and 13 h on stream**

| 1/WHSV<br>(h) | Conv. (%) |        | Selectivity (%) |     |                               |      |        |     |                               |      | Deactivation<br>rate (%) |
|---------------|-----------|--------|-----------------|-----|-------------------------------|------|--------|-----|-------------------------------|------|--------------------------|
|               | Initial   | t=13 h | Initial         |     |                               |      | t=13 h |     |                               |      |                          |
|               |           |        | MEA             | DEA | C <sub>2</sub> H <sub>4</sub> | AcN  | MEA    | DEA | C <sub>2</sub> H <sub>4</sub> | AcN  |                          |
| 1.10          | 82.4      | 82.2   | 3.0             | 2.5 | 1.9                           | 92.6 | 3.2    | 1.2 | 2.0                           | 93.6 | 0.2                      |
| 0.91          | 73.3      | 71.2   | 4.5             | 2.4 | 1.8                           | 91.3 | 4.3    | 2.3 | 1.7                           | 91.7 | 2.9                      |
| 0.55          | 51.5      | 50.2   | 3.9             | -   | 1.3                           | 94.8 | 2.8    | -   | 1.2                           | 96.0 | 2.5                      |
| 0.39          | 37.2      | 34.2   | 3.6             | -   | 1.2                           | 95.2 | 2.6    | -   | 1.2                           | 96.3 | 8.1                      |
| 0.30          | 31.5      | 29.9   | 3.6             | -   | 0.8                           | 95.6 | 2.1    | -   | 1.0                           | 96.9 | 5.1                      |
| 0.27          | 27.0      | 25.2   | 3.4             | -   | 0.8                           | 95.8 | 2.0    | -   | 0.8                           | 97.2 | 6.7                      |

Reaction conditions: NH<sub>3</sub>/EtOH (molar ratio)=2, partial pressure of EtOH=3 kPa, and T=210 °C