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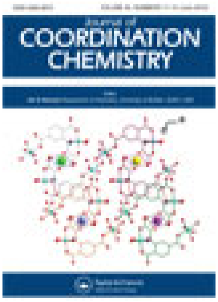

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Reaction of NO at low temperature by ACF loading urea and rare-earth element oxides (La_2O_3, CeO_2)

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Reaction of NO at low temperature by ACF loading urea and rare-earth element oxides (La_2O_3, CeO_2)

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Loaded catalysts of 10–50% (w/w) urea loaded on activated carbon fibers (ACF), referred to as urea/ACF, and 10%urea–5–15% (w/w) La_2O_3/ACF and CeO_2/ACF were prepared by an impregnation method and used for removal of NO at low temperature (30–120°C). The experimental results showed that the catalytic activity of urea/ACF could be greatly improved by loaded rare-earth element oxides. Furthermore, 10%urea–5%La_2O_3/ACF and 10%urea–10%CeO_2/ACF could maintain high and stable catalytic activity at 100°C.

Keywords: NO; La_2O_3; CeO_2; ACF; Urea

1. Introduction

Nitrogen oxides (NO, NO_2) emitted from stationary industrial sources or mobile vehicles are harmful atmospheric pollutants that contribute to acid rain, photochemical smog, depletion of the stratospheric ozone layer, and chronic inflammatory airway diseases [1–3]. Although selective catalytic reduction (SCR) has been regarded as an efficient method to treat NO_x from a stationary emission source, there are two main problems [4]. First, the high reaction temperature requires reheating of the flue gas and second, the process requires NH_3 gas as an indispensable reagent which has high toxicity and flammability [5].

For the first problem, many previously reported catalysts, such as MnO_2/Al_2O_3, CuO/AC, and Fe_2O_3/AC, showed high activities for SCR at 120–250°C [6–8]. However, research of SCR at lower temperatures (<120°C) is still rare.

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For the second one, urea is a practical reagent for SCR system because it is consumed only through reaction with NO, not decomposition, an improvement over NH_3 [9]. Another reason is that it has much higher storage capacity for reducing agent than NH_3 [10].

The urea has been used in SCR for NO for many years. Sullivan [11] reported catalysts, prepared by CuO loaded on TiO_2, Al_2O_3, and SiO_2, activated for the SCR–NH_3 reaction on NO in the presence of H_2O, showing very low activity in SCR-urea reaction on NO, and the decrease was not mainly due to H_2O. Seker [12] also used alumina loaded Pt and Au for SCR-urea reaction of NO, and the presence of SO_2 had fewer effects. However, the Pt and Au were both noble metals which could not be widely used. Meanwhile, Xu [13] reported that Cu-zeolite with urea also could yield high NO conversion. However, the urea used in most of the reported papers was in solution. Shirahama [9] reported that activated carbon loaded urea could yield ideal NO conversion, too. However, the samples prepared by Shirahama had less catalytic activity on NO than NO_2. The former study by using urea loaded on activated carbon fibers (ACF) of Shirahama [10] also showed similar results. Recently, Miyawaki [14] reported that NO could be turned into N_2 using pitch-based ACF, in which TiO_2 and urea were co-supported. TiO_2 could convert NO into NO_2 due to its photocatalytic effect. However, UV light or daylight was necessary in the process.

Since lanthanides, such as La and Ce, are abundant in China, the authors have studied NO purification ability of La_2O_3 and CeO_2 loaded on ACF at low temperature [15–18]. However, all of them have been investigated using NH_3 as an indispensable reagent or only at room temperature. In this article, the NO conversions of urea/ACF, urea-La_2O_3/ACF, and urea-CeO_2/ACF were studied and the NO catalytic mechanisms also discussed, respectively.

2. Experimental

2.1. *Catalysts preparation*

The catalysts urea/ACF, urea-La_2O_3/ACF, and urea-CeO_2/ACF were prepared as previous papers [15, 17] reported. Surface area of the catalysts was measured by the BET method illustrated in table 1. Figure 1 also shows the SEM microphotographs of two catalysts.

Table 1. Values of S_{BET} of the catalysts.

Sample	S_{BET} ($m^2 g^{-1}$)
ACF	1476
10%urea–5%La_2O_3/ACF	1304
10%urea–10%CeO_2/ACF	1168

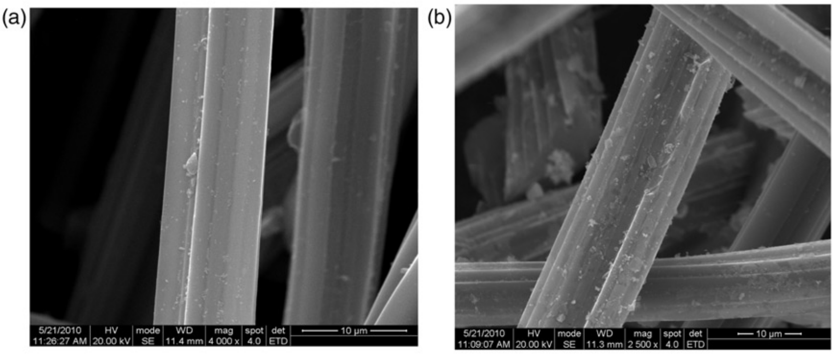

Figure 1. SEM microphotographs of different catalysts: (a): 10%urea–5%La_2O_3/ACF; (b): 10% urea–10%CeO_2/ACF.

2.2. *Measurement of reactivity*

In each experiment, 0.5000 g of catalyst was loaded. The experiment was carried out under NO: 500 ppm, O_2: 9%, N_2: balance, gas space velocity = 20,000 $m^3\,h^{-1}\,m^{-3}$, flow = 533.4 mL min^{-1}, temperature = 30–120°C, relative humidity = 0%. The NO and NO_2 concentrations were measured continuously by Testo flue gas analyzer (Testo 350XL, GER).

3. Results and discussion

3.1. *Reaction of NO with urea supported on ACF*

Figure 2 shows 30%urea/ACF yielded the highest NO conversion of all catalysts from 30°C to 120°C. The NO conversion of 20%urea/ACF was just slightly lower than that of 30%urea/ACF. Meanwhile, the NO conversion of 10%urea/ACF also yielded high and stable activity even with less urea loaded mass than those of 40%urea/ACF and 50%urea/ACF. In contrast, 40%urea/ACF and 50%urea/ACF had low activity due to too much urea loaded on ACF. All samples yield more NO conversion from 100°C to 120°C. Although the NO conversion was slightly lower than that of Miyawaki [14], it was obviously higher than those of the reported results of Sullivan Seker and Xu [11–13].

3.2. *Reaction of NO with urea supported on series of La_2O_3/ACF and CeO_2/ACF*

Figure 3 shows 10%urea/ACF, modified by metal oxides, greatly affected NO conversion. In figure 3, 10%urea–10%CeO_2/ACF yielded more than 96% NO conversion from 30°C to 120°C. On the other hand, 10%urea–5%La_2O_3/ACF yielded the highest and most stable NO conversion in the series of 10%urea-La_2O_3/ACF, higher than catalytic activity of Cu/AC prepared by electroless plating [19] and no less than that of previous reported results [9, 11–13, 20].

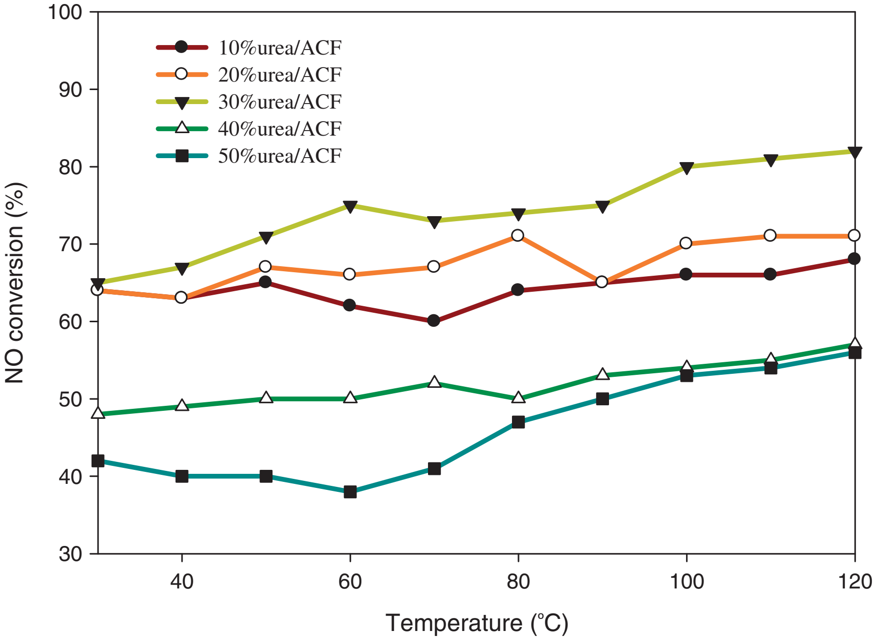

Figure 2. Effect of loading methods of urea/ACF on NO reaction.

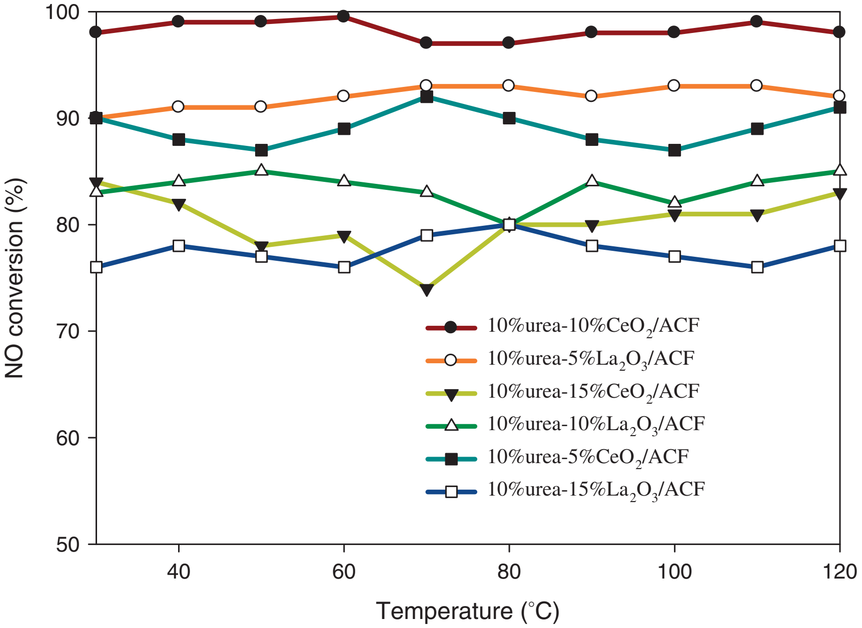

Figure 3. Effect of loading methods of 10%urea-La$_2$O$_3$/ACF and 10%urea-La$_2$O$_3$/ACF on NO reaction.

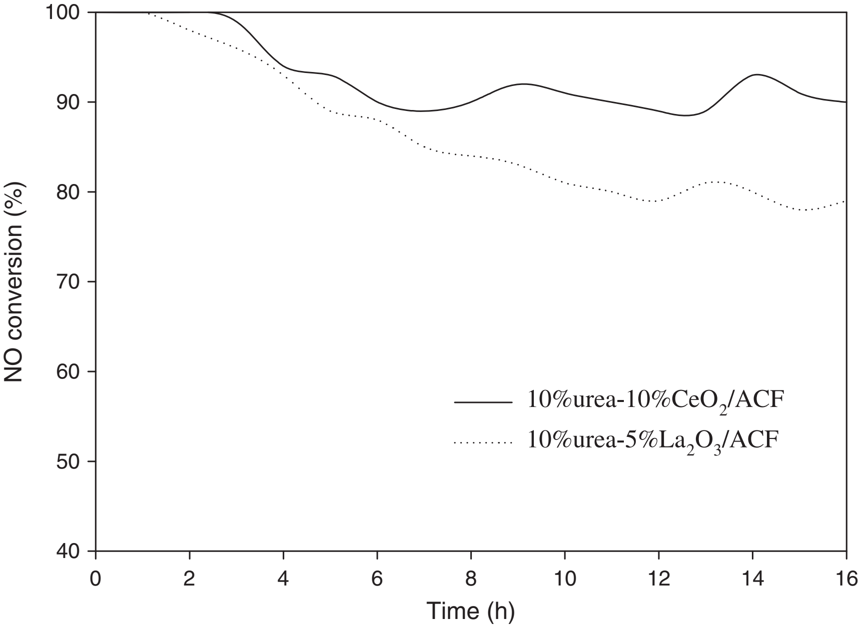

Figure 4. Reaction of NO with 10%urea–5%La_2O_3/ACF and 10%urea–10%CeO_2/ACF.

3.3. *Catalytic stability experiments*

Figure 4 shows the catalytic activity of 1.0000 g 10%urea–5%La_2O_3/ACF and 10%urea–10%CeO_2/ACF at 100°C under conditions of 500 ppm NO concentration and 9% O_2 concentration; 10%urea–10%CeO_2/ACF and 10%urea–5%La_2O_3/ACF yield 100% in 3 h and 1 h at 100°C, respectively. Moreover, 10%urea–10%CeO_2/ACF yielded higher and more stable NO conversion than 10%urea–5%La_2O_3/ACF at 100°C, which was consistent with previous research [15]. Above all, 10% urea–5%La_2O_3/ACF and 10%urea–10%CeO_2/ACF still yielded 90% and 79% after 16 h.

3.4. *Mechanism of SCR of NO*

The reduction of NO with urea on ACF was completed through the following steps.

$$2NO + O_2 \rightarrow 2NO_2, \tag{1}$$

$$NO + NO_2 + (NH_2)_2CO \rightarrow 2N_2 + CO_2 + 2H_2O, \tag{2}$$

$$2NO_2 + O_2 + 2(NH_2)_2CO \rightarrow 3N_2 + 2CO_2 + 4H_2O. \tag{3}$$

Oxidation of NO into NO_2 was the key step, since the presence of NO_2 significantly accelerated reactions (2) and (3). Moreover, $(NH_2)_2CO$ could be treated as reducing agent like the action of NH_3 for SCR [9]. Since urea occupied the surface of ACF, it restricted the adsorption of O_2 and oxidation of NO. Therefore, the amount of urea should be optimized to balance NO removal, which was consistent with the result illustrated in figure 2.

However, the NO conversion mechanism on urea-MO/ACF (La_2O_3 and $CeO_2 = MO$) was different from that of urea/ACF at low temperature (30–120°C). The catalytic centers would be the metal oxides [21].

$$2MO + O_2 \rightarrow 2MO_2^{\cdot}, \tag{4}$$

$$MO_2^{\cdot} + NO \rightarrow NO_2 + MO, \tag{5}$$

$$6MO_2^{\cdot} + 4(NH_2)_2CO + 6NO \rightarrow 6MO + 4CO_2 + 7N_2 + 8H_2O, \tag{6}$$

$$2MO_2^{\cdot} + 2(NH_2)_2CO + 2NO_2 \rightarrow 2MO + 2CO_2 + 3N_2 + 4H_2O. \tag{7}$$

Reaction (1) can be enhanced by urea-MO/ACF because of the addition of MO, as shown by reactions (4) and (5). Therefore, the NO oxidation activity over the catalysts played an important role in improving the catalytic activity since reactions (2) and (3) could simultaneously take place, significantly enhancing NO conversion. Moreover, the sample loaded mass of MO and the specific surface area of the prepared catalyst should be balanced [22], in line with the result of figure 3. Furthermore, thermal gravimetric experiments showed high chemical stability of La_2O_3/ACF and CeO_2/ACF [15, 16]. Thus, they could maintain high and stable catalytic activity at 100°C, consistent with the result of figure 4.

4. Conclusions

The catalytic activity of urea/ACF was greatly improved by loading rare-earth element oxides (La_2O_3 and CeO_2), of which the best loaded mass percentages are 5% and 10%, respectively. Furthermore, 10%urea–5%La_2O_3/ACF and 10%urea–10%CeO_2/ACF could maintain high and stable catalytic activity at 100°C. SCR of NO by urea-MO/ACF is a desirable method to treat NO from a stationary emission source. Furthermore, the influence of SO_2 and H_2O is the target of the next research.

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References

[1] I. Su, J.C.S. Wu. *Catal. Commun.*, **10**, 1534 (2009).
[2] W. Xu, S. Zheng, R.A. Dweik, S.C. Erzurum. *Free Radic. Biol. Med.*, **41**, 19 (2006).

[3] B. Gaston, J.M. Drazen, J. Loscalzo, J.S. Stamler. *Am. J. Respir. Crit. Care Med.*, **149**, 538 (1994).
[4] I. Mochida, Y. Kawabuchi, S. Kawano, Y. Matsumura, M. Yoshikawa. *Fuel*, **76**, 543 (1997).
[5] G.C. Bond, P. Forzatti, J.C. Védrine. *Catal. Today*, **56**, 329 (2000).
[6] L. Singoredjo, R. Korver, F. Kapteijn, J. Moulijn. *Appl. Catal. B: Environ.*, **1**, 297 (1992).
[7] Z.P. Zhu, Z.Y. Liu, S.J. Liu, H.X. Niu, T.D. Hu, T. Liu, Y.N. Xie. *Appl. Catal. B: Environ.*, **26**, 25 (2000).
[8] T. Grzybek, H. Papp. *Appl. Catal. B: Environ.*, **1**, 271 (1992).
[9] N. Shirahama, I. Mochida. *Appl. Catal. B: Environ.*, **57**, 237 (2005).
[10] N. Shirahama, I. Mochida. *Appl. Catal. B: Environ.*, **52**, 173 (2004).
[11] J.A. Sullivan, J.A. Doherty. *Appl. Catal. B: Environ.*, **55**, 185 (2005).
[12] E. Seker, E. Gulari, R.H. Hammerle, C. Lambert, J. Leerat, S. Osuwan. *Appl. Catal. A: Gen.*, **226**, 183 (2002).
[13] L.F. Xu, R.W. McCabe, R.H. Hammerle. *Appl. Catal. B: Environ.*, **39**, 51 (2002).
[14] J. Miyawaki, T. Shimohara, N. Shirahama, A. Yasutake, M. Yoshikawa, I. Mochida, S.H. Yoon. *Appl. Catal. B: Environ.*, **110**, 273 (2011).
[15] P. Lu, C.T. Li, G.M. Zeng, L.J. He, D.L. Peng, H.F. Cui, S.H. Li, Y.B. Zhai. *Appl. Catal. B: Environ.*, **96**, 157 (2010).
[16] C.T. Li, P. Lu, G.M. Zeng, Q.J. Wang, Q. Li, L.J. He, Y.B. Zhai. *Environ. Sci. China*, **29**, 3280 (2008).
[17] P. Lu, Z. Zeng, C.T. Li, G.M. Zeng, J. Guo, X. Jiang, Y.B. Zhai, X.P. Fan. *Environ. Technol.*, **33**, 1029 (2012).
[18] Z. Zeng, P. Lu, C.T. Li, G.M. Zeng, X. Jiang, Y.B. Zhai, X.P. Fan. *Environ. Technol.*, DOI. 10.1080/09593330.2011.626799.
[19] L. Olsson, H. Sjovall, R.J. Blint. *Appl. Catal. B: Environ.*, **81**, 203 (2008).
[20] H.F. Cui, C.T. Li, P. Lu, D.L. Peng, J. Guo, L. Chen. *Environ. Sci. China*, **31**, 29 (2010).
[21] M. Kang, E.D. Park, J.M. Kim, J.E. Yie. *Appl. Catal. A: Gen.*, **327**, 261 (2007).
[22] Z. Zeng, P. Lu, L. Mai. *Guangzhou Chem. Ind.*, **38**, 20 (2010).