

New insight into hydroxyl-mediated NH₃ formation on the Rh-CeO₂ catalyst surface during catalytic reduction of NO by CO

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ARTICLE INFO

Article

Article history: Received 20 March 2017 Accepted 4 May 2017 Published 5 August 2017

Keywords: NH₃ formation NO reduction CO oxidation In-situ DRIFTS Water gas shift

1. Introduction

The catalytic reduction of NO to N₂ by CO has been widely applied in emission control for automotive exhaust [1]. In recent years, CeO₂ has generally been used as an oxygen buffer in three-way catalytic converter systems owing to its oxygen storage/release capacity, undergoing redox processes involving the Ce⁴⁺/Ce³⁺ couple, CeO₂ \Rightarrow CeO_{2-x} + (x/2)O₂, that can greatly promote CO oxidation [2]. Among transitional metals, rhodium shows the strongest ability for specifically enhancing NO reduction due to its ability to efficiently dissociate NO, which is the main reason for Rh addition to commercial three-way catalysts [3,4]. Additionally, Rh/ceria interactions improve both resistance to thermally induced catalyst sintering and catalytic activity due to additional bifunctional sites at the

ABSTRACT

Vibrational IR spectra and light-off investigations show that NH_3 forms via the "hydrogen down" reaction of adsorbed CO and NO with hydroxyl groups on a CeO_2 support during the catalytic reduction of NO by CO. The presence of water in the reaction stream results in a significant increase in NH_3 selectivity. This result is due to water-induced hydroxylation promoting NH_3 formation and the competitive adsorption of H_2O and NO at the same sites, which inhibits the reactivity of NO reduction by NH_3 .

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metal-support interfaces [4,5].

Few reports exists concerning the formation of NH₃ during the catalytic reduction of NO by CO, but N₂O selectivity has been discussed [2,4,6,7], resulting in a misunderstanding of the reaction mechanisms [8–11]. N₂ selectivity is defined as 'the percentage of NO conversion to N₂ (total reduced NO concentration minus double N₂O concentration) in total NO conversion' [7,12], indicating that only N₂, N₂O, and CO₂ products are taken into consideration during the catalytic reduction of NO by CO on Rh catalyst. Dropsch *et al.* [13] suggested that CO could react with hydroxyl groups on the support to release hydrogen gas. Until now, NH₃ detection in the effluent gas has not been used to analyze N₂ selectivity, resulting in an improper mechanistic and kinetic understanding of the NO/CO reaction on Rh catalyst [11,14].

This work was supported by the National Natural Science Foundation of China (21463015), the Provincial Applied Fundamental Research Program of Yunnan (2014FA045), and the National High Technology Research and Development Program of China (863 Program, 2015AA034603).

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DOI: 10.1016/S1872-2067(17)62856-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 8, August 2017

NH₃ emission from automobiles is principally due to the reduction of nitrogen oxides (NO_x) by H₂ generated from water-gas shift and steam-reforming reactions [15–17]. Recent studies [18,19] have emphasized that NH₃ is among the main factors causing the formation of secondary inorganic aerosols (NH₄⁺, SO₄^{2–}, and NO₃[–]). Therefore, an exact understanding of the NH₃ formation mechanism in the catalytic reduction of NO to N₂ by CO plays a significant role in effective NH₃ emission control for gasoline-fueled vehicles under transient driving conditions. This work focuses on determining the behavior of NH₃ generation and proposing a possible reaction mechanism for NH₃ formation during the catalytic reduction of NO by CO, leading researchers to a more accurate analysis of light-off test results.

2. Experimental

CeO₂ was synthesized using a precipitation method. A slight excess of 25% NH₄OH solution was added dropwise into the requisite amount of aqueous solution of Ce(NO₃)₃·5H₂O under continuous stirring. The obtained gelatinous precipitate was aged at 80 °C for 3 h under vigorous stirring, filtered, and washed with distilled water several times until no pH change was observed. The precipitate was dried at 120 °C overnight and then calcined at 300 °C in static air for 1 h. The resultant powder was calcined at 550 °C for 4 h under an air atmosphere.

Rh-CeO₂ catalyst was prepared by mixing the obtained gelatinous precipitate with Rh nanoparticles (NPs), followed by aging, drying, and calcinating using the same method outlined for CeO₂ preparation. For Rh NP synthesis, polyvinylpyrrolidone (PVP) and citric acid (CA) were added into 85 mL of Rh(NO₃)₃ aqueous solution with a PVP monomer unit:CA:Rh molar ratio of 5:4:1, and then placed in a 250-mL three-necked flask. The mixture was preheated under a nitrogen atmosphere and magnetic stirring to 60 °C for 5 min and the pH was adjusted to 3.0 by the addition of 10% NH₄OH solution. The requisite borane *tert*-butylamine (TBAB), which served as a reducing agent in the reaction, was dissolved in 15 mL of distilled water and added to the above mixture with a TBAB:Rh molar ratio of 5:1. The reaction proceeded at 60 °C for 10 min.

Fourier transform infrared (FT-IR) measurements of the solid samples were carried out in transmission mode on a Nicolet iS10 FT-IR spectrometer with a resolution of 2 cm⁻¹ using the KBr wafer technique and scanning 36 times. For wafer preparation, catalyst sample (10 mg) was mixed with KBr (200 mg, Specpure) and pressed under a pressure of 20 MPa for several minutes. The actual Rh loading amount was analyzed on a PerkinElmer Optima 8000 ICP-OES instrument.

In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed on a Nicolet 6700 FT-IR spectrometer equipped with a mercury cadmium telluride (MCT) detector. Each sample (100 mg) was pretreated at 500 °C for 60 min in a N₂ stream and then cooled to room temperature. Before starting the experiment, background spectra were recorded at 100 °C intervals from 100 to 500 °C in a N₂ stream at a heating rate of 10 °C/min. Each corresponding spectrum was measured in a reaction gas stream containing 0.1% CO and/or 0.1% NO for transient experiments. The total flow rate of the mixed gas stream in these experiments was 100 mL/min.

The catalytic activity and selectivity of the catalyst samples were studied in the catalytic reduction of NO by CO in a continuous flow fixed-bed microreactor. Catalyst samples (500 mg) with an average diameter of 40–60 mesh were placed in a stainless-steel tube with an inner diameter of 5 mm to conduct activity tests, and CO temperature-programmed reduction (CO-TPR) and NO temperature-programmed oxidation (NO-TPO) measurements. The reaction mixture gas, as shown in Table 1, was supplied at a flow rate of 500 mL/min and the space velocity was 60000 mL/(g·h). The temperature dependence of the reaction was determined in temperature-programmed mode by heating from ambient temperature to 500 °C at a heating rate of 10 °C/min. The composition of the effluent gas was analyzed online using a 2030DBG2EZKS13T MultiGas FT-IR Analyzer purchased from MKS Instruments, Inc.

The conversion rate of NO, *X*(NO), was calculated using equation (1):

 $X(NO) = ([NO]_{in} - [NO]_{out})/[NO]_{in} \times 100\%$ (1) where $[NO]_{in}$ and $[NO]_{out}$ are the concentrations of injected and effluent NO gas, respectively. The conversion rate of CO, X(CO), was calculated using the same method. The selectivities to N₂O and NH₃, $S(N_2O)$ and $S(NH_3)$, respectively, were calculated using equations (2) and (3), based on the concentrations of N₂O and NH₃ products, respectively.

$$S(N_2O) = 2[N_2O]/([NO]_{in} - [NO]_{out}) \times 100\%$$
(2)

$$S(NH_3) = [NH_3]/([NO]_{in} - [NO]_{out}) \times 100\%$$
 (3)

Activation energies were estimated for CO conversion using the Arrhenius equation. About 200 mg of catalyst sample was used in each measurement. The samples were first activated at 400 °C in a CO/NO or CO/NO/H₂O reaction mixture gas stream at a total flow rate of 500 mL/min and then cooled to room temperature. The composition of the effluent gas was analyzed online at 10 °C interval in the (5–20)% CO conversion temperature range. The specific reaction rate was defined as the total number of moles of CO₂ produced per second per mass of catalyst at a specific temperature.

3. Results and discussion

The catalytic reduction of NO by CO is an important model reaction for simulating three-way catalysis. In this work, model CO/NO and CO/NO/ H_2O reactions were carried out using a

Table 1

Composition of reaction mixture gas stream for catalytic properties test.

Reaction	CO (%)	NO (%)	H ₂ O (%)	H ₂ (%)	N ₂
CO-TPR	0.1	0	0	0	balance
NO-TPO	0	0.1	0	0	balance
CO/NO	0.1	0.1	0	0	balance
CO/H ₂ O	0.1	0	5	0	balance
NO/H ₂ O	0	0.1	5	0	balance
CO/NO/H ₂ O	0.1	0.1	5	0	balance
NO/H ₂	0	0.1	0	0.05 a	balance

 $^{\rm a}$ Total conversion of 0.1% CO via a water-gas shift reaction would produce 0.05% ${\rm H}_2$



Fig. 1. (a) CO and NO conversion and (b) NH₃ selectivity curves during catalytic reduction of NO by CO.

typical fixed-bed flow reactor under a CO/NO stoichiometric mixture. CO and NO conversion curves for the model reactions are shown in Fig. 1(a). T_{50} values for CO and NO conversions in the CO/NO reaction over Rh-CeO₂ catalyst with an actual Rh loading amount of 0.296% were 152 and 156 °C (Table 2), respectively, which were significantly lower than those over the CeO₂ catalyst. This was further confirmed by the lower apparent activation energy (E_a) of 36 kJ/mol for the Rh-CeO₂ catalyst, which

Table 2

 $T_{\rm 50}$ and $T_{\rm 90}$ values for CO and NO conversion in the catalytic reduction of NO to N_2 by CO.

Desetien	Decetant	CeO ₂			Rh-CeO ₂		
Reaction	Reactant	T ₅₀ ^a (°C)	T ₉₀ b (°C)		T ₅₀ (°C)	T ₉₀ (°C)	
CO (NO	CO	321	407		152	247	
CO/NO	NO	325	379		156	250	
	CO	no data	no data		155	266	
	NO	no data	no data		162	266	

^a Light-off temperature for 50% conversion.

^b Light-off temperature for 90% conversion.



Fig. 2. Arrhenius curves of the NO/CO reaction on (1) CeO₂ surface, (2) Rh-CeO₂ surface, and (3) the NO/CO/H₂O reaction on Rh-CeO₂ surface.

explained the lack of intrinsic reactivity for base metals compared with precious metals [3,20]. For the Rh-CeO₂ catalyst, water-induced active inhibition of CO and NO conversions was explained by the corresponding increases in T_{90} and E_a (up to 21 kJ/mol) compared with results under dry conditions.

NO is partially reduced to N_2O as the main product on the Ce site below 250 °C, and N_2O selectivity decreased with increasing temperature in the CO/NO reaction (Fig. 3). Notably, Fig. 1(b) shows that clear NH₃ gas detection started at about 190 °C and a maximum NH₃ selectivity of 14.8% was obtained on the CeO₂ support at 268 °C in the H₂O-free reaction mixture. Furthermore, CO and NO conversions of 17.1% and 12.6%, respectively, were achieved at the same temperature. By contrast, N₂O selectivity strongly decreased when Rh nanoparticles were supported because N₂O was more readily formed and binded less strongly. Therefore, N₂O was more likely to desorb into the gas phase on CeO₂ surfaces than on Rh sites [11]. The Rh-CeO₂ catalyst also showed higher NH₃ selectivity up to 236 °C, but gave lower NH₃ selectivity at higher temperatures due to a rhodium-mediated increase in reactivity.



Fig. 3. N_2O selectivity curves of the NO/CO reaction on (1) CeO₂ surface , (2) Rh-CeO₂ surface, and (3) the NO/CO/H₂O reaction on Rh-CeO₂ surface.

Fig. 4(b) shows that the amount of NH₃ product on the Rh-CeO₂ catalyst increased in the following order: CO/NO/H₂O (0.0158% NH₃ at 203 °C) > CO/NO (0.0094% NH₃ at 222 °C) > NO/H₂ (0.004% NH₃ at 240 °C). There was no clear NH₃ formation during the NO-TPO and NO/H₂O reactions at low temperatures. The results indicated that CO and NO might react with hydroxyl groups on the surface of the CeO₂ support to release NH₃ gas via a water-gas shift reaction, comprising the chemisorption and reaction of CO with hydroxyl species, followed by NO reduction, as described in equations (4) and (5) [13,21,22].

$$20H + 2CO \rightarrow CO_2 + H_2 \tag{4}$$

$$2NO_x + (2x+3)H_2 \rightarrow 2xH_2O + 2NH_3$$
 (5)

Results concerning the influence of water on NH₃ selectivity are shown in Fig. 1(b). Two peaks for NH3 formation, centered at 199 and 342 °C with NH₃ selectivities of 25.2% and 20.9%, respectively, were observed in the water mixed feed stream. The maximum NH₃ selectivity at low temperature was attributed to OH groups, while NH₃ was formed at high temperatures due to the reduction of NO_x by H_2 , where CO reacts with water to produce H₂ and CO₂ according to the water-gas shift reaction, as shown in equation (6). Compared with the CO-TPR results, CO conversion rates increased with increasing temperature above 230 °C due to the water-gas shift reaction, as shown in Fig. 5. Theoretically, 0.05% H₂ would be released when a total conversion of 0.1% CO was achieved in the water-gas shift reaction. The competitive reaction of H₂O and NO with CO during the CO/NO/H₂O reaction might form H₂ as a product.

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{6}$$

As shown in Figs. 4 and 5, CO conversion was observed during the CO-TPR experiment, illustrating that CO indeed reacted with active species on the catalyst surface. There was little NO conversion and NH₃ production under the NO/H₂O stream, which indicated that H₂O inhibited NO adsorption due to the competitive adsorption of H₂O and NO at the same sites [23]. This inhibition effect would reduce the reactivity of NO reduction by NH₃, leading to increased NH₃ emission.

FT-IR spectroscopy was used to further confirm that adsorbed CO and NO reacted with hydroxyl groups on the surface

100 90 80 CO TPR CO/NO 70 CO/H₂O CO conversion (%) 60 CO/NO/H₂O 50 40 30 20 1(100 150 200 250 300 350 400 450 500 Reaction temperature (°C)

Fig. 5. CO conversion curves on Rh-CeO₂ catalyst in temperature-programmed experiments using different gas mixtures.

of CeO₂ to release NH₃. The FT-IR spectrum of pristine Rh-CeO₂ catalyst (Fig. 6) showed three main bands at 3693, 3650, and 3506 cm⁻¹, which were assigned to Ce-OH terminal hydroxyl groups (type I), Ce₂-OH double-bridging groups (type II), and cerium oxyhydroxide impurities, respectively [24,25]. After the CO/NO/H₂O reaction, three main stretching vibrations of OH groups were still detected, while the Ce-OH vibration showed a sharp decrease in intensity and shifted to higher wavenumber (3704 cm⁻¹). However, no band was observed in the range 3800–3400 cm⁻¹ after CO/NO cycling. This was explained by the interaction of adsorbed H₂O with basic OH groups. Demoulin *et al.* [22] suggested that hydroxylated surfaces resulted from water vapor dissociatively chemisorbing to become hydroxyl ions. Surface water molecules can also react with chemisorbed CO species to form H⁺ and formate ions [26].

Surface species evolutions of CO and/or NO on pretreated Rh-CeO₂ catalyst were also investigated using *in-situ* DRIFTS measurements. The stretching vibrations of hydroxyl groups exhibited a significant wavenumber shift after CO adsorption at 100 °C, as shown in Fig. 7(a). This was mainly due to the presence of surface hydroxyls on the CeO₂ support, which (1) al-



Fig. 4. (a) NO conversion and (b) NH₃ formation curves on Rh-CeO₂ catalyst in temperature-programmed experiments using different gas mixtures.



Fig. 6. FT-IR spectra of (1) Rh-CeO₂ catalyst, and used catalysts from (2) CO/NO and (3) CO/NO/H₂O reactions.

lows the migration of adsorbed CO on Rh across the CeO₂ surface to isolated OH sites to form carbonates (1583, 1453, and 1402 cm⁻¹), and (2) alters the coordination of chemisorbed CO at the oxygen end, weakening the C-O bond followed by facilitating CO dissociation during CO oxidation [24,25,27,28]. At this temperature, the features at 2168, 2073, 2010, and 1760 cm⁻¹ were attributed to Ce⁴⁺-carbonyls, gem-dicarbonyls, linear carbonyls, and bridged carbonyls on Rh, respectively [27]. The vibrational IR spectra of carbonyl species, and type I and II hydroxyls, showed a decrease in intensity, which indicated the consumption of adsorbed CO. The band at 3616 cm⁻¹ was assigned to O-H stretching vibrations of hydrogen carbonate species formed by the interaction of CO with basic OH⁻ ions [10,28]. In summary, the reaction of type I and II hydroxyls with adsorbed CO led to a weakening of their vibrations and hydrogen carbonate formation.

Figs. 7(b) and (c) show *in-situ* DRIFTS results for temperature-programmed experiments in NO and CO/NO streams, respectively. Under NO, the obvious consumption of three types of hydroxyl groups was accomplished by the reaction with NO, with a peak apparition appearing at 3622 cm⁻¹ (when the temperature was raised to 300 °C). This was associated with N–H stretching in coordinated ammonia from NH₃ product adsorbed on the oxide surface [29]. The consumption of adsorbed NO on Rh (band at 1922 cm⁻¹) and the formation of nitrates on CeO₂ (1594, 1568, and 1530 cm⁻¹) were observed with increasing temperature [23,30]. These results suggested that NO reacted with OH groups to form nitrates and release NH₃, explaining NH₃ formation and clear NO conversion during the NO-TPO experiment. In contrast, the peak at 3622 cm⁻¹ started to appear at a lower temperature (200 °C) and showed a higher intensity at the same temperature when CO and NO were introduced simultaneously, illustrating that CO played an important role in NH₃ formation during the NO reaction. These results were in good agreement with those in Fig. 4(b).

4. Conclusions

NH₃ production in the catalytic reduction of NO to N₂ by CO under dry conditions was ascribed to NO reduction by molecular hydrogen present in hydroxyl groups on the CeO₂ surface. *In-situ* DRIFTS results suggested that the consumption of cerium oxyhydroxide impurities was directly accomplished by NO reduction, whereas type I and II hydroxyls were consumed *via* a water-gas shift reaction followed by NO_x reduction, which led to NH₃ generation. In the presence of water, water-induced hydroxylation could promote NH₃ formation, whereas the competitive adsorption of H₂O and NO on the same sites would inhibit the reactivity of NO reduction by NH₃, leading to increased NH₃ emission.

Acknowledgments

This work was supported by Xiaodong Wu (School of Materials Science and Engineering, Tsinghua University) for *in-situ* DRIFTS characterization.

References

- J. J. He, C. X. Wang, T. T. Zheng, Y. K. Zhao, Johnson Matthey Technol. Rev., 2016, 60, 196–203.
- [2] J. R. Kim, W. J. Myeong, S. K. Ihm, J. Catal., 2009, 263, 123–133.
- [3] H. S. Gandhi, G. W. Graham, R. W. McCabe, J. Catal., 2003, 216, 433–422.
- [4] P. Fornasiero, G. R. Rao, J. Kašpar, F. L'Erario, M. Graziani, J. Catal., 1998, 175, 269–279.
- [5] F. Fajardie, J. F. Tempère, J. M. Manoli, O. Touret, G. Blanchard, G. Djéga-Mariadassou, J. Catal., 1998, 179, 469–476.
- [6] A. Tou, H. Einaga, Y. Teraoka, Catal. Today, 2013, 201, 103–108.



Fig. 7. In-situ DRIFTS spectra of Rh-CeO2 catalyst in (a) CO/N2, (b) NO/N2, and (c) CO/NO/N2 steams as a function of temperature in transient mode.



A hydroxyl-induced water-gas shift reaction results in NH_3 formation on the surface of $Rh-CeO_2$ catalyst, suggesting that NH_3 production should be considered in the catalytic reduction of NO by CO in future studies. Water vapor in the gas mixture stream has a significant influence on NH_3 release.

- [7] M. Li, X. D. Wu, Y. D. Cao, S. Liu, D. Weng, R. Ran, J. Colloid Interf. Sci., 2013, 408, 157–163.
- [8] L. J. Liu, B. Liu, L. H. Dong, J. Zhu, H. Q. Wan, K. Q. Sun, B. Zhao, H. Y. Zhu, L. Dong, Y. Chen, *Appl. Catal. B*, **2009**, 90, 578–586.
- [9] D. Li, Q. Yu, S. S. Li, H. Q. Wan, L. J. Liu, L. Qi, B. Liu, F. Gao, L. Dong, Y. Chen, *Chem. Eur. J.*, **2011**, 17, 5668–5679.
- [10] Y. Y. Lü, L. C. Liu, H. L. Zhang, X. J. Yao, F. Gao, K. A. Yao, L. Dong, Y. Chen, J. Colloid Interf. Sci., 2013, 390, 158–169.
- [11] W. C. Ding, W. X. Li, Chin. J. Catal., 2014, 35, 1937–1943.
- [12] B. K. Cho, B. H. Shank, J. E. Bailey, J. Catal., 1989, 115, 486–499.
- [13] H. Dropsch, M. Baerns, *Appl. Catal. A*, **1997**, 158, 163–183.
- [14] V. P. Zhdanov, B. Kasemo, *Surf. Sci. Rep.*, **1994**, 20, 113–189.
- [15] D. C. Carslaw, G. Rhys-Tyler, Atmos. Environ., 2013, 81, 339–347.
- [16] A. J. Kean, D. Littlejohn, G. A. Ban-Weiss, R. A. Harley, T. W. Kirchstetter, M. M. Lunden, *Atmos. Environ.*, 2009, 43, 1565–1570.
- [17] M. Shelef, H. S. Gandhi, Ind. Eng. Chem. Prod. Res. Dev., 1974, 13, 80–85.
- [18] S. N. Behera, M. Sharma, Sci. Total Environ., 2010, 408, 3569–3575.
- [19] M. Sharma, S. Kishore, S. N. Tripathi, S. N. Behera, J. Atmos. Chem., 2007, 58, 1–17.

- [20] M. Bowker, Chem. Soc. Rev., 2008, 37, 2204–2211.
- [21] S. D. Jackson, B. M. Glanville, J. Willis, G. D. Mclellan, G. Webb, R. B. Moyes, S. Simpson, P. B. Wells, R. Whyman, *J. Catal.*, **1993**, 139, 207–220.
- [22] O. Demoulin, M. Navez, P. Ruiz, Appl. Catal. A, 2005, 295, 59–70.
- [23] G. Pekridis, N. Kaklidis, V. Komvokis, C. Athanasiou, M. Konsolakis, I. V. Yentekakis, G. E. Marnellos, J. Phys. Chem. A, 2010, 114, 3969–3980.
- [24] C. Li, Y. Sakata, T. Arai, K. Domen, K. I. Maruya, T. Onishi, J. Chem. Soc., Faraday Trans. 1, 1989, 85, 929–943.
- [25] C. Binet, M. Daturi, J. C. Lavalley, Catal. Today, 1999, 50, 207–225.
- [26] S. Emiroglu, N. Bårsan, U. Weimar, V. Hoffmann, *Thin Solid Films*, 2001, 391, 176–185.
- [27] V. Schwartz, A. Campos, A. Egbebi, J. J. Spivey, S. H. Overbury, ACS Catal., 2011, 1, 1298–1306.
- [28] A. Hornés, P. Bera, A. L. Cámara, D. Gamarra, G. Munuera, A. Martínez-Arias, J. Catal., 2009, 268, 367–375.
- [29] K. Liu, F. D. Liu, L. J. Xie, W. P. Shan, H. He, *Catal. Sci. Technol.*, 2015, 5, 2290–2299.
- [30] B. Azambre, L. Zenboury, A. Koch, J. V. Weber, J. Phys. Chem. C, 2009, 113, 13287–13299.

Rh-CeO2催化剂表面CO还原NO反应中羟基介导NH3生成问题的探讨

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摘要: CO催化还原NO是发生在汽车尾气净化催化剂中的一个重要化学反应. CeO₂容易发生氧化还原反应CeO₂ ⇔ CeO_{2-x} + (*x*/2)O₂而具有氧储存/释放作用,可以有效地促进CO氧化,因而CeO₂作为储氧材料和催化助剂被广泛应用于汽车催化剂 中. 在过渡金属元素中,铑对NO的解离活性最高,是目前汽车三效催化剂中最为重要的还原性活性组分.目前,有关 Rh-CeO₂基催化剂表面CO还原NO的文献仅关注催化反应活性和N₂O选择性,对CO还原NO反应机理的理解还不够深入准 确,无法为轻型汽油车NH₃排放控制提供正确有用的理论基础. NH₃排放至大气中会以NH₄⁺形式与SO₄²⁻和NO₃⁻离子结合,导致二次颗粒物污染,因此,研究CO还原NO反应中NH₃生成机理对轻型汽油车NH₃排放控制具有非常重要的理论意义. 我

们研究组强调了CO催化还原NO反应的表面羟基介导NH3生成问题,并通过原位漫反射傅里叶变换红外光谱(*in-situ* DRIFTS),傅里叶变换红外光谱(FT-IR),程序升温还原/氧化(TPR/TPO)等现代分析表征技术深入研究了CO还原NO反应机 理,并首次提出了催化剂表面"羟基脱氢"反应的NH3生成机理.

研究发现, Rh-CeO₂催化剂表面CO还原NO反应的NH₃选择性最高可达9.7%, 其反应表观活化能仅为36 kJ/mol, *in-situ* DRIFTS, FT-IR和NO-TPO测试结果表明, NH₃的生成可归因于催化剂表面"羟基脱氢"反应,即CO与催化剂表面端位羟基和桥式羟基发生"水煤气转化"反应生成H₂,反应产生的H₂还原NO生成NH₃; CeO₂中非骨架铈双羟基化形成的类氢氧化铈物种则会直接与NO发生脱氢反应生成NH₃,但需要更高的反应温度.值得注意的是,当反应气中额外通入5%水蒸气时,其反应表观活化能提高了21 kJ/mol (同比增加58.3%),更重要的是NH₃选择性明显提高,最高可达25.3%(同比增加160.8%), FT-IR测试结果表明,这是由于水蒸气作用促使催化剂表面羟基化,表面活性氢源得以不断补充.这从动力学角度促进了端位羟基和桥式羟基的"水煤气转化"反应而提高NH₃选择性.同时,对比NO/H₂,CO/NO和CO/NO/H₂O反应的NH₃生成浓度,我们还发现,H₂O分子与NO的竞争吸附会抑制未解离吸附的NH₃进一步还原NO,减少反应生成NH₃的消耗,促使更多生成的NH₃从催化剂表面脱附至气相中,这也是水蒸气导致NH₃选择性明显增加的重要原因.以上结果清晰地表明了催化剂表面"羟基脱氢"作用和水蒸气分子与NO的竞争吸附行为对CO还原NO反应中NH₃生成的重要影响. 关键词:NH₃生成;NO还原;CO氧化;原位漫反射傅里叶变换红外光谱;水煤气转化

收稿日期: 2017-03-20. 接受日期: 2017-05-04. 出版日期: 2017-08-05.

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基金来源:国家自然科学基金(21463015);云南省应用基础研究计划项目(2014FA045);国家高技术研究发展计划项目(863计划, 2015AA034603).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(http://www.sciencedirect.com/science/journal/18722067).