Novel Ru–Mg–Al–O Catalyst Derived from Hydrotalcite-like Compound for NO Storage/Decomposition/Reduction

Lan Dong Li,[†] Jun Jie Yu,[†] Zheng Ping Hao,^{*,†} and Zhi Ping Xu^{*,‡}

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, People's Republic of China, and Australian Research Council (ARC) Centre for Functional Nanomaterials, School of Engineering and Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, QLD 4072, Australia

Received: November 25, 2006; In Final Form: March 12, 2007

Ru–Mg–Al hydrotalcite-like anionic clay (Mg/Al/Ru = 90:29:1) was successfully prepared with a constant-pH coprecipitation method. Calcination of a hydrotalcite-like precursor at 600 °C in the air gave rise to the well-mixed oxide Ru–Mg–Al–O that possesses a good dispersion of Ru species. Ru–Mg–Al–O catalyst after suitable pretreatment exhibits quite high NO_x storage capability in the temperature range of 250–400 °C, and the highest NO_x storage capability of about 220 μmol g⁻¹ is obtained at 350 °C with flowing 790 ppm NO and 8% O₂ in N₂ stream. Meanwhile, the decomposition of 25–60% NO to N₂ as well as N₂O is clearly observed on the catalyst at 300–400 °C. In situ diffuse reflectance Fourier transform (DRIFT) spectra indicate that NO_x is adsorbed and stored on a catalyst mainly in the form of various coordinated nitrites/nitrates. On the basis of the NO_x adsorption–desorption profiles as well as the in situ DRIFTS spectra, we have proposed a schematic outline for NO_x storage and NO decomposition. Finally, the reduction of stored NO_x species on the catalyst by H₂ was carried out at 350 °C, indicating that all adsorbed NO_x species can be readily reduced by hydrogen.

1. Introduction

Current strategies attempting to minimize fuel consumption and CO₂ emission prompt the use of lean-burn engines instead of conventional engines in automobiles. However, the three-way catalysts used to treat the exhaust of conventional engines suffer from severe loss of activity for NO_x reduction under lean-burn conditions (in excess oxygen).¹ Selective catalytic reduction (SCR) of NO_x by hydrocarbons is a potential approach to remove NO_x under lean-burn conditions and receives much attention. Nevertheless, a breakthrough in the SCR technology is hindered by the insufficient activity and insufficient durability of SCR catalysts.² Thus, NO_x storage–reduction (NSR) technology is considered as a more promising alternative for NO_x removal under lean-burn conditions and has already been commercialized in relevant applications.³

NSR technology is used in the engines that alternately operate under lean-burn and rich-burn conditions.⁴ Under lean-burn conditions, NO is oxidized and stored on catalysts, while the stored NO_x species are reduced and the NSR catalysts are regenerated periodically under rich-burn conditions. A model NSR catalyst is composed primarily of three components: (i) a high-surface-area support material; (ii) alkali or alkaline-earth metal oxides for NO_x storage; and (iii) a noble metal as the catalytic redox component. As a model NSR catalyst, Pt–Ba/Al₂O₃ has been extensively studied.^{5–13} In the recent search for promising NSR catalysts, well-mixed oxide catalysts derived from hydrotalcite-like compounds have received considerable attention due to their high NO_x storage capability and good SO_x

tolerance.^{14–19} Pt–Mg–Al–O,^{14,17} Pt–Cu–Mg–Al–O,^{14–16} Pd–Mg–Al–O,¹⁸ and Co–Mg–Al–O¹⁹ catalysts derived from their corresponding hydrotalcite-like compounds have been reported to exhibit quite good NSR performance.

Supported Ru materials are well-known heterogeneous catalysts for ammonia synthesis²⁰ and decomposition.²¹ Ru surfaces have been proved as active sites for the chemisorption, activation, and dissociation of small molecules, such as NH₃,²² NO,²³ CH₄,²⁴ and CO.²⁵ However, to the best of our knowledge, Ru-based catalysts have not been applied in NSR reactions yet. In the present work, a well-mixed Ru–Mg–Al–O oxide derived from its hydrotalcite-like precursor has been prepared and tested as an NSR catalyst for the first time. The performances in NO storage/reduction/decomposition demonstrate that Ru–Mg–Al–O oxide is a novel promising NSR catalyst.

2. Experimental

2.1. Catalyst Preparation. The Mg/Ru–Al hydrotalcite-like compound was prepared with a constant-pH coprecipitation method. In a typical synthesis, Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, and RuCl₃·3H₂O were mixed with distilled water at a Mg/Al/Ru atomic ratio of 90:29:1. The mixed salt solution (150 mL) and Na₂CO₃ solution (150 mL) were simultaneously added into 100 mL of distilled water under vigorous stirring. The pH was maintained at 10 ± 0.5 by adding an appropriate amount of 1 M NaOH. After aging in the suspension for 2 h under stirring at room temperature, precipitates were collected by filtration and thoroughly washed with distilled water. The cake was dried at 80 °C overnight and then calcined in air at 600 °C for 6 h to derive the corresponding Ru–Mg–Al–O oxide.

2.2. Catalyst Characterization. Powder X-ray diffraction (XRD) measurement was carried out at a scanning rate of 4°

* Corresponding authors. Prof. Zheng Ping Hao: Tel.: +86-10-6292354; fax: +86-10-62923564; e-mail: zpinghao@rcees.ac.cn. Dr. Zhi Ping Xu: Tel: +61-7-33463809; fax: +61-7-33463973; e-mail: gordonxu@uq.edu.au.

[†] Chinese Academy of Sciences.

[‡] The University of Queensland.

Figure 1. XRD patterns of the Mg/Ru–Al hydrotalcite-like compound and the derived Ru–Mg–Al–O composite.

min^{-1} from 10 to 70° using a Rigaku D/max RB diffractometer equipped with a graphite monochromator and using Cu K α radiation ($\lambda = 0.1542 \text{ nm}$).

The textural properties of Ru–Mg–Al–O oxide were analyzed by low-temperature N_2 adsorption/desorption using a Quantachrome NOVA-1200 gas absorption analyzer. The specific surface area was calculated with the Brunauer–Emmett–Teller (BET) equation, and the pore volume was derived with the Barrett–Joyner–Halenda (BJH) method from the adsorption isotherm.

2.3. NO_x Adsorption/Desorption. NO_x adsorption experiments were performed on a fixed-bed flow reactor with an

TABLE 1: Textural Properties of the Ru–Mg–Al–O Composite

sample	surface area ($\text{m}^2 \text{ g}^{-1}$)	pore volume ($\text{cm}^3 \text{ g}^{-1}$)	Mg/Al ratio ^a	Ru loading (%) ^a	Ru dispersion (%) ^b
Ru–Mg–Al–O	280	0.54	2.89	1.89	90

^a By weight. ^b Determined by a CO chemisorption experiment.

8-mm-i.d. quartz tube. A Ru–Mg–Al–O sample (0.8 g, 1 mL, 20–40 mesh) was fixed in the quartz tube, pretreated by flowing H_2/N_2 (1% H_2 ; flow rate = 100 mL min^{-1}) at 400°C for 1 h, and then cooled down to a preset adsorption temperature. A gaseous mixture of 790 ppm NO, 8% O_2 , and the balance N_2 was introduced to pass the sample at a total flow rate of 500 mL min^{-1} for 30 min at this temperature for adsorption. The concentrations of NO and NO_2 in the outlet were monitored online with a chemiluminescence NO_x analyzer (Ecotech EC 9841).

After NO_x adsorption, the flow gas was switched to pure N_2 (flow rate = 500 mL min^{-1}) for 30 min to remove the weakly adsorbed species at the same temperature. Then the temperature was cooled down to 100°C , and the temperature-programmed desorption (TPD) was conducted by heating the sample from 100°C to 600°C at a heating rate of $5^\circ \text{C min}^{-1}$. The concentrations of NO and NO_2 in the outlet were measured with a chemiluminescence NO_x analyzer, and the storage capability of NO_x on the sample was thus calculated.

2.4. NO Decomposition. A NO decomposition experiment was also performed on the fixed-bed flow reactor. Similarly, a Ru–Mg–Al–O sample (0.8 g, 1 mL, 20–40 mesh) was fixed

Figure 2. NO_x adsorption profiles on a Ru–Mg–Al–O composite at different temperatures.

in the quartz tube and pretreated in H_2/He (1% H_2 ; flow rate = 100 mL min^{-1}) at 400°C for 1 h. After the temperature was cooled down to a preset temperature, a gas mixture of 790 ppm NO, 8% O_2 , and the balance He was introduced at a total flow rate of 500 mL min^{-1} to react with the catalyst for 1 h, and gaseous nitrogen species in the outlet stream were monitored. Particularly, N_2O and N_2 in the outlet stream were analyzed online using a gas chromatograph (HP 6820 series, TCD detector, a molecular sieve 5A column and a porapak Q column), and NO and NO_2 were detected with a chemiluminescence NO_x analyzer (Ecotech EC 9841).

2.5. In Situ Fourier Transform Infrared (FTIR) Studies of NO_x Adsorption. In situ FTIR studies were performed in a spectrometer (Bruker Tensor 27) at a resolution of 4 cm^{-1} with an accumulation of 128 scans. Self-supporting pellets (about 50 mg) were made from the sample and used directly in the IR flow cell. The sample was pretreated in H_2/N_2 (1% H_2 ; flow rate = 30 mL min^{-1}) at 400°C for 1 h prior to each experiment and cooled to the preset temperature. After recording a reference spectrum, a gas mixture of 790 ppm NO, 8% O_2 , and the balance N_2 was introduced at a total flow rate of 30 mL min^{-1} , and then time-dependent FTIR spectra were recorded.

2.6. N_2 -TPD on Ru–Mg–Al–O. The N_2 -TPD experiment was performed with a mass spectrometer (Hiden QIC20) as the detector. The reduced Ru–Mg–Al–O sample was pretreated at 600°C for 1 h and cooled to room-temperature, both in He. Then pure N_2 was introduced to the sample. After 30 min of N_2 adsorption, the gas flow was switched to pure He. The catalyst was heated to 600°C at a rate of 5°C min^{-1} in He flow (30 mL min^{-1}), and the N_2 -TPD profile was recorded.

2.7. Reduction of Adsorbed NO_x Species. The catalyst was first exposed to $\text{NO}-\text{O}_2/\text{N}_2$ (790 ppm NO, 8% O_2 ; flow rate = 30 mL min^{-1}) for 1 h and purged with pure N_2 for 30 min at 350°C . After the feed gas was switched to H_2/N_2 (1% H_2 ; flow rate = 30 mL min^{-1}), time-dependent FTIR spectra were recorded every 2 min, and the intensity of characteristic IR bands was analyzed.

3. Results and Discussion

3.1. Ru–Mg–Al–O Composite. The XRD pattern of an as-synthesized Mg/Ru–Al compound in Figure 1a shows the hydrotalcite structure (JCPDS 22-0700) as the only crystalline phase. The well-defined diffraction peaks at 11.5° , 23° , 34° , 61° , and 62° revealed a good dispersion of Al^{3+} and Ru^{3+} in the hydroxide layers.²⁶ Calcination at 600°C for 6 h completely transformed the hydrotalcite structure to the oxide phase: mainly a MgO periclase phase (JCPDS 43-1022) with a possible spinel phase $\text{Mg}(\text{Al,Ru})_2\text{O}_4$ (JCPDS 86-2258), as shown in Figure 1b. No diffraction peaks corresponding to crystalline RuO_x phase can be observed, owing to the good dispersion of Ru species in the oxide matrices, which was 90% as determined by CO chemisorption (Table 1). The element analysis of the mixed oxide reveals that the mass ratio of Mg/Al is 2.89 and Ru loading is 1.89% (Table 1), in good agreement with the data in desired oxide $\text{Mg}_{90}\text{Al}_{29}\text{RuO}_{135}$ (2.79 and 1.93%, respectively). In addition, the derived oxide possesses a specific surface area of $280 \text{ m}^2/\text{g}$ and a pore volume of $0.54 \text{ cm}^3/\text{g}$ (Table 1).

3.2. NO_x Adsorption/Desorption. NO_x adsorption profiles on a Ru–Mg–Al–O catalyst at 250 – 400°C are presented in Figure 2. In general, NO was completely trapped by the catalyst in the initial 100–450 s. In the next period, NO was continuously trapped, but NO as well as NO_2 concentrations in the outlet gradually increased to a certain level. In the final 1500–2000 s, NO and NO_2 concentrations reached a constant. In

Figure 3. N_2 and N_2O concentrations vs time during the adsorption process.

particular, at 250°C , NO very quickly started to recover to about 700 ppm, and almost no NO_2 ($<10 \text{ ppm}$) was detected in the outlet. At higher temperatures (300 – 400°C), a considerable amount of NO_2 was detected, while the NO concentration recovered only to 200–400 ppm. Interestingly, the NO_2 concentration in the outlet increased to a maximum and then decreased to a stable level (Figure 2).

We further noted that, at 250°C , the total concentration of NO_x ($\text{NO} + \text{NO}_2$) was nearly recovered to the inlet NO concentration (790 ppm) after 20 min of adsorption. However, at higher temperatures, the amount of NO_x could only be recovered to 250–500 ppm. This indicates that a large proportion of NO is transformed/decomposed to other nitrogen compounds, such as N_2 and N_2O . As shown in Figure 3, N_2 and N_2O were detected at 250 – 400°C by gas chromatography when the balance gas was switched to He under the same conditions. N_2O was formed only at 300°C as well as 350°C in a small amount ($<40 \text{ ppm}$), while N_2 was transferred in a high amount at 300 – 400°C . It appears that the concentrations of N_2 and N_2O formed at each temperature arrive at a constant after 1500 s, which, together with the nearly constant concentrations of NO and NO_2 after 1500 s shown in Figure 2, indicates that the NO adsorption reaches a steady state after 1500 s.

Figure 4. NO_x desorption profiles from a Ru–Mg–Al–O composite after NO_x adsorption at different temperatures.

NO_x desorption profiles on Ru–Mg–Al–O oxide after NO_x adsorption at different temperatures are presented in Figure 4. In all cases, a similar strong NO desorption peak (centered at 350–400 °C) was observed, and a weak NO₂ desorption peak centered at about 350 °C was also noted. The NO_x storage capabilities on Ru–Mg–Al–O catalysts derived from the NO_x desorption profile are 120, 155, 220, and 165 $\mu\text{mol g}^{-1}$ catalyst at 250, 300, 350, and 400 °C, respectively. Generally, the storage capability is quite high, comparable with that of a model Pt–Ba/Al₂O₃ catalyst.^{5,27} Once again, the maximum NO_x storage (220 $\mu\text{mol g}^{-1}$) occurs at 350 °C. Since Mg–Al–O catalysts prepared with a similar method showed very low NO_x storage capability,¹⁸ it is suggested that Ru species play an essential role for NO_x storage on Ru–Mg–Al–O catalysts.

3.3. NO Decomposition. As discussed previously, a large proportion of NO_x is transferred to N₂ and N₂O on Ru–Mg–Al–O catalysts (Figure 3). As further shown in Figure 5, a considerable amount of N₂ (100–250 ppm) was detected at 300–400 °C, while N₂O was in a quite small quantity (<40 ppm) after 1500 s adsorption. As can also be seen, the outlet nitrogen equivalent of four nitrogen species (i.e., “outlet N” in Figure 5), $[\text{NO}]_{\text{outlet}} + [\text{NO}_2]_{\text{outlet}} + 2[\text{N}_2\text{O}]_{\text{outlet}} + 2[\text{N}_2]_{\text{outlet}}$, is almost equal to that of the supplied NO (i.e., “inlet N” in Figure 5) in all our experiments at 250–400 °C. We thus conclude that (i) NO decomposition takes place on Ru–Mg–Al–O catalysts during NO adsorption, (ii) the main decomposition products are N₂ and N₂O, and (iii) the adsorption/desorption/decomposition reaches a steady state after 1500 s. In particular, at 350 °C, most N₂ (250 ppm) was transferred from the inlet NO, meaning that 63% ($2 \times 250/790 \times 100\%$) of the NO is

Figure 5. Steady-state outlet nitrogen species concentrations during NO adsorption at 250–400 °C, where outlet N = $[\text{NO}] + [\text{NO}_2] + 2[\text{N}_2\text{O}] + 2[\text{N}_2]$.

directly decomposed. This is a remarkable amount of NO directly decomposed, which is comparable to the activity of catalysts only for NO thermal decomposition²⁸ and is not apparent for NSR catalysts. Meanwhile, the NO storage amount at 350 °C is the highest (220 $\mu\text{mol g}^{-1}$). These two points thus explain why the complete trapping time (450 s) is the longest and the recovered NO_x concentration is the lowest. Therefore,

Figure 6. DRIFT spectra of NO_x adsorption on Ru-Mg-Al-O oxide at different temperatures.

the optimum NO adsorption temperature on Ru-Mg-Al-O catalysts seems to be $\sim 350^\circ\text{C}$, at which most of the NO is either adsorbed by the catalyst or decomposed to N_2 . This temperature is also lower than the operation temperature in using a commercial NSR catalyst.²⁹

3.4. Adsorbed NO_x Species on a Catalyst. The in situ diffuse reflectance Fourier transform (DRIFT) spectra of NO adsorption on Ru-Mg-Al-O at different temperatures are shown in Figure 6. In these spectra, two downward peaks at ~ 1600 and $\sim 1400\text{ cm}^{-1}$ were observed, probably due to the replacement of carbonate in the initial catalyst.³⁰

At 250°C , bridging bidentate nitrite (peak at 1220 cm^{-1}), monodentate/linear nitrites (peak at 1480 cm^{-1}), and chelating bidentate nitrate (peak at 1290 cm^{-1}) were immediately observed upon $\text{NO}-\text{O}_2$ adsorption. The peaks of chelating nitrate and linear nitrites become more intense while the peak intensity of bridging nitrites remains constant after a 20-min adsorption. The adsorbed NO species on Ru (peak at 1850 cm^{-1}) is also recognized.

The IR spectra of NO adsorption on the catalyst at 300°C and above also show that the major species are various nitrites/nitrates (peaks at 1290 , 1480 , and 1030 cm^{-1}). Moreover, higher temperatures favor the formation of nitrates, either due to the instability of nitrites at these temperatures or the transformation of nitrites to nitrates³¹ with Ru catalysts. Therefore, the time-

TABLE 2: Assignments of IR Bands Observed on Ru-Mg-Al-O upon NO_x Adsorption at Different Temperatures

wavenumber	assignment	structure ^a	reference
1030 cm^{-1}	$\nu_{\text{sym}}(\text{ONO})$	$\begin{array}{c} \text{M}-\text{O} \\ \\ \text{M}-\text{O}-\text{N}=\text{O} \end{array}$	30
	bridging nitrates		
1220 cm^{-1}	$\nu_{\text{sym}}(\text{ONO})$	$\begin{array}{c} \text{M}-\text{O} \\ \\ \text{M}-\text{O}-\text{N} \end{array}$	31, 32
	bridging nitrites		
1290 cm^{-1}	$\nu_{\text{sym}}(\text{ONO})$	$\begin{array}{c} \text{O} \\ // \\ \text{M}-\text{O}-\text{N}=\text{O} \end{array}$	33, 34
	chelating nitrates		
1480 cm^{-1}	$\nu(\text{ONO})$	$\text{M}-\text{O}-\text{N}=\text{O}$	31, 32
	linear nitrites		
1850 cm^{-1}	$\nu(\text{NO})$	$\text{Ru}^{\text{II}}-\text{N}=\text{O}$	35
	adsorbed NO		

^a M = metal ions: Mg^{2+} or Al^{3+} .

resolved FTIR spectra at $250\text{--}400^\circ\text{C}$ indicate that NO is adsorbed and stored on the Ru-Mg-Al-O catalyst mainly as various coordinated nitrites and nitrates. A detailed assignment of IR bands observed on the Ru-Mg-Al-O catalyst is listed in Table 2.

3.5. NO_x Adsorption/Desorption Mechanism. Under adsorption conditions, O_2 can be adsorbed on the surface of Ru, followed by the disassociation to O, as on Pt:³²

Gaseous NO can then react with surface O to form nitrites/nitrates, which then migrate to the basic sites adjacent to Ru species. Thus, NO_x was stored on the Ru-Mg-Al-O catalyst as nitrites/nitrates, and the adsorption sites on Ru were regenerated:

Obviously, the dispersion of Ru species in catalyst is very important for NO_x storage, because a higher dispersion of Ru species provides more active sites to convert NO to nitrates/nitrates, which, in our belief, is the major route to store NO_x on the catalyst.

In addition, surface O on Ru can also oxidize gaseous NO to gaseous NO_2 on the catalyst surface. Some NO_2 can then be trapped on the basic sites available on the catalyst (most probably those nonadjacent to Ru species), forming nitrites and nitrates,³³ and the other NO_2 goes to the outlet:

On the other hand, the desorption process of adsorbed NO_x species mainly releases NO through decomposing nitrites and

Figure 7. Proposed NO_x storage/decomposition pathway on a Ru–Mg–Al–O catalyst.

nitrites.^{13,34} The decomposition of nitrates to NO can be facilitated by Ru:

3.6. NO Decomposition Mechanism. As shown in Figure 5, a large proportion of NO decomposed to N₂ at 300–400 °C. Under NO_x adsorption conditions, NO can be strongly adsorbed on the surface of Ru, as indicated by the high NO adsorption energy on Ru sites.³⁵ The dissociation of chemisorbed NO is readily activated on Ru stepped surfaces;^{23,35} for example, the adsorbed NO can easily dissociate to adsorbed N and O:

The adsorbed N diffuses on the Ru surface and two such N atoms form a chemisorbed N₂ molecule:

The desorption of N₂ from the Ru surface can occur further, but it is regarded as the rate-determining step for NO decomposition on Ru²⁸ at temperatures below 300 °C. We found that, on Ru–Mg–Al–O catalysts, N₂ desorption can start at 250 °C,

Figure 8. Time dependence of the integrated area of the FTIR bands (a) and the proportion of adsorbed species reduced (b) at 350 °C in flowing H₂/N₂ (1% H₂) after NO_x adsorption.

but only at 300 °C can a considerable amount of N₂ be released. The N₂ desorption peak is centered at about 350 °C. As a result, the Ru–Mg–Al–O catalyst does not exhibit obvious catalytic activity for NO decomposition at 250 °C, but exhibits high catalytic activity at 300 °C or higher temperatures. Generally, NO decomposition on the noble metal surface is severely inhibited by surface oxygen that is strongly bonded to the metal surface.³⁶ Under the current conditions, surface O can react with gaseous NO to form nitrites/nitrates that spill over to the basic sites adjacent to Ru species.

As discussed above, both NO_x storage and NO decomposition take place on Ru–Mg–Al–O catalysts at 300–400 °C. For a schematic view, the storage–decomposition pathway is illustrated in Figure 7.

3.7. Reduction of Adsorbed NO_x Species. Our experiments further indicate that the stored NO_x can be readily reduced to N₂ by H₂ at 350 °C on Ru–Mg–Al–O catalysts. We noted that the intensities of all IR bands corresponding to adsorbed NO_x species decreases with time significantly in H₂/N₂ at 350 °C. Figure 8a presents the decrease in the area of peaks at 1290, 1480, 1850, and 1030 cm⁻¹. In particular, two peaks at 1290 and 1480 cm⁻¹ decrease in intensity quickly with time. In 15–20 min, most NO_x species are reduced, which is more obviously shown in Figure 8b.

Since most adsorbed NO_x species are thermally stable at 350 °C, we believe that most adsorbed NO_x species are reduced to

air N₂, which is assisted by Ru. In the first step of reduction, the gaseous H₂ scavenges the adsorbed oxygen from Ru surfaces:

Then, H₂ adsorbs on the reduced Ru sites, followed by the dissociation to adsorbed H:

The formed adsorbed H can directly reduce the adsorbed NO on the Ru surface. Moreover, the active H could spill over to the adjacent basic sites to reduce the adsorbed nitrites/nitrates, similarly to that on Pd surfaces:³⁷

As usual, nitrites/nitrates on the basic sites (Mg-O and Al-O) can be reduced by gaseous H₂ directly:¹³

Overall, the reduction is not so prompt. The possible reason is due to the fewer Ru redox sites available, so that the last two reactions without catalysis may take place in a higher portion. Therefore, the incorporation of some cheap transition metals, such as Co, Cu, and Fe, into the catalysts has been under way in order to facilitate the reduction of the stored NO_x.

4. Conclusion

A Ru-Mg-Al hydrotalcite-like compound (Mg/Al/Ru = 90:29:1) was successfully prepared with a constant-pH coprecipitation method, and its calcination at 600 °C in the air derived the mixed Ru-Mg-Al-O oxide with a good Ru dispersion. The Ru-Mg-Al-O catalyst exhibits very good performance for NO_x storage in the temperature range of 250–400 °C, with a maximum storage of 220 μmol g⁻¹ at 350 °C. We have also noted that 25–60% of NO is decomposed to N₂ on the catalyst at 300–400 °C during the adsorption. Moreover, the adsorbed NO_x species on the Ru-Mg-Al-O catalyst can be reduced by H₂ at 350 °C, and the catalyst can thus be regenerated. In situ DRIFT spectra reveal that NO_x is stored on catalyst mainly in the form of various coordinated nitrites/nitrates, with a little NO adsorbed on Ru.

Acknowledgment. This work was financially supported by the National Basic Research Program of China (2004CB-719500). and Z.P.X. appreciates the support from the ARC Centre for Functional Nanomaterials funded by the Australia Research Council under its Centre of Excellence Scheme.

References and Notes

(1) Shelef, M.; McCabe, R. W. Twenty-five years after introduction of automotive catalysts: What next? *Catal. Today* **2000**, *62*, 35–50.

(2) Burch, R. Knowledge and know-how in emission control for mobile applications. *Catal. Rev. Sci. Eng.* **2004**, *46*, 271–333.

(3) Matsumoto, S. DeNOx catalyst for automotive lean-burn engine. *Catal. Today* **1996**, *29*, 43–45.

(4) Epling, W. S.; Campbell, L. E.; Yezerets, A.; Currier, N. W.; Parks, J. E., II. Overview of the fundamental reactions and degradation mechanisms of NOx storage/reduction catalysts. *Catal. Rev. Sci. Eng.* **2004**, *46*, 163–245.

(5) Lietti, L.; Forzatti, P.; Nova, I.; Tronconi, E. NOx storage reduction over Pt-Ba/γ-Al₂O₃ catalyst. *J. Catal.* **2001**, *204*, 175–191.

(6) Nova, I.; Castoldi, L.; Lietti, L.; Tronconi, E.; Forzatti, P. On the dynamic behavior of “NOx-storage/reduction” Pt-Ba/Al₂O₃ catalyst. *Catal. Today* **2002**, *75*, 431–437.

(7) Sedlmair, C.; Seshan, K.; Jentys, A.; Lercher, J. A. Elementary steps of NOx adsorption and surface reaction on a commercial storage–reduction catalyst. *J. Catal.* **2003**, *214*, 308–316.

(8) Liu, Z. Q.; Anderson, J. A. Influence of reductant on the regeneration of SO₂-poisoned Pt/Ba/Al₂O₃ NOx storage and reduction catalyst. *J. Catal.* **2004**, *228*, 243–253.

(9) Piacentini, M.; Maciejewski, M.; Baiker, A. Supported Pt–Ba NOx storage–reduction catalysts: Influence of support and Ba loading on stability and storage efficiency of Ba-containing species. *Appl. Catal. B* **2006**, *65*, 157–167.

(10) Piacentini, M.; Strobel, R.; Maciejewski, M.; Pratsinis, S. E.; Baiker, A. Flame-made Pt-Ba/Al₂O₃ catalysts: Structural properties and behavior in lean-NOx storage–reduction. *J. Catal.* **2006**, *243*, 43–56.

(11) Zhou, G.; Luo, T.; Gorte, R. J. An investigation of NOx storage on Pt–BaO–Al₂O₃. *Appl. Catal. B* **2006**, *64*, 88–95.

(12) Szailer, T.; Kwak, J. H.; Kim, D. H.; Hanson, J. C.; Peden, C. H. F.; Szanyi, J. Reduction of stored NOx on Pt/Al₂O₃ and Pt/BaO/Al₂O₃ catalysts with H₂ and CO. *J. Catal.* **2006**, *239*, 51–64.

(13) Nova, I.; Lietti, L.; Castoldi, L.; Tronconi, E.; Forzatti, P. New insights in the NOx reduction mechanism with H₂ over Pt–Ba/γ-Al₂O₃ lean NOx trap catalysts under near-isothermal conditions. *J. Catal.* **2006**, *239*, 244–254.

(14) Centi, G.; Fornasari, G.; Gobbi, C.; Livi, M.; Trifirob, F.; Vaccari, A. NOx storage–reduction catalysts based on hydrotalcite: Effect of Cu in promoting resistance to deactivation. *Catal. Today* **2002**, *73*, 287–296.

(15) Fornasari, G.; Trifiro, F.; Vaccari, A.; Prinetto, F.; Ghiotti, G.; Centi, G. Novel low temperature NOx storage–reduction catalysts for diesel light-duty engine emissions based on hydrotalcite compounds. *Catal. Today* **2002**, *75*, 421–429.

(16) Basile, F.; Fornasari, G.; Livi, M.; Trini, F.; Trifiro, F.; Vaccari, A. Performance of new Pt and Pt-Cu on hydrotalcite-derived materials for NOx storage/reduction. *Top. Catal.* **2004**, *30*, 223–227.

(17) Fornasari, G.; Glockler, R.; Livi, M.; Vaccari, A. Role of the Mg/Al atomic ratio in hydrotalcite-based catalysts for NOx storage/reduction. *Appl. Clay Sci.* **2005**, *29*, 258–266.

(18) Silletti, B. A.; Adams, R. T.; Sigmon, S. M.; Nikolopoulos, A.; Spivey, J. J.; Lamb, H. H. A novel Pd/MgAlOx catalyst for NOx storage–reduction. *Catal. Today* **2006**, *114*, 64–71.

(19) Yu, J. J.; Jiang, Z.; Zhu, L.; Hao, Z. P.; Xu, Z. P. Adsorption/desorption studies of NOx on well-mixed oxides derived from Co–Mg/Al hydrotalcite-like compounds. *J. Phys. Chem. B* **2006**, *110*, 4291–4300.

(20) Topsøe, H.; Boudart, M.; Nørskov, J. K. *Frontiers in Catalysis: Ammonia Synthesis and Beyond*; Baltzer: Basel, Switzerland, 1994.

(21) Yin, S. F.; Xu, B. Q.; Zhou, X. P.; Au, C. T. A mini-review on ammonia decomposition catalysts for on-site generation of hydrogen for fuel cell applications. *Appl. Catal. A* **2004**, *277*, 1–9.

(22) Mortensen, H.; Diekhoner, L.; Baurichter, A.; Jensen, E.; Luntz, A. C. Dynamics of ammonia decomposition on Ru(0001). *J. Chem. Phys.* **2000**, *113*, 6882–6887.

(23) Hammer, B. Bond activation at monatomic steps: NO dissociation at corrugated Ru (0001). *Phys. Rev. Lett.* **1999**, *83*, 3681–3684.

(24) Mortensen, H.; Diekhoner, L.; Baurichter, A.; Luntz, A. C. CH₄ dissociation on Ru(0001): A view from both sides of the barrier. *J. Chem. Phys.* **2002**, *116*, 5781–5794.

(25) Cioabica, I. M.; van Santen, R. A. Carbon monoxide dissociation on planar and stepped Ru(0001) surfaces. *J. Phys. Chem. B* **2003**, *107*, 3808–3812.

(26) Basile, F.; Fornasari, G.; Gazzona, M.; Vaccari, A. Synthesis and thermal evolution of hydrotalcite-type compounds containing noble metals. *Appl. Clay Sci.* **2000**, *16*, 185–200.

(27) Elbouazzaoui, S.; Corbos, E. C.; Courtois, X.; Marecot, P.; Duprez, D. A study of the deactivation by sulfur and regeneration of a model NSR Pt/Ba/Al₂O₃ catalyst. *Appl. Catal. B* **2005**, *61*, 236–243.

- (28) Garin, F. Mechanism of NO_x decomposition. *Appl. Catal. A* **2001**, 222, 183–219.
- (29) Takeuchi, M.; Matsumoto, S. NO_x storage-reduction catalysts for gasoline engines. *Top. Catal.* **2004**, 28, 151–156.
- (30) Yanga, W.; Kima, Y.; Liub, P. K. T.; Sahimia, M.; Tsotsisa, T. T. A study by in situ techniques of the thermal evolution of the structure of a Mg–Al–CO₃ layered double hydroxide. *Chem. Eng. Sci.* **2002**, 57, 2945–2953.
- (31) Sedlmair, Ch.; Seshan, K.; Jentys, A.; Lercher, J. A. Elementary steps of NO_x adsorption and surface reaction on a commercial storage–reduction catalyst. *J. Catal.* **2003**, 214, 308–316.
- (32) Olsson, L.; Persson, H.; Fridell, E.; Skoglundh, M.; Andersson, B. A kinetic study of NO oxidation and NO_x storage on Pt/Al₂O₃ and Pt/BaO/Al₂O₃. *J. Phys. Chem. B* **2001**, 105, 6895.
- (33) Schmitz, P. J.; Baird, R. J. NO and NO₂ adsorption on barium oxide: Model study of the trapping stage of NO_x conversion via lean NO_x traps. *J. Phys. Chem. B* **2002**, 106, 4172–4180.
- (34) Liu, Z.; Anderson, J. A. Influence of reductant on the thermal stability of stored NO_x in Pt/Ba/Al₂O₃ NO_x storage and reduction traps. *J. Catal.* **2004**, 224, 18–27.
- (35) Hammer, B. Adsorption, diffusion, and dissociation of NO, N and O on flat and stepped Ru (0001). *Surf. Sci.* **2000**, 459, 323–348.
- (36) Parvulescu, V. I.; Grange, P.; Delmon, B. Catalytic removal of NO. *Catal. Today* **1998**, 46, 233–316.
- (37) Machida, M.; Kurogi, D.; Kijima, T. Role of hydrogen spillover in H₂–NO reaction over Pd-supported NO_x adsorbing material, MnO_x–CeO₂. *J. Phys. Chem. B* **2003**, 107, 196–202.