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E.C. Corbos, M. Haneda, Xavier Courtois, P. Marecot, D. Duprez, et al.. Cooperative effect of Pt–Rh/Ba/Al and CuZSM-5 catalysts for NO reduction during periodic lean-rich atmosphere. *Catalysis Communications*, 2008, 10 (2), pp.137-141. 10.1016/j.catcom.2008.06.014 . hal-03107558

HAL Id: hal-03107558

<https://hal.science/hal-03107558>

Submitted on 12 Jan 2021

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Catalysis Communications 10 (2008) 137–141.
DOI: 10.1016/j.catcom.2008.06.014

Cooperative effect of Pt-Rh/Ba/Al and CuZSM-5 catalysts for NO_x reduction during periodic lean-rich atmosphere

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Abstract

NO_x removal efficiency was investigated with a combination of model Pt–Rh/Ba/Al and Cu-ZSM-5 catalysts using periodic fluctuations between lean (100 s) and rich (10 s) atmosphere. NO_x removal is greatly improved at 250°C and 300°C by physically mixing the two catalysts. The mixed catalyst shows a NO_x removal activity almost double as compared to a system where Pt–Rh/Ba/Al catalyst is situated upstream and CuZSM-5 downstream the gas flow. FT-IR characterization shows that CuZSM-5 catalyst enhances the formation of NCO species on alumina during rich conditions. These NCO are further hydrolyzed to NH₃ under lean condition which acts as a reductant for NO_x.

Keywords: NSR, NH₃-SCR, Pt-Rh/Ba/Al, NO_x reduction, NH₃, isocyanate, Cu, ZSM-5,

1. Introduction

The general demand for lower CO₂ emissions led to the development of diesel and lean-burn automotive engines. Diesel engine emissions contain NO_x in excess of O₂ which makes NO_x reduction to N₂ very difficult. In the last decade, two main approaches toward NO_x reduction in lean conditions have been explored: the NO_x storage–reduction technology (NSR) and the Selective Catalytic Reduction of NO_x (SCR). The NSR catalysts operate alternatively under lean and rich conditions. During the lean conditions, NO is oxidized to NO₂ on precious metals and then stored as nitrites/nitrates on a basic component (alkaline and/or alkaline earth oxides). Before that an unacceptable amount of NO_x slips through the catalyst, the engine switches to rich conditions (excess of hydrocarbons) for a short period where the stored NO_x are released and reduced into N₂ over the precious metals [1]. The NO_x removal efficiency depends on both NO_x storage and NO_x reduction activity of the NSR catalyst. Generally, at low temperature the NO_x removal is limited by both the NO_x storage and reduction, whereas at high temperature, it is restricted mainly by the storage function [1]. The reduction of nitrates strongly depends on both the nature of reductant (H₂, CO, hydrocarbons) and by the length of the reduction pulse. In real conditions the reduction step is very short (typically from 2% to 10% from the lean phase) and must take place with a high selectivity towards N₂ production without emitting CO and HC. If the reducing pulse is too short, the regeneration of storage sites is incomplete and thus the activity of NO_x trap decreases. On the contrary, if the pulse is too long undesirable products, like ammonia are produced [2]. To avoid the NH₃ break-out, one possibility is to combine the NSR catalyst with a SCR system. The NH₃ is stored during the rich phase on the SCR catalyst sites and used as a reducer for SCR reaction at the beginning of the next lean cycle [3,4]. In this approach, we investigated the influence of the addition of CuZSM-5 to a model Pt–Rh/Ba/Al NSR catalyst in order to determine if the NO_x removal under lean-rich atmosphere can be efficiently improved. The activity of the catalysts for NO_x removal is estimated by periodically switching between lean and rich cycles with a time length of 100 s lean and 10 s rich.

2. Experimental

The Pt-Rh/Ba/Al catalyst was prepared by successive wet impregnation method. First barium (20 wt% BaO) was impregnated from a Ba(NO₃)₂ solution to commercial Al₂O₃ (Mizusawa Chemical, GB-45, 190 m² g⁻¹). The resulting material was dried at 110°C and calcined at 700°C for 4h in air. The platinum (1 wt%) was impregnated by using a Pt(NH₃)₄(NO₃)₂ solution to the Ba/Al₂O₃ previously obtained, and the catalyst was treated at 700°C for 4h under N₂ flow before Rh impregnation (0.013 wt%) with a RhCl₃ solution. Eventually, the Pt-Rh/Ba/Al (noted Pt-RhBa) was treated at 700°C under N₂ and then aged at the same temperature with wet air (5 % H₂O/air) for 4 hours. A 5 wt% Cu-ZSM-5, was prepared by wet impregnation of H-ZSM-5 (Tosoh, HSZ-830NHA, SiO₂/Al₂O₃=28) with an aqueous solution of Cu(NO₃)₂.2H₂O. After drying for 1 night the catalyst was calcined in air at 500°C for 5h. This catalyst is noted CuZSM-5.

The catalytic tests were performed on physical mixture of CuZSM-5 and Pt-RhBa catalysts using equal amounts of each catalyst (30 mg/30 mg). When the individual activity of the Pt-RhBa and CuZSM-5 catalyst was measured, 30 mg of each catalyst was diluted with 30 mg of inert α -alumina. The NO_x removal activity was determined by alternatively switching

between lean and rich conditions. The gas composition and total flow used are described in Table 1. The lean period and rich periods were of 100s and 10s, respectively. The total flow rate was 90 ml.min⁻¹, giving a space velocity of ca. 5 000 h⁻¹ for 60 mg of powder. The activity of the catalysts was followed until stabilization. The NO, NO₂, N₂O, NH₃, CO and C₃H₆ concentrations were measured using a GASMET DX-4000 FT-IR apparatus. Before measurement the catalysts were treated at 550°C as follow. They were first treated for 10 min at 550°C under the rich mixture without NO and then for another 10 min under lean mixture (without NO) after flushing under CO/H₂. Eventually, after flushing (CO₂/He) the catalysts were treated again under the rich mixture for 10 min at 550°C. This pretreatment normalized the state of the catalysts before each test and allowed one to have a clean surface. After pretreatment, the samples were cooled down to test temperatures (150°C, 200°C, 250°C, 300°C and 400°C) under CO₂/He. The NO_x removal efficiency (%) was calculated after stabilization for at least 5 rich/lean cycles as follows: NO_x removal efficiency = (1- [Average NO_x outlet]/[Average NO_x inlet])*100. The term NO_x is used for NO and NO₂, N₂O being considerate as a reduction product. Additionally, the CO removal efficiency was calculated in the same way.

Diffuse reflectance FT-IR spectra were taken with a Nicolet Nexus 670 FT-IR spectrometer with a resolution of 4 cm⁻¹. Before recording the spectra the catalysts were treated at 550°C in the same conditions as for the NO_x removal activity measurement (rich / lean / rich, 10 min each, and flushing under He before changing from rich to lean or *vice versa*). The gas composition was 500 ppm NO and 6 % O₂ for lean periods (100s) and 3 % CO and 1% H₂ for rich ones (15s). The background was recorded at each temperature after treatment. The spectra recording started after a first lean cycle, using 10 scans/spectra during 2 rich-lean cycles.

Table 1: Gas composition for the lean and rich mixtures

Gas	NO	O ₂	CO - H ₂ (75 % / 25 %)	CO ₂	C ₃ H ₆	He	Total flow
Lean (100s)	500 ppm	10 %	0.13 %	1 %	167 ppm	Balance	90 ml.min ⁻¹
Rich (10s)	100ppm	-	8.53 %	1 %	-	Balance	

3. Results and discussion

3.1. Activity measurement

Figure 1 shows the NO_x and CO removal efficiencies (%) during the lean-rich cycles as a function of the temperature for Pt-RhBa, CuZSM-5 catalysts and physically mixed catalyst Pt-RhBa+CuZSM-5. Excluding 400°C, the NO_x removal efficiency during the lean-rich cycles is greatly improved when the Pt-RhBa catalyst is mixed with CuZSM-5. The NO_x removal efficiency of mixed catalyst is higher than the summation of individual activities, showing a synergy effect of Pt-RhBa and CuZSM-5. The most dramatic difference is observed at 250°C and 300°C where the NO_x removal efficiency increases from 39 % and 50 % for Pt-RhBa to 86 % and 79 % with the mixed sample, respectively. Additionally, the CO removal efficiency (Figure 1-B) is also increased for the mixed catalyst as compared to the reference.

As water is always present in the exhaust gas, we further check if the mixed catalyst still shows a higher activity in more realistic conditions, *i.e.* in presence of water. To perform these experiments, 1 % H₂O was added in the feed gas. The NO_x removal activity was 42 % at 250°C and 55 % at 300°C for Pt-RhBa catalyst, and 62 % and 69 %, respectively, for Pt-RhBa + CuZSM-5. Adding water in the feed gas did not cause big difference in the NO_x removal activity for Pt-RhBa catalyst. On the other hand, a decrease of the activity is observed for the mixed Pt-RhBa + CuZSM-5 catalyst. Nevertheless, even in the presence of water, the activity of mixed catalyst is still significantly higher than that of Pt-RhBa catalyst.

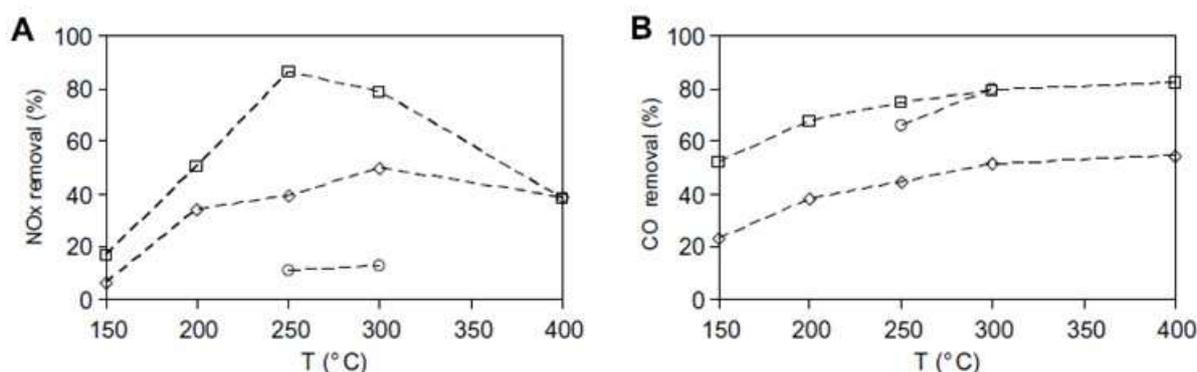


Figure 1: (A) NO_x removal efficiency (%) and (B) CO removal efficiency (%) during the lean-rich cycles for physically mixed catalysts (\diamond) Pt-RhBa+ α -Al₂O₃, (\square) Pt-RhBa+CuZSM-5 and (\circ) CuZSM-5+ α -Al₂O₃. Reaction conditions: lean 100s, 1 % CO₂, 500 ppm NO, 10 % O₂ 0.13 % CO/H₂ (75/25), 167 ppm C₃H₆ and rich 10s with 8.53 % CO/H₂ (75/25) He balance, 100 ppm NO, 1 % CO₂, He balance. Catalyst weight: 30 mg Pt-RhBa diluted with 30 mg of α -Al₂O₃ or with 30 mg of CuZSM-5.

The raw data recorded for NO_x, NH₃ and N₂O during the rich pulses at 250°C and 300°C (Figure 2) reveal that mainly NH₃ is formed during rich cycles with Pt-RhBa. The NH₃ concentration increases after the 2nd rich pulse, and reaches a maximum at 300°C. Conversely, N₂O formation decreases with the raise of the temperature and shows a maximum at low temperature (250°C), in agreement with the literature [6,7]. Note that the N₂O concentration is much lower than ammonia. When the Pt-RhBa is mixed with CuZSM-5, ammonia is no longer observed at the outlet of the reactor regardless of the temperature. However, an increase in N₂O concentration is noticed for the mixed catalyst, especially at 250°C. Shinjoh et al. [3] reported recently an increase of the NO_x removal activity between 230°C and 310°C by using a combination of three catalysts, Pd/Alumina (upstream) + NSR + Cu/ZSM-5 (downstream). They ascribed this effect to NH₃-SCR on CuZSM-5: during the rich pulse, the NO_x stored on NSR catalyst are reduced to NH₃ which is adsorbed on CuZSM-5 and subsequently reacts at the beginning of the next lean phase with NO_x, in agreement with the work of Nakatsuji et al. [4]. Thus, since our results showed no NH₃ at the outlet of the reactor for the Pt-RhBa + CuZSM-5 mixed catalyst the increase of NO_x removal can be ascribed to NH₃-SCR on CuZSM-5.

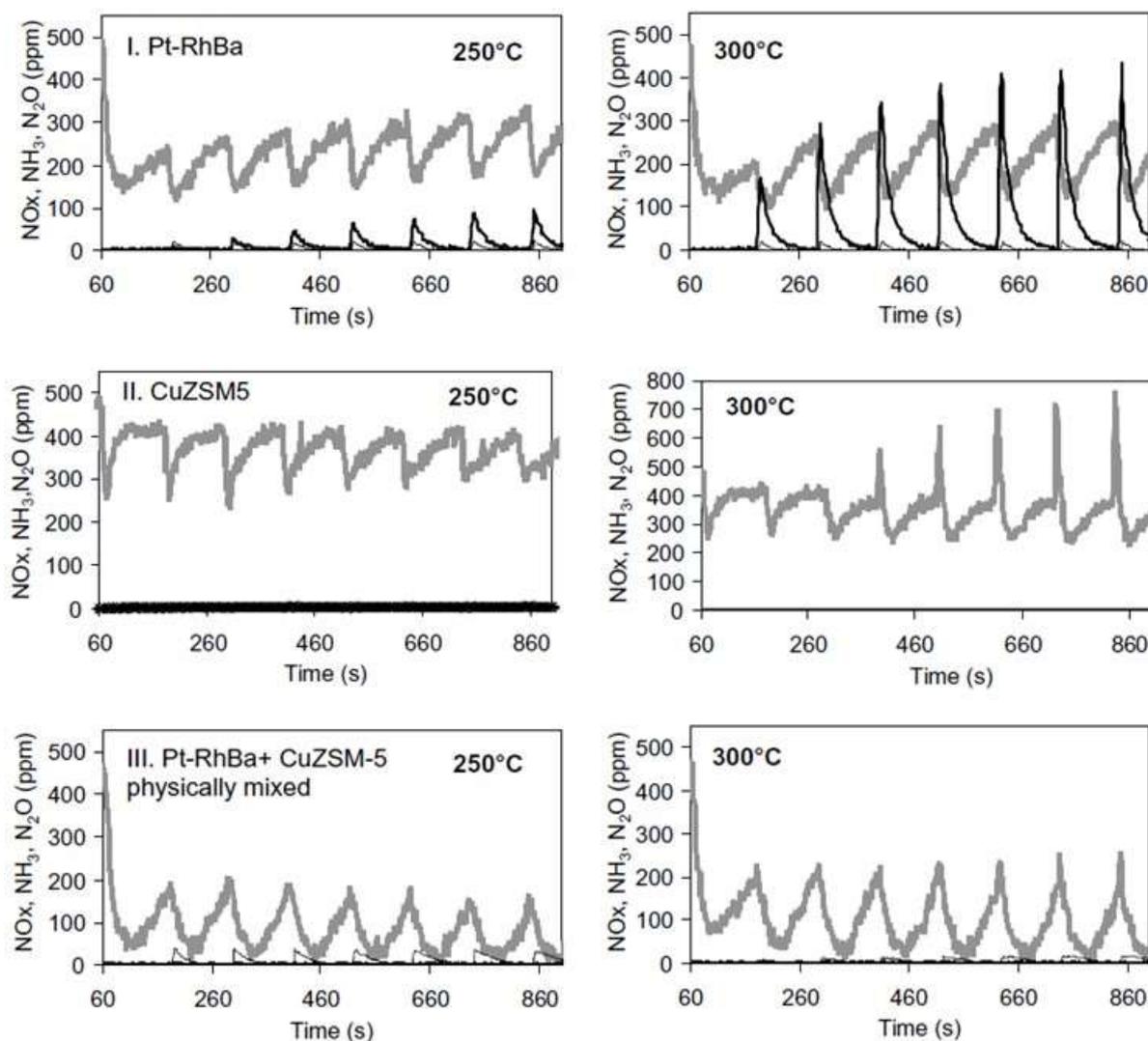


Figure 2: Experimental NO_x , NH_3 and N_2O curve (ppm) at 250°C and 300°C versus time for (I) Pt-RhBa+ $\alpha\text{-Al}_2\text{O}_3$, (II) CuZSM-5+ $\alpha\text{-Al}_2\text{O}_3$ and (III) mixed catalyst Pt-RhBa+CuZSM-5; (—) NO_x , (---) NH_3 and (· · ·) N_2O .

As seen in Figure 2, the integrated area of NH_3 peaks for Pt-RhBa catalyst at 250°C is at maximum around 2000 ppm. Assuming that NH_3 is totally consumed for NO reduction during the consecutive lean step according to the equation: $2\text{NO} + 2\text{NH}_3 + 1/2\text{O}_2 = 2\text{N}_2 + 3\text{H}_2\text{O}$, this amount cannot explain the increase of NO_x removal efficiency with the mixed catalyst, which is more than doubled. In order to check if only the NH_3 -SCR is responsible for the increase of NO_x removal, we performed an experiment by using two catalytic beds: upstream Pt-RhBa and downstream CuZSM-5. If the enhancement of NO_x removal efficiency is due to NH_3 -SCR on CuZSM-5, the activity of two bed catalyst and mixed one should be close. The results obtained for NO_x and CO removal efficiencies at 250°C , 300°C and 400°C are reported in Table 2, together with the NO_x removal efficiencies of Pt-RhBa and CuZSM-5 catalysts. The NO_x removal activity using two catalytic beds is higher than that of the Pt-RhBa (46 % versus 39 % at 250°C and 61 % versus 50 % at 300°C). Since NH_3 is not observed at the outlet of the reactor and the N_2O concentration is not significantly changed (results not shown), the higher activity of two bed system can be explained by NH_3 -SCR activity on the CuZSM-5 catalyst

located downstream of the Pt-RhBa, in agreement with previous results [3,4]. Notwithstanding, the NO_x removal activity of physically mixed catalyst is much higher than that of the system with 2 catalytic beds: 86 % versus 46 % at 250°C and 79 % versus 61 % at 300°C. This result suggests that in addition to NH₃-SCR, the CuZSM-5 catalyst must play another role in the NO_x reduction under the reaction conditions used in this study. A detailed study of the experimental curves recorded at 300°C revealed that the main difference between the two systems (two catalytic bed and physically mixed catalyst) is the presence of a NO slip occurring on two catalytic beds (results not shown). A similar behavior was also obtained with CuZSM-5 alone (Figure 2), while no NO slip was observed with the reference Pt-RhBa catalyst. Moreover, Figure 2 shows an increase in NO breakthrough with the time over CuZSM-5, indicating a deactivation of CuZSM-5 catalyst. Similar results were also obtained by Hammache et al. [8] for bimetallic Pt-Cu/Ba/Al and Cu/Al catalysts. They ascribed the result to a slower kinetic of NO_x reduction on Pt-Cu due to a decrease of the metal efficiency for adsorbing NO_x. Another possibility for an increase in NO slip would be due to either the reduction of NO₂ desorbed from Pt-RhBa catalytic to NO on CuZSM-5, or the oxidation of ammonia stored on CuZSM-5 into NO [4]. At 400°C, the NO_x removal activity of Pt-RhBa and mixed catalyst is similar, despite the fact that NH₃ is produced in high amount on the Pt-RhBa (results not shown). This can be explained by a competition between NH₃ oxidation (which is very fast at this temperature [4]) and NO_x reduction by NH₃.

Table 2: NO_x and CO removal efficiencies under various conditions for Pt-RhBa, CuZSM-5, physically mixed Pt-RhBa and CuZSM-5 catalyst and two bed catalyst (upstream Pt-RhBa and downstream CuZSM-5).

Reaction conditions	Catalyst	NO _x removal (%)			CO removal (%)		
		Temperature			Temperature		
		250°C	300°C	400°C	250°C	300°C	400°C
With CO/H ₂ in rich mixture. Lean mixture (Table 1)	Pt-RhBa	39	50	39	45	53	54
	CuZSM-5	11	13	-	66	80	-
	Pt-RhBa/CuZSM-5 2 beds	46	61	37	67	76	78
	Pt-RhBa+CuZSM-5 Physically mixed	86	79	38	74	79	82
Without H ₂ in rich mixture. Lean mixture (Table 1)	Pt-RhBa	39	43	36	32	45	51
	Pt-RhBa/CuZSM-5 2 beds	39	58	-	55	68	-
	Pt-RhBa+CuZSM-5 Physically mixed	54	66	-	59	77	-

- Tests were not performed

To summarize, when the Pt-RhBa and CuZSM-5 catalysts are physically mixed, a synergistic effect is observed for the NO_x removal during lean-rich cycles, at 250°C and 300°C. This cannot be explained only by NH₃-SCR on CuZSM-5, since the activity of the sample with two catalytic beds is significantly lower than physically mixed catalysts. Another role of CuZSM-5 for the enhancement of NO_x reduction performance has to be considered.

3.2. FT-IR measurements

In order to understand why proximity between Pt-RhBa and CuZSM-5 catalysts is needed to enhance the NO_x removal activity, the catalysts were characterized individually and in mixture by FT-IR. Note that for FT-IR experiments, a simplified mixture was used (see experimental part). Figure 3 shows the IR spectra recorded during the lean-rich cycles with Pt-RhBa, CuZSM-5 and mixed Pt-RhBa + CuZSM-5 catalyst. For Pt-RhBa (Figure 3-A), switching from lean to rich gas leads to an increase of the bands at 2230 - 2250 cm⁻¹ and 2168 cm⁻¹ ascribed to NCO vibration on alumina and barium sites, respectively [9-11]. These species are not completely removed when the gas composition was changed from rich to lean. During the rich pulse, a small band at 2070 cm⁻¹ ascribed to adsorbed CO on platinum [11] is also observed but it rapidly disappears when switching to lean gas. The FT-IR spectra of adsorbed species formed on CuZSM-5 during the rich phase (Figure 3-B) show only one intense band at 2155 cm⁻¹ which is ascribed to CO adsorbed on Cu⁺ sites [12]. Note that this specie is quite stable at 250°C, since it still can be seen after changing to lean atmosphere. For the mixed Pt-RhBa + CuZSM-5 catalyst during the rich conditions one can observe the bands corresponding to NCO vibration on alumina and barium at 2230 – 2250 cm⁻¹ and 2168 cm⁻¹ respectively, and those corresponding to CO-Cu⁺ at 2155 cm⁻¹. These bands are still present in a lower extent after switching to lean conditions. Otherwise, the characteristic bands for ammonia adsorption were not observed either in rich or lean conditions.

Since NCO species are considered to be an important intermediate for NO_x reduction [9,10], we focus on the IR region where these species appear. Figure 4-A shows the time evolution of integrated peak areas in the 2300 – 2200 cm⁻¹ range (corresponding to the vibrations of NCO species on alumina) at 250°C. It is important to specify that the weight of each catalyst is kept constant (10 mg of Pt-RhBa mixed with 10 mg of CuZSM-5). For a better comparison, the Pt-Rh catalyst (10 mg) was diluted with α-Al₂O₃ (10 mg). As can be seen in Figure 4-A, the peak area of NCO species on alumina for mixed catalyst is much larger than for the Pt-RhBa catalyst. Since NCO species were not observed for CuZSM-5 alone (Figure 3-B), one can conclude that CuZSM-5 promotes the formation of NCO species on Pt-RhBa catalyst. The NCO species are easily hydrolyzed to NH₃ in the presence of small amounts of water [9,10] which is further used for NO_x reduction. A higher quantity of NCO would lead to higher NO_x reduction, thus explaining the increase of the NO_x removal for the mixed catalyst. Figure 4-B also shows a change in the integrated area of the band intensity due to CO species adsorbed on Cu⁺ at 2155 cm⁻¹ on the mixed catalyst. Apparently, its IR band intensity rapidly increases as rich gas was introduced. When the gas composition was switched to lean gas, not only a decrease of CO species but also the formation of NCO species was observed. CO species adsorbed on Cu⁺ sites can be considered to be consumed for the formation of NCO on Pt-RhBa catalyst. The role of CuZSM-5 would be to provide the sites for CO adsorption and activation.

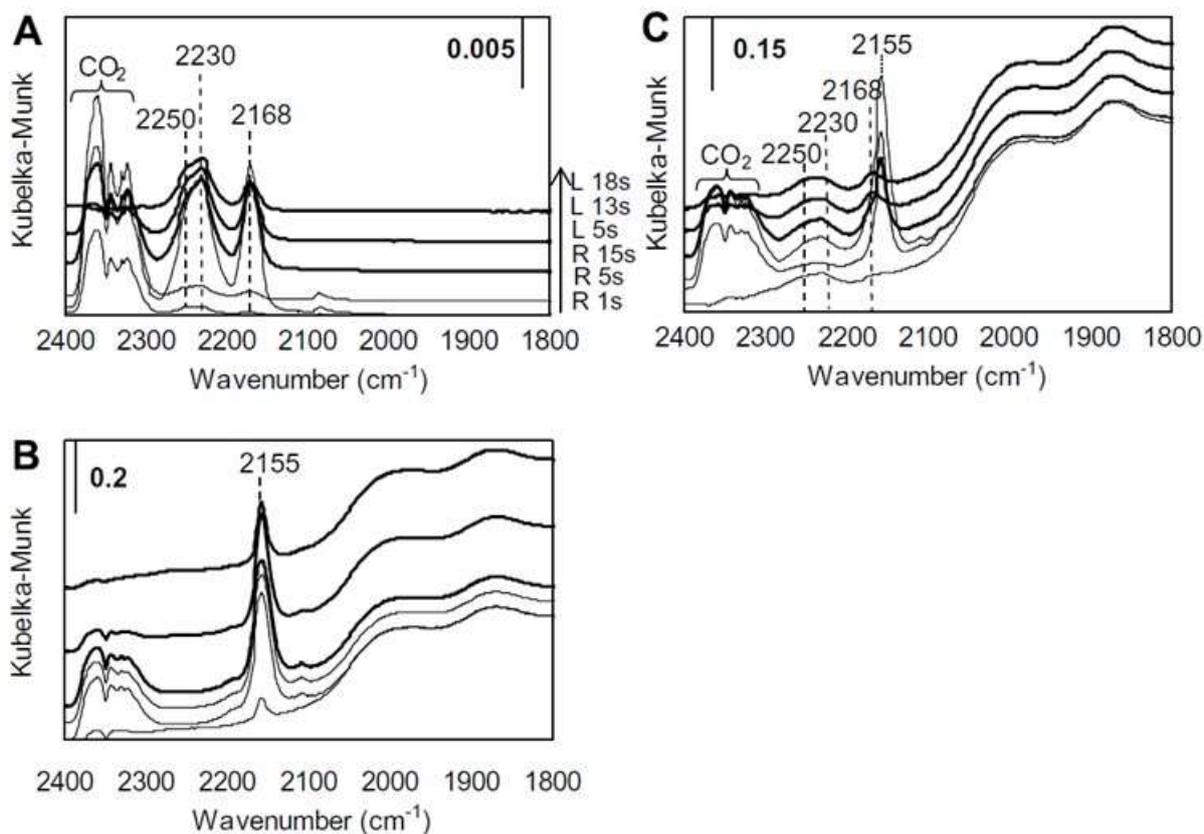


Figure 3: FT-IR spectra of (A) Pt-RhBa catalyst, (B) CuZSM-5 and (C) Pt-RhBa + CuZSM-5 mixed catalyst. (—) spectra recorded in rich conditions and (---) spectra recorded in lean conditions.

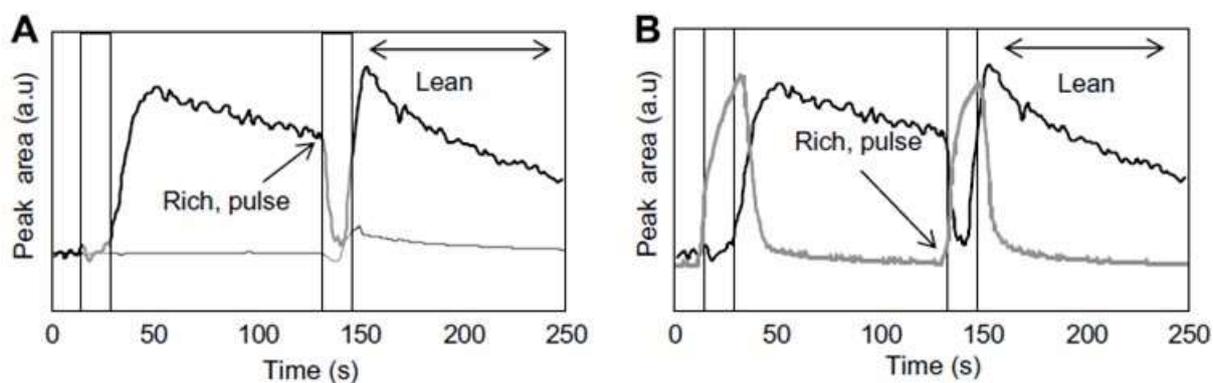


Figure 4: (A) Time dependence of integrated area of the bands for NCO vibrations on alumina (2300 cm^{-1} and 2200 cm^{-1}) formed during the rich/lean cycles at 250°C on (---) Pt-RhBa catalyst and (—) Pt-RhBa+CuZSM-5 physically mixed catalyst; (B) Time dependence of integrated area of the bands for (---) NCO vibrations on alumina 2300 cm^{-1} and 2200 cm^{-1} and (—) CO-Cu⁺ (2155 cm^{-1}) and NCO on Ba (2168 cm^{-1}) formed during the rich/lean cycles at 250°C on Pt-RhBa+CuZSM-5 mixed catalyst. Conditions: Lean NO = 500 ppm, O₂ = 6 %, Rich CO = 3 % H₂ = 1 %; catalyst weight 20 mg (Pt-RhBa: 10 mg Pt-RhBa + 10 mg $\alpha\text{-Al}_2\text{O}_3$ and Pt-RhBa+CuZSM-5 physically mixed: 10 mg Pt-RhBa + 10 mg CuZSM-5).

To further check this hypothesis we performed an activity test by using only CO. In this case, NH₃ formation would come only from the NCO hydrolysis since H₂ is no longer present in the gas composition. The experiments were carried out on the reference Pt-RhBa catalyst, the physically mixed and two bed catalysts. The results are reported in Table 2. Removing H₂ from the rich gas leads only to a slight decrease of the NO_x removal activity for Pt-RhBa catalyst. The NO_x removal activity at 250°C for the two bed catalyst was identical to that obtained with Pt-RhBa catalyst while at 300°C the activity increases from 43 % for the Pt-RhBa catalyst to 58 % for the two-bed one. Nevertheless, when the two catalysts are mixed the NO_x removal efficiency increases by 38 % at 250°C (from 39 to 54%) and by 53 % at 300°C (from 43 to 66 %) even using only CO as a reducing gas. Note that with Pt-RhBa catalyst at 300°C and 400°C, NH₃ was observed during the rich cycles even without H₂ in rich mixture. However, the NH₃ concentration was about five times smaller than when CO/H₂ was used as reductant. These results indicate that the reduction of NO_x should take place with intermediate formation of NCO species and their formation is favored by the proximity between Pt-RhBa and CuZSM-5 catalysts, in agreement with the FT-IR results.

4. Conclusion

In conclusion, the NO_x reduction over Pt-RhBa catalyst under lean-rich atmosphere is greatly promoted by physically mixing with CuZSM-5. This effect was much lower when the catalysts are separated in two beds. The role of CuZSM-5 is not only to store NH₃ formed on Pt-RhBa catalyst in rich conditions and catalyze the NH₃-SCR but also to provide enough amount of CO which reacts with NO_x to form NCO species as intermediate on Pt-RhBa catalyst, resulting thus in an increase of NH₃ formation.

Acknowledgements

The authors gratefully thanks to Y. Kintaichi for the realisation of the experimental device. This work was carried out in the framework program with scientific collaboration between France and Japan (ECSAW France–Japan). Miss. Corbos acknowledge the financial support of the Advanced Industrial Science and Technology (AIST).

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