Influence of Copper on the Catalytic Activity of Supported Rhodium Catalysts in the Reactions of CO Oxidation and NO Reduction

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Abstract

The catalytic activity of Cu, Rh, and Rh/Cu, catalysts supported on Al₂O₃, CeO₂ and CeO₂/Al₂O₃ in reactions of CO oxidation and NO reduction has been studied in temperature-programmed regime. Addition of Cu to Rh catalysts decreases temperature at which 5 and 50% degree of conversion, while end of reaction temperature is not influenced by presence of Cu. The presence of Cu has positive effect on the activity of Rh containing catalysts in the low temperature region. Cu has noticeable promoting effect mainly for the catalytic activity in the reaction of CO oxidation and in smaller extent for the reaction of NO reduction. Preliminary redox treatment of the catalysts decreases the light off temperature in the reactions of CO oxidation and in NO reduction. Thermal treatment at temperatures up to 973 K does not have sensible effect on the catalytic activities of all studied catalysts. Calcination at 1073 K, however, strongly decreases the catalytic activity of Rh/Cu/CeO₂/Al₂O₃ catalysts.

Introduction

The Three Ways Catalysts (TWC) are now universally used for controlling carbon monoxide, hydrocarbons, and nitrogen oxide content in automotive exhaust gases. The Rh is indispensable element used in industry for preparing of TWC [1,2]. Usually TWC are promoted by ceria [3,4]. Unfortunately Rh is very expensive and scarcely spread in the nature. Therefore, it is of great importance to find the new catalyst formulations in order to replace at least part of Rh used in TWC composition. The copper is one of the promising potential substitutes of noble metals in TWC. Its catalytic properties have been widely studied but still it is not clear its influence on the TWC performance [5-7].

In this paper data on influence of copper on the performance of Rh catalysts in reactions of CO oxidation and NO reduction are presented.

Experimental

Catalyst preparation

All catalysts were prepared by impregnation of spherical alumina pellets (Condea, high purity Puralox grade $S_{BET} = 210 \text{ m}^2/\text{g}$) with salts of corresponding metals. The Rh containing catalysts were prepared by alumina impregnation with solution of Rh(NO₃)₃ (Johnson Mathey product). After the impregnation the sample was dried and calcinated at 723 K. The Cu containing catalysts were prepared by alumina impregnation with solution of Cu(NO₃)₂ (Johnson Mathey product). After the impregnation the sample was dried and calcinated at 723 K. The CeO₂ containing catalysts were prepared by impregnation of the carrier with solution of Ce(III)-nitrate hexahydrate Ce(NO₃)₃·6H₂O (Fluka product). After the impregnation the sample was dried and calcinated at 723 K. The compositions of the studied catalysts in wt.% are given in the catalyst names. For example 1Cu/0.1Rh/10CeO₂/Al₂O₃ means that the sample contains in wt.%: 1% Cu, 0.1% Rh, 10% CeO₂ which are supported on the Al₂O₃ in the order CeO₂, Rh, Cu.

Pre-treatment procedures of the samples before the catalytic activity measurements are indicated by corresponding letter and used temperature:

i) only calcination - by C,
ii) calcination and oxidation - by O,
iii) calcination and reduction - by R,
iv) calcination and connectives oxidation and reduction procedures - by RO.

**Catalytic experiments**

The catalytic activity measurements were carried out in a glass flow reactor in temperature-programmed regime. The rate of temperature rise was 5 K min in the temperature range from 350 to 803 K. The reactor had internal diameter of 13 mm. Inside of the reactor the thermocouple with external diameter of 5 mm was located. The catalyst charges of 1.0-5.0 g were diluted with 4 cm³ nonporous carborund with the average particle size of 2 mm. Above and below of the diluted catalyst bed 15 cm³ grounded carborund were placed. The following reaction mixtures were used:

(i) Reaction mixture No 1: 1 mol% CO, 0.5 mol% O₂ and balance nitrogen.
(ii) Reaction mixture No 2: 1 mol% CO, 0.1 mol% NO, 0.45 mol% O₂ and balance nitrogen.

The feed flow rates of the reaction mixture components were maintained constant by four mass flow controllers. The GHSV for the inlet reaction mixture was changed in the range from GHSV = 10000 h⁻¹ to GHSV = 200000 h⁻¹.

To characterize the catalyst performance at given space velocities of studied catalysts we have used three specific temperatures - the temperatures at which the 5, 50, and 95% degree of conversion were obtained. The temperature for 5% degree of conversion was used as a measure for the light-off temperature (LOT), the temperature for 50% degree of conversion as a measure for the catalyst’s medium performance (MPT) is observed (some authors used this temperature as a measure for LOT), and the temperature for 95% degree of conversion was used as a measure for the temperature at which the reaction was ended (EORT).

**Analytical**

The analysis of the NO, N₂O, NO₂, CO, and CO₂ concentrations in the inlet and outlet gas stream was performed by using the Perkin Elmer FT IR spectrometer mod. 1725 equipped with multiple reflections transmission cell (Infrared Analysis Inc. “long path gas minicell”, 2.4 m path length and 130 cm³ internal volume) with experimental error of 5% relative. Oxygen concentration was determined with a paramagnetic analyzer (Servomex 540A) with experimental error of 7% relative. Nitrogen was used as a carrier gas and changes in its concentration due to NO reduction was not followed during the reaction.

All analytical devises are connected with a computer, which calculates the concentrations in the inlet and outlet gas stream and corresponding degrees of conversion by means of specially written program. Experimentally full curve degree of conversion/temperature is measured and then the necessary points are presented in the tables.

**Results and Discussion**

**Catalytic activity of CeO₂, Al₂O₃ and CeO₂/Al₂O₃ in CO oxidation and NO reduction**

Before studying the catalytic properties of supported catalysts, catalytic activity of the carriers should be measured. In Table 1 an experimental data on influence of GHSV of the reaction mixture No 1 on characteristic temperatures of Al₂O₃, CeO₂/Al₂O₃ and CeO₂ in CO oxidation is presented.

Pure Al₂O₃ has low activity in CO oxidation. At lowest GHSV = 10000 h⁻¹ used in this study, the LOT is equal to 673 K and MPT at 787 K.

The catalytic activity measurements have shown that CeO₂ is much more active in CO oxidation than the alumina. Its LOT and MPT at GHSV = 10000 h⁻¹ are with 220 K lower than corresponding temperatures for pure Al₂O₃. At GHSV = 100000 h⁻¹ CeO₂ still possess a good activity. The LOT and MPT increase linearly with increasing of the GHSV in the range from GHSV = 10000 up to GHSV = 100000 h⁻¹. At GHSV up to GHSV = 50000 h⁻¹ the EORT increase linearly with increasing of the GHSV, but then this dependence became highly non-linear.

The washcoats of the industrial TWCs usually contain ceria and alumina. The pure alumina has low activity but permits to obtain catalysts with optimal metal dispersity. Ceria is used as a promoter. It has multiple promotion functions: to be a storage of oxygen, to prevent the noble metal deactivation, to enhance the reaction rate of water gas-shift, CO oxidation and NO reduction reactions, to increase the thermostability of washcoat composition for monolithic catalyst [1].

The impregnation of alumina with small quantity of ceria drastically increases the alumina catalytic activity. From Table 1 one can see that the Sample 2
with composition 10% CeO$_2$/Al$_2$O$_3$ has activity in the middle between the activity of pure CeO$_2$ and activity of pure Al$_2$O$_3$ with characteristic temperatures decreased by 100 K comparing to characteristic temperatures of pure alumina. The addition of 20 and 30% of ceria to alumina (Sample 3 and Sample 4) had an effect not very much different from that of addition of 10% ceria.

In our previous paper [8] we have studied the effect of CeO$_2$ dispersion on alumina on its activity for CO oxidation and NO reduction and gave explanation for the lower activity of ceria supported on alumina in comparison with pure ceria. The main reason for this phenomenon on well dispersed CeO$_2$/Al$_2$O$_3$ are the difficulties of generating the associated oxygen vacancy centers, observed on pure ceria, which are able to activate NO and CO molecules. From the Tab. 1 one can see that the sample 10CeO$_2$/Al$_2$O$_3$ have relatively high activity and low ceria content, so, we decided in all further experiments when ceria containing catalyst carriers is needed, to use alumina impregnated with 10% CeO$_2$.

The activity of all samples in NO reduction is very low. Only 14% degree of NO conversion at GHSV = 100000 h$^{-1}$ on pure ceria was obtained at 773 K. On alumina, at the same temperature and GHSV = 10000 h$^{-1}$ the degree of conversion was 47%.

Table 1

| No | Sample          | Treatment | GHSV, h$^{-1}$ | LOT, K | MPT, K | EORT, K |
|----|-----------------|-----------|---------------|-------|--------|---------|
| 1  | Al$_2$O$_3$     | RO773     | 10000         | 673   | 787    | -       |
| 2  | 10CeO$_2$/Al$_2$O$_3$ | C673     | 10000         | 569   | 664    | 794     |
| 3  | 2.0CeO$_2$/Al$_2$O$_3$ | C673     | 10000         | 550   | 634    | 749     |
| 4  | 30CeO$_2$/Al$_2$O$_3$ | C673     | 10000         | 533   | 613    | 716     |
| 5  | 50CeO$_2$/Al$_2$O$_3$ | C673     | 10000         | 509   | 590    | 694     |
| 6  | CeO$_2$         | C673      | 10000         | 593   | 618    | 653     |
| 7  | CeO$_2$         | RO773     | 10000         | 456   | 564    | 641     |
| 8  | CeO$_2$         | RO773     | 25000         | 476   | 578    | 647     |
| 9  | CeO$_2$         | RO773     | 50000         | 503   | 599    | 659     |
| 10 | CeO$_2$         | RO773     | 100000        | 565   | 628    | 786     |

The experimental data on the catalytic activity of supported Cu catalysts in CO oxidation and NO reduction using reaction mixture No 2 is presented on Table 2.

The ceria supported Cu catalysts are more active than the ceria/alumina supported Cu catalysts and much more active than the alumina supported Cu catalysts. The difference in favor of ceria supported catalysts for the EORT is larger then for LOT and MPT. For ceria/alumina supported catalysts the LOT are close to LOT for ceria-supported catalysts, while the EORT are close to those of alumina-supported samples.

All Cu supported catalysts have very low LOT even at GHSV = 100000 h$^{-1}$, but their MPT and EORT are rather high.

The efficiency of Cu supported catalysts in CO oxidation reaction is higher than the efficiency in the reaction of NO reduction. The characteristic temperatures for NO reduction of all catalysts are higher than the corresponding characteristic temperature for CO oxidation reaction with about 50 K.

The calcination at the temperature of 973 K does not have well defined influence on the catalytic activity in CO oxidation of the 1Cu/10CeO$_2$/Al$_2$O$_3$ catalyst comparing with the calcination at lower temperatures. At GHSV = 10000 h$^{-1}$ the calcination increase only the EORT while at GHSV = 30000 h$^{-1}$ the effect is the decreasing of EORT.

The calcination at 973 K improve the performance in NO reduction at GHSV = 10000 h$^{-1}$, but slightly decrease the performance at GHSV = 30000 h$^{-1}$ comparing with the samples calcinated at 673 K.
The effect of preliminary redox cycling also did not have the strong and clear impact on the 1Cu/10CeO₂/Al₂O₃ catalyst performance. In the same time, this procedure strongly enhanced the activity of Cu/Al₂O₃ in both reactions.

**Catalytic activity of supported Rh catalysts in CO oxidation and NO reduction**

Rhodium is a key component of the TWC. It has high activity in both CO oxidation and NO reduc-

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**Table 2**

Characteristic temperatures for the reaction of CO oxidation and NO reduction on Cu supported catalysts

| No | Sample | Treatment | GHSV, h⁻¹ | LOT, K | MPT, K | EORT, K |
|----|--------|-----------|-----------|-------|--------|---------|
| CO oxidation | | | | | | |
| 1 | 1Cu/Al₂O₃ | C723 | 30000 | 433 | 594 | 841 |
| 2 | 1Cu/Al₂O₃ | RO623 | 30000 | 408 | 504 | 853 |
| 3 | 1Cu/CeO₂ | C723 | 30000 | 346 | 500 | 690 |
| 4 | 3Cu/CeO₂ | C723 | 30000 | 333 | 440 | 640 |
| 5 | 6Cu/CeO₂ | C723 | 30000 | 325 | 432 | 596 |
| 6 | 1Cu/10CeO₂/Al₂O₃ | C673 | 10000 | 333 | 397 | 481 |
| 7 | 1Cu/10CeO₂/Al₂O₃ | C973 | 10000 | 313 | 404 | 543 |
| 8 | 1Cu/10CeO₂/Al₂O₃ | RO673 | 10000 | 332 | 397 | 503 |
| 9 | 1Cu/10CeO₂/Al₂O₃ | C673 | 30000 | 353 | 470 | 823 |
| 10 | 1Cu/10CeO₂/Al₂O₃ | R673 | 30000 | 379 | 485 | 823 |
| 11 | 1Cu/10CeO₂/Al₂O₃ | C973 | 30000 | 357 | 488 | 803 |
| 12 | 1Cu/10CeO₂/Al₂O₃ | C973, R673 | 30000 | 386 | 493 | 813 |
| 13 | 1Cu/10CeO₂/Al₂O₃ | C673 | 100000 | 403 | 753 | - |
| 14 | 1Cu/10CeO₂/Al₂O₃ | RO773 | 100000 | 413 | 740 | - |
| 15 | 1Cu/10CeO₂/Al₂O₃ | RO673 | 100000 | 432 | 732 | - |
| NO reduction | | | | | | |
| 1 | 1Cu/Al₂O₃ | C723 | 30000 | 523 | 623 | - |
| 2 | 1Cu/Al₂O₃ | RO623 | 30000 | 473 | 504 | - |
| 3 | 1Cu/CeO₂ | C723 | 30000 | - | 500 | - |
| 4 | 3Cu/CeO₂ | C723 | 30000 | - | 440 | - |
| 5 | 6Cu/CeO₂ | C723 | 30000 | - | 432 | - |
| 6 | 1Cu/10CeO₂/Al₂O₃ | C673 | 10000 | 477 | 590 | - |
| 7 | 1Cu/10CeO₂/Al₂O₃ | C973 | 10000 | 444 | 503 | - |
| 8 | 1Cu/10CeO₂/Al₂O₃ | RO673 | 10000 | 463 | 492 | - |
| 9 | 1Cu/10CeO₂/Al₂O₃ | C673 | 30000 | 478 | 667 | - |
| 10 | 1Cu/10CeO₂/Al₂O₃ | R673 | 30000 | 414 | 498 | - |
| 11 | 1Cu/10CeO₂/Al₂O₃ | C973 | 30000 | 481 | 673 | - |
| 12 | 1Cu/10CeO₂/Al₂O₃ | C973, R673 | 30000 | 447 | 507 | - |
| 13 | 1Cu/10CeO₂/Al₂O₃ | C673 | 100000 | 510 | - | - |
| 14 | 1Cu/10CeO₂/Al₂O₃ | RO773 | 100000 | 447 | - | - |
| 15 | 1Cu/10CeO₂/Al₂O₃ | RO673 | 100000 | 458 | - | - |
Numerous papers are devoted to the study of his properties and catalytic performance [1]. The experimental data (Table 3) on the catalytic activity of supported Rh catalysts does not contradict to the data published [9,10], but few things are worth of mentioning.

### Table 3

| No | Sample                  | Treatment | GHSV, h⁻¹ | LOT, K | MPT, K | EORT, K |
|----|-------------------------|-----------|-----------|--------|--------|---------|
| CO oxidation | | | | | | |
| 1  | 0.1Rh/Al₂O₃             | C723      | 100000    | 546    | 586    | 663     |
| 2  | 0.1Rh/10CeO₂/Al₂O₃      | C723      | 100000    | 527    | 554    | 583     |
| 3  | 0.1Rh/1Cu/10CeO₂/Al₂O₃  | C723      | 100000    | 404    | 545    | 603     |
| 4  | 1Cu/0.1Rh/10CeO₂/Al₂O₃  | C723      | 100000    | 413    | 548    | 628     |
| NO reduction | | | | | | |
| 5  | 0.1Rh/Al₂O₃             | C723      | 100000    | 546    | 579    | 640     |
| 6  | 0.1Rh/10CeO₂/Al₂O₃      | C723      | 100000    | 506    | 523    | 643     |
| 7  | 0.1Rh/1Cu/10CeO₂/Al₂O₃  | C723      | 100000    | 523    | 547    | 576     |
| 8  | 1Cu/0.1Rh/10CeO₂/Al₂O₃  | C723      | 100000    | 499    | 548    | 603     |

The characteristic temperature for Rh containing catalysts in both CO oxidation and NO reduction reactions are practically equal. The presence of ceria in the catalyst composition improves its catalytic performance in both reactions. Preliminary redox treatment improves only LOT and MPT but not EORT for both reactions. The calcination of the Rh/Al₂O₃ and Rh/CeO₂/Al₂O₃ catalysts at 1073 K causes the substantial decrease of the catalysts activity in both reactions. The experiments with catalysts Rh/CeO₂/Al₂O₃ prepared by changing the order of addition of Rh and ceria to the carrier showed that their activities were comparable.

**Catalytic activity of Cu/Rh/CeO₂/Al₂O₃ and Rh/Cu/CeO₂/Al₂O₃ supported catalysts**

The experimental data on the catalytic activity of supported Rh-Cu catalysts using reaction mixture No 2 is presented in Table 3.

The order of introduction of Rh and Cu in the process of catalysts preparation has a minor influence on the catalytic activities of the bimetal Rh and Cu containing supported catalysts in both reactions. The Rh/Cu/CeO₂/Al₂O₃ catalysts have slightly better performance than the Cu/Rh/CeO₂/Al₂O₃ catalysts. The performance of the Rh/Cu/CeO₂/Al₂O₃ and Cu/Rh/CeO₂/Al₂O₃ catalysts is better than the performances of the Rh/CeO₂/Al₂O₃ catalyst. The presence of Cu has positive effect on low percentage Rh containing catalysts in the low temperature region. Cu has noticeable promoting effect mainly for the catalytic activity in the reaction of CO oxidation and in smaller extent for the reaction of NO reduction.

Preliminary treatment with RO cycles improves the LOT of both types of catalyst in the CO oxidation and in NO reduction. Thermal treatment at temperatures up to 973 K does not have sensible effect on the catalytic activities of all studied catalysts. Calcination at 1073 K, however, strongly decreases the catalytic activity of Rh/Cu/CeO₂/Al₂O₃ catalysts.

**Conclusion**

The addition of Cu to the Rh catalysts supported on ceria/alumina improves their catalytic activities in both reactions in all temperature regions but strong decrease is observed only for LOT and MPT.

Thermal pre-treatment of the catalysts at temperatures up to 973 K does not have sensible effect on the catalytic activities of all studied catalysts. Calcination at 1073 K of Rh containing catalysts, however, causes substantial decreases the catalytic ac-
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