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CATALYTIC ABATEMENT OF COLD-START VEHICULAR CO EMISSIONS

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1. Introduction

Rapid urbanization coupled with increased demand for transportation for day-to-day activities has led to the unrestrained increase in the number of vehicles in the world, especially in developing countries [1]. Huge amount of fuel is burnt in motorized transport [2]. In vehicles the incomplete combustion of fuels causes air pollution. The major primary pollutants present in the emissions are carbon monoxide (CO), nitrogen oxides (NO_x) and unburned hydrocarbons (HCs) [3]. These primary pollutants are toxic themselves and contribute to the formation of more toxic secondary pollutants in sunlight, e.g. peroxy-acetyl nitrate (PAN), poly-aromatic hydrocarbons (PAH), ozone (O_3), smog, acid rain, and may also increase the greenhouse effect [4]. The pollutants cause health problems, pollution of water and soil, deterioration of buildings, reductions in visibility, and negative impact on agricultural productivity and are known to be mutagenic and carcinogenic [5]. Out of all these pollutants, CO is the most poisonous and it has been termed «the unnoticed poison of the 21st century». It is particularly detrimental to human beings and in general to all life forms that respire. It also adversely affects vegetation and environment.

Thus, the increasing concern on atmospheric pollution derived from road transportation has led to the introduction of stringent clean air regulations. Bharat Stage (BS VI) equivalent to the European Emission (EU VI) standard requires reducing CO emissions below 1.0 g/km from petrol-driven car [6]. As a consequence effective control devices need to be developed to enable vehicles to meet the increasingly stringent limits. Various primary measures (engine modifications, fuel modifications, fuel/air ratio, etc.) failed to match the emission requirements. To meet the emission norms, automotive catalytic converter (ACC) has been proposed to be the most effective end-of-the pipe treatment technology [7]. Here catalysts play a major role to convert CO to non-toxic CO_2 as represented by the following Eq. 1:

$$CO + 1/2O_2 \rightarrow CO_2. \qquad (1)$$

CO_2 is present in the atmosphere and used in photosynthesis by plants and vegetation.

Commercial catalysts usually consist of very costly noble metals (Pt, Pd, Rh) [8]. Availability of the noble metals in our country is only by import causing heavy burden on the exchequer. One of the major challenges is the «cold-start» problem: controlling the unwanted emissions produced before the catalytic converter reaches operational temperatures [9]. During cold-start phase, about 60—80 % of CO is emitted from a motor vehicle even equipped with a three-way catalyst (TWC) [10]. TWC which uses noble metals are not being able to function effectively until it reaches the light-off temperature of 200 °C as the conversion efficiency depends strongly on the working temperature and is practically zero during the starting and warming up period. Thus, efforts have been always put towards the development of low cost non-noble metal-based catalysts [11, 12] which can also overcome the problem of cold-start.

Among base metal catalysts, copper and supported copper catalysts are known to be highly active in view of availability, lower cost, less sensitive to sulfur poisoning and comparable activity for purification of vehicular exhaust [12—14]. To enhance the performance of the Cu catalyst, addition of appropriate promoter is essential. The addition of ceria (CeO_2) to the Cu increases catalyst performance due to its excellent oxygen storage capacity (OSC) provided by the redox couple: $2CeO_2 \leftrightarrow Ce_2O_3 + O$, making active oxygen available for the acceleration of oxida-

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tion reactions [15, 16] and structural enhancement of the metal dispersion. Further, gold-based catalysts exhibit high activity at low temperatures, good stability under moisture and resistance to sulfur poisoning [17]. It is also reported that Au is about 1000 times more active than Pt in the catalytic oxidation of CO under basic but not acidic environments [18]. Highly dispersed gold on suitable metal oxides exhibits extraordinarily high activity in low-temperature CO oxidation [19, 20]. By promoting Au catalysts great improvements in activity can be obtained [21—23] and the temperature range of CO conversion can be enlarged. Results reported in the literature [19, 24] shows that ceria has a promoting effect on the activity of the Au/Al_2O_3 catalyst in CO oxidation. India has sufficient Au reserves, therefore application of Au in place of Pt would be attractive proposition for catalytic control of vehicular CO emissions under cold-start conditions.

Several authors have investigated $Cu\text{-}CeO_2$, $Cu\text{-}CeO_2/Al_2O_3$, Au/CuO, Au/CeO_2 and $Au/CuO\text{-}CeO_2$ catalysts for low temperature CO oxidation [25—31]. Qin et al. [25] reported the Ce-Cu binary precursor synthesized by an improved urea method resulted in CO oxidation at temperature lower then 71 °C. Liu and Stephanopoulos have investigated the CO oxidation over La promoted Au/CeO_2 containing 5 wt.% Au at room temperature [32]. Hoflund and co-workers have shown Au/CeO_2 containing 10 % Au as an active catalyst for the low temperature (< 0 °C) oxidation of CO [33]. Bera and Hegde have reported CO oxidation over 1 % Au/CeO_2 prepared by combustion method [34]. However, the catalyst is shown to be active for the reaction at high temperature of 250—300 °C. Majority of the gold catalysts shown to be highly active for CO oxidation typically contain 2—10 wt.% gold. Pillai and Deevi [35] worked on Au/CeO_2 catalyst containing as low as 1 wt.% Au, and they found that it is a highly active catalyst for the room temperature oxidation of CO to CO_2 with complete conversion of CO and sustains its high activity for a period of 24 h.

However, little attention has been paid on the stability of catalyst for a considerable period of time. It is well known fact that stability is a desirable characteristic. Therefore, using alumina support stability of the catalyst could be increased without sacrificing the performance in the reaction. Because of the abundant pores and large surface area present in alumina, it has a great potential in further improving the catalytic performance. Hence, the objective of the present study was to develop Au promoted $Cu\text{-}Ce/\gamma\text{-}Al_2O_3$ catalyst and to test the activity and durability of prepared samples for CO oxidation at low temperature.

2. Experimental

2.1. Catalyst preparation

First ceria (CeO_2) powder was prepared by thermal decomposition of precipitated cerium (III) oxalate $[Ce_2(C_2O_4)_3 \cdot 10H_2O]$. Then, the copper was supported on prepared ceria by wet impregnation with required amount of copper nitrate solution. The slurry thus obtained was evaporated to dryness followed by further drying in an oven at 110 °C overnight. The dried precursor was calcined under controlled conditions and environment to prepare $CuCe_xO_y$ (molar ratio Cu : Ce = = 1 : 8) catalyst. Further, the above slurry was also impregnated over 15 wt.% $\gamma\text{-}Al_2O_3$ followed by the heat treatment steps.

To prepare gold-promoted $CuCe/\gamma\text{-}Al_2O_3$ catalyst, Au was incorporated into the ceria supported copper catalyst by incipient wetness method with required amount of $1.3 \cdot 10^{-2}$ M aqueous solution of chloroauric acid ($HAuCl_4$) followed by evaporation, drying and calcinations under controlled conditions and environment. The composition of Au in the catalysts was 3 % by weight, with Cu : Ce = = 1 : 8 molar ratios remain unchanged.

This paper reports only the optimum composition of the catalyst with respect to performance in CO oxidation. The prepared catalyst was calcined at 600 °C under controlled conditions and environment for 2 hours. For durability test prepared catalyst was further heated to 800 °C for 2 hours and then its CO oxidation activity was plotted against time-on-stream for continuous 50 h run with the temperature kept constant at its 100 % conversion.

2.2. Catalyst characterization

Surface area measurement and textural characterization of the catalyst sample was done by nitrogen adsorption at –196 °C using Quantachrome Nova 2200e surface area analyzer. X-ray diffraction (XRD) patterns of the catalyst were collected on 18 kV rotating anode Rigaku powder diffractometer, using CuK_α radiation for phase identification of the catalysts. The patterns were recorded at room temperature with a 2θ range from 20 to 80°. X-Ray photoelectron spectroscopy (XPS) analysis was performed on an Amicus spectrometer equipped with MgK_α X-ray radiation. For typical analysis, the source was operated at a voltage of 15 kV and current of 12 mA. Pressure in the analysis chamber was less than 10^{-5} Pa. The binding energy scale was calibrated by setting the main C1s line of adventitious impurities at 284.7 eV, giving an uncertainty in peak positions of ±0.2 eV.

2.3. Catalytic activity

The oxidation of CO was studied in a fixed bed tubular down-flow compact reactor [12]. Following reaction conditions were maintained: 100 mg catalyst, 100—150 mesh size (150—100 μm particle size), using a lean mixture of 2.5 % CO (volume ratio) in the air, maintaining total flow rate of 60 ml/min. The reaction was carried out in the temperature range of ambient to the temperature till 100 % CO conversion was attainted. Air fed was made free of moisture and CO_2 by passing it through CaO and KOH pellets drying towers. The catalytic experiments were carried out under steady state conditions. Typically, the reactor was heated to the desired temperature with the help of a micro-processor based temperature controller. A temperature control of ±0.5 °C was achieved. The flow rates of CO and air were monitored with the help of digital gas flow meters. Reactants and products were analyzed for the concentration of CO and CO_2 with the help of an online gas chromatograph equipped with porapack Q-column, FID detector and methaniser. The conversion (X_{CO}) was calculated on the basis of values of CO concentration in the reactor input ($C_{CO_{in}}$) and output ($C_{CO_{out}}$) samples by the following Eq. 2:

$$X_{CO} = (C_{CO_{in}} - C_{CO_{out}})/C_{CO_{in}}. \qquad (2)$$

The activity of the catalyst was expressed as conversion of CO. Multiple samples of the gases were analyzed to ensure that the catalytic system had reached a steady state.

3. Results and discussion

3.1. Textural characterization

BET surface area of Au-CuCe/γ-Al_2O_3 catalyst was found to be 103.48 m^2/g and pore size was 28.664 nm. The pore volume of the catalyst was 0.07 cm^3/g measured by N_2 sorption at its relative pressure, $P/P_0 = 0.99$. The nitrogen adsorption-desorption isotherms of the Au-CuCe/γ-Al_2O_3 catalyst are shown in Fig. 1. The isotherms are of type IV according to IUPAC classification [36]. A hysteresis loop with a sloping adsorption and desorption curves is observed at a high relative pressure (P/P_0) range.

The pore size distribution of the catalyst is shown in Fig. 2. It can be seen that pores are distributed in a narrow range of 1.7—15 nm, with dominating pore diameter around 4—5 nm.

3.2. X-ray diffraction

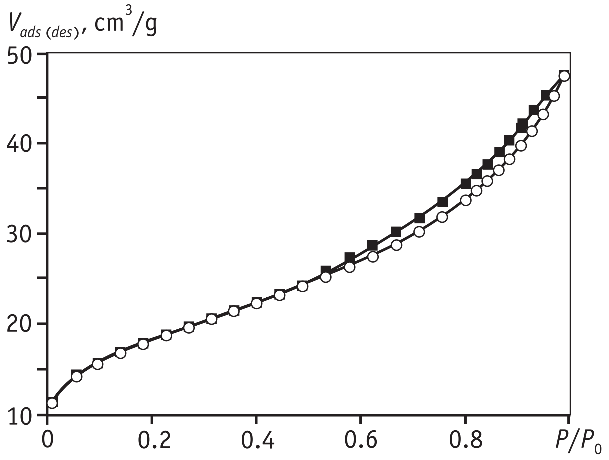

Fig. 1. N_2 adsorption-desorption isotherms of Au-CuCe/γ-Al_2O_3 catalyst

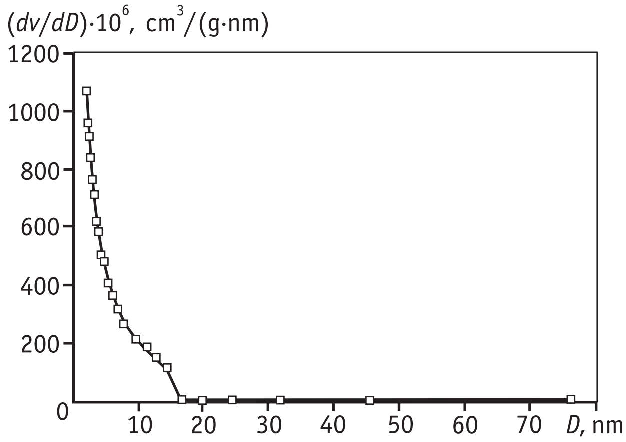

Fig. 2. Pore size distribution of Au-CuCe/γ-Al_2O_3 catalyst

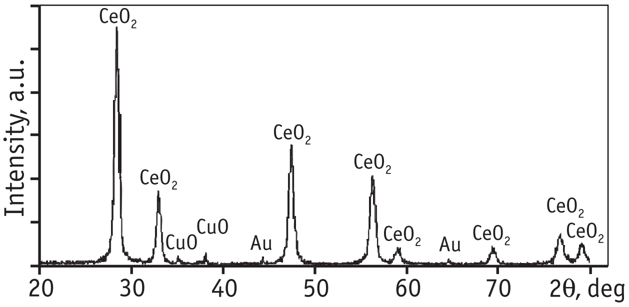

Fig. 3. XRD pattern of Au-CuCe/γ-Al_2O_3 catalyst

XRD pattern of the catalyst containing Au-CuCe/γ-Al_2O_3 is shown in Fig. 3. The diffraction peaks corresponding to the 2θ values of 28.5, 33.1, 47.5, 56.3, 59.1, 69.4, 76.7 and 78.9° can be indexed to the (111), (200), (220), (311), (222), (400), (331) and (420) planes of the fluorite structure of CeO_2 crystals (JCPDS 43-1002). For the catalysts, the small diffraction peaks at 35.42 and 38.7° are attributed to the (111) plane of CuO crystals of tenorite phase. Very small peaks of Au are observed at 44.3 and 64.5° representing its amorphous nanosize nature. There is no indication of the presence of other phases like Au-Cu alloy which is found at 39.2°. This shows that they are present in almost amorphous state. The dominant phase present in the catalyst is of CeO_2.

3.3. X-Ray photoelectron spectroscopy

The Au 4*f* ionization process is characterized by the doublet of the two spin-orbit components, Au $4f_{7/2}$ and Au $4f_{5/2}$, with a splitting of 3.7 eV. As indicated in the Fig. 4, the experimental curves were fitted with two doublets. The prepared sample presents a main Au $4f_{7/2}$ component at a binding energy of 84.1 eV typical of metallic gold [34], and a negligible component at 86.1 eV, likely due to oxidized surface Au species.

As shown in Fig. 5, two principal peaks of Ce $3d_{5/2}$ and Ce $3d_{3/2}$ (centred at 882 and 898 eV) and four satellite peaks raising from ionization can be attributed to the Ce(IV). However, main peaks of Ce $3d_{5/2}$ and Ce $3d_{3/2}$ in the catalyst sample is lower than that of the reported in literature [37, 38], due to the coexistence of Ce^{3+}/Ce^{4+} in the catalyst [39, 40].

The Cu 2*p* XPS spectra in Fig. 6 consist of two main peaks of Cu $2p_{3/2}$ deconvoluted by using three components at 932.0, 934.2, and 936.0±0.2 eV which have been found to correspond to Cu(I), Cu(II) in octahedral sites and Cu(II) in tetrahedral sites respectively and Cu $2p_{1/2}$ (centred at 951.8—952.6 eV) [41—43]. The existence of Cu^+ and Ce^{3+} observed in the catalyst is induced by substitution of Ce with Cu or by strong interaction at the interface of two oxides [44]. The reduced species of copper and cerium oxides demonstrate the synergistic interaction between CuO and CeO_2 in the Au-CuCe/γ-Al_2O_3 catalyst, which have significant effects on the catalytic activity [45]. O 1*s* spectra of the sample (not shown) have similar pattern with the main peak appearing at 528.4 eV with a shoulder peak at 531.5 eV indicating the presence of two different types of metal-oxygen sites. Peak at 528.4 eV is due to the lattice oxygen from the CeO_2.

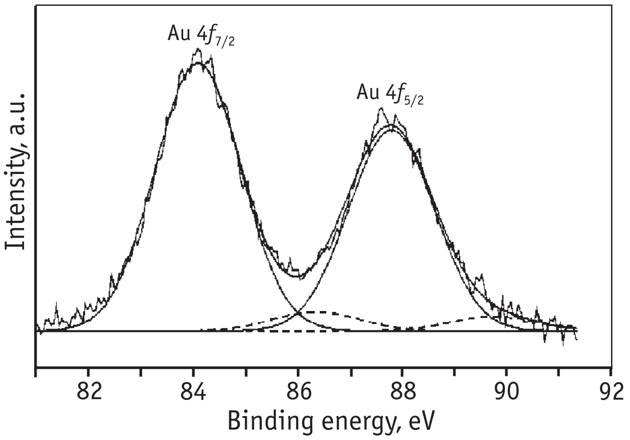

Fig. 4. Experimental and fitted Au 4*f* photoelectron peaks of Au-CuCe/γ-Al_2O_3 catalyst

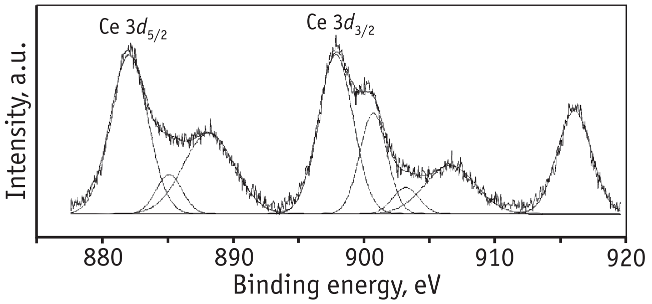

Fig. 5. Experimental and fitted Ce 3*d* photoelectron peaks of Au-CuCe/γ-Al_2O_3 catalyst

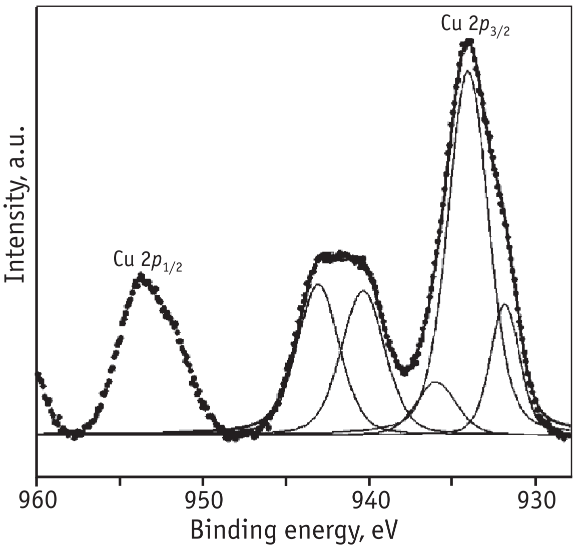

Fig. 6. Experimental and fitted Cu 2*p* photoelectron peaks of Au-CuCe/γ-Al_2O_3 catalyst

3.4. Activity measurement

It is evident from Fig. 7 that Au promoted CuCe/γ-Al_2O_3 catalysts are highly active for CO oxidation exhibiting 100 % CO conversion at 80 °C with light-off temperature at 60 °C. The presence of CuO, Cu_2O and dominance of CeO_2 phases as evidenced from XRD and XPS studies may be the possible reason for the high activity of the catalyst. CeO_2 phase accelerates the oxidation reactions making lattice oxygen available. Structural oxygen is more active than molecular oxygen of air. Further, Au catalyst is known to be very active at ambient temperature [18]. Thus, Cu/γ-Al_2O_3 catalyst promoted with Au and supported with CeO_2 shows very high activity at low temperature.

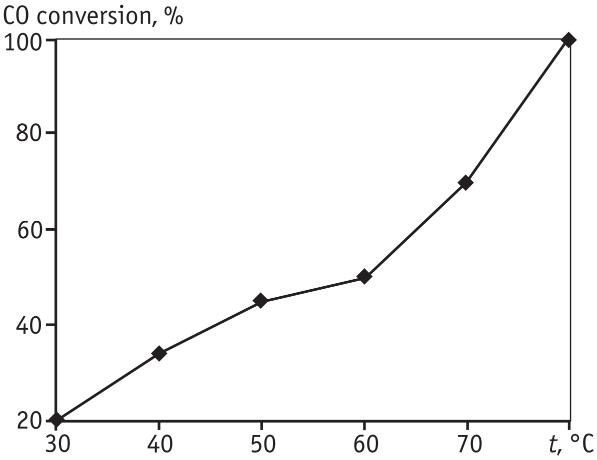

Fig. 7. CO oxidation over Au-CuCe/γ-Al_2O_3 catalyst

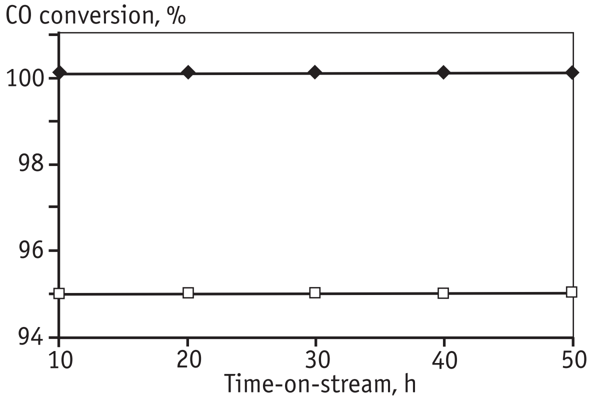

Fig. 8. Durability tests of Au-CuCe/γ-Al_2O_3 catalyst for CO oxidation at 80 °C

Calcination temperature: ◆ – 600 °C; □ – 800 °C

3.5. Durability test

For durability test, the conditions were kept the same as mentioned above in the activity test and the reaction temperature was fixed at 80 °C. It is clear from Fig. 8 that the catalyst calcined at 600 °C showed 100 % CO conversion for 50 hours continuous run while the catalyst calcined at 800 °C showed activity at little lower level of 95 % conversion for the whole time-on-stream. It can be concluded that the catalyst showed quite good durability and negligible deactivation after 50 hours run.

4. Conclusion

In this paper, Au-CuCe/γ-Al_2O_3 catalyst was found to convert total CO into CO_2 at cold start temperature, around 80 °C. The durability test showed no deactivation of catalyst confirming its sturdy nature. It is a well stabilized fact that stability is more desirable characteristic of a catalyst than its activity for application in the catalytic converter. Thus, it can be concluded that Au-CuCe/γ-Al_2O_3 catalyst might be used for CO oxidation in vehicular exhaust at cold-start temperature. Furthermore, its low cost and easy availability support for its use as pollution controls catalyst.

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КАТАЛИТИЧЕСКОЕ СНИЖЕНИЕ АВТОМОБИЛЬНЫХ ВЫБРОСОВ СО ПРИ ХОЛОДНОМ ЗАПУСКЕ ДВИГАТЕЛЯ

Пратичи Сингх и Рам Прасад

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Быстрая урбанизация в сочетании с увеличением спроса на перевозки в повседневной деятельности привела к безудержному росту численности автомобилей в мире, особенно в развивающихся странах. Огромное количество топлива сжигается моторизованным транспортом. Неполное сгорание топлива в двигателях вызывает загрязнение воздушного бассейна. Основные первичные загрязнители, присутствующие в выбросах, — монооксид углерода (CO), оксиды азота (NO_x) и несгоревшие углеводороды (УВ). Эти вещества токсичны сами по себе, а кроме того, приводят к образованию под действием солнечного света более токсичных вторичных загрязнителей, например пероксиацетилнитрата (ПАН), полициклических ароматических углеводородов (ПАУ), озона (O_3), смога, кислотных дождей, и могут также способствовать усилению парникового эффекта. Загрязняющие вещества вызывают серьезные проблемы со здоровьем, отравляют воду и почву, ухудшают состояние зданий, снижают видимость, а также отрицательно сказываются на продуктивности сельского хозяйства. Кроме того, они, как известно, обладают мутагенными и канцерогенными свойствами. Из названных загрязнителей монооксид углерода — самый ядовитый, он получил название «незаметный яд XXI века».

Таким образом, растущая озабоченность по поводу загрязнения атмосферы, вызванного автомобильным транспортом, привела к введению более жестких требований к чистоте воздуха. Bharat Stage (BS VI), эквивалентный европейскому стандарту на выбросы (Евро-6), требует от автомобиля, работающего на бензине, снижения выбросов СО до уровня ниже 1,0 г/км. В связи с этим должны быть разработаны эффективные устройства, обеспечивающие соответствие транспортных средств столь жестким требованиям. Для соблюдения норм выбросов предложен автомобильный каталитический конвертер (АКК) — эффективный дожигатель, где катализаторы играют важную роль в превращении СО в нетоксичный CO_2, присутствующий в атмосфере и используемый растениями в процессе фотосинтеза.

Коммерческие катализаторы обычно содержат очень дорогостоящие благородные металлы (Pt, Pd, Rh). Наличие благородных металлов в нашей стране обеспечивается только импортом. Одной из основных задач является проблема «холодного запуска»: регулирование нежелательных выбросов, образующихся до того, как каталитический дожигатель достигает рабочих температур. В фазе холодного старта около 60—80 % СО выбрасывается из двигателя автомашины, даже если она оснащена катализатором TWC, в которым используются благородные металлы. Он не способен эффективно работать до тех пор, пока не достигнет температуры зажигания 200 °С, так как величина конверсии сильно зависит от рабочей температуры и практически равна нулю во время пуска и прогрева. Поэтому усилия разработчиков всегда были направлены на создание недорогих металлических катализаторов, которые также могут решить проблемы холодного запуска.

Таким образом, цель настоящего исследования состояла в определении активности и продолжительности срока службы промотированного золотом $Cu\text{-}Ce/\gamma\text{-}Al_2O_3$ катализатора в реакции окисления СО при низкой температуре. Образец был приготовлен методом пропитки и прокален при 600 °С, а для тестирования на продолжительность срока службы — при 800 °С. Катализатор был охарактеризован методами низкотемпературной адсорбции азота, рентгеновской дифракции и рентгеновской фотоэмиссионной спектроскопии (РФС). Окисление СО изучали в проточном трубчатом реакторе с неподвижным слоем катализатора: навеска — 100 мг, размер частиц — 100—150 меш (150—100 мкм), используя обедненную смесь (2,5 об.% СО в воздухе) с общей скоростью потока 60 мл/мин. Реагенты и продукты анализировали на содержание СО и CO_2 с помощью газового хроматографа, оснащенного колонкой с порапаком, пламенно-ионизационным детектором и метанатором.

Определенная методом БЭТ удельная поверхность $Au\text{-}Cu\text{-}Ce/\gamma\text{-}Al_2O_3$ катализатора составила 103,48 $м^2/г$, размер пор — 28,664 нм и объем пор — 0,07 $см^3/г$. Дифракционная картина катализатора показала, что в аморфном состоянии преобладают кристаллы CeO_2 флюоритной структуры, присутствуют кристаллы CuO теноритной фазы и наблюдаются два очень небольших пика от наноразмерных частиц Au. Методом РФС (XPS) выявлено совместное существование Ce^{3+}/Ce^{4+} в катализаторе.

Полная конверсия СО на $Au\text{-}Cu\text{-}Ce/\gamma\text{-}Al_2O_3$ наблюдается при температуре около 80 °С. Повышенная активность катализатора может быть обусловлена присутствием CuO, Cu_2O и доминированием CeO_2 фаз. Кроме того, известно, что катализаторы, содержащие Au, очень активны при температуре окружающей среды. Так, $Au\text{-}Cu\text{-}Ce/\gamma\text{-}Al_2O_3$ проявил высокую каталитическую активность при низкой температуре. В ходе испытаний на продолжительность срока службы конверсию СО измеряли на протяжении 50 ч непрерывной работы, дезактивации катализатора при этом не наблюдалось. Благодаря низкой стоимости и доступности, $Au\text{-}Cu\text{-}Ce/\gamma\text{-}Al_2O_3$ может быть рекомендован для использования в качестве катализатора окисления автомобильных выхлопных газов при температуре холодного запуска двигателя.