

PROMOTING ASPECT OF PALLADIUM NANOPARTICLES ON SPINEL Pd@CuCr₂O₄/γ-Al₂O₃ CATALYTIC SYSTEM IN CARBON MONOXIDE OXIDATION

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ABSTRACT

In this report, the promoting aspect of Pd on the activity of spinel CuCr₂O₄ and Pd catalytic systems in CO oxidation is investigated. Catalysts with compositions of 10 % spinel CuCr₂O₄ synthesized via modified sol–gel *in situ* on γ-Al₂O₃ support and Pd nanoparticles (0.11 ÷ 0.68) % then decorated on CuCr₂O₄/γ-Al₂O₃ via impregnation method by decomposed palladium (II) acetate solution at 280 °C for 2 h. Promoting aspect of Pd nanoparticles evaluating by Temperature Program Surface Reaction (TPSR) method in temperature range of 30 ÷ 450 °C and 15 L.h⁻¹ flow gases consist of 1 % CO, 20 % O₂ and 79 % N₂ on 0.100 g catalysts. The experimental results reveal that the as-prepared materials completely convert CO at temperatures below 140 °C with 0.68 % Pd compare to 300 °C without Pd in the component. CO conversion highly increases with increasing amounts of Pd, with gas hourly space velocity reached by 1500 L.h⁻¹.g⁻¹ that exhibits promising application of these catalytic systems in exhausts treatment containing CO at low temperatures.

Keywords: spinel CuCr₂O₄, palladium catalyst, sol–gel PVA, CO oxidation.

1. INTRODUCTION

Spinel CuCr₂O₄ has attracted much research interest in applying as catalyst materials to the treatment of CO since it was discovered by Lory [1] in 1933. Some catalytic systems based on CuCr₂O₄ have been registered as material for handling CO emissions of internal combustion engines by Albert and Frazer [2]. Some researchers [3] concluded that the spinel CuCr₂O₄ is

appropriate catalyst for CO oxidation. Yurieva [4] supposed that the spinel CuCr_2O_4 is active phase in CO oxidation reactions and has better catalytic activity than mechanical mixture of two oxides CuO and Cr_2O_3 or separate oxide mentioned above.

Spinel CuCr_2O_4 crystal structure consists of O^{2-} ions with face-centered cubic structure in Bravais lattice system while Cu^{2+} and Cr^{3+} cations distribute in tetrahedral and octahedral cavities of the crystal lattice. Each unit cell consists of 8 CuCr_2O_4 molecules including 32 O^{2-} anions, 8 Cu^{2+} and 16 Cr^{3+} cations (Figure 1). This structural surface is covered by a lot of oxygen anions that facilitates spinel CuCr_2O_4 materials dominating good catalytic property for CO oxidation conducting on the crystalline surface. Spinel CuCr_2O_4 structure can stabilize activity under the variety reacting conditions so this catalytic system can be able to maintain activity during chemical reaction process.

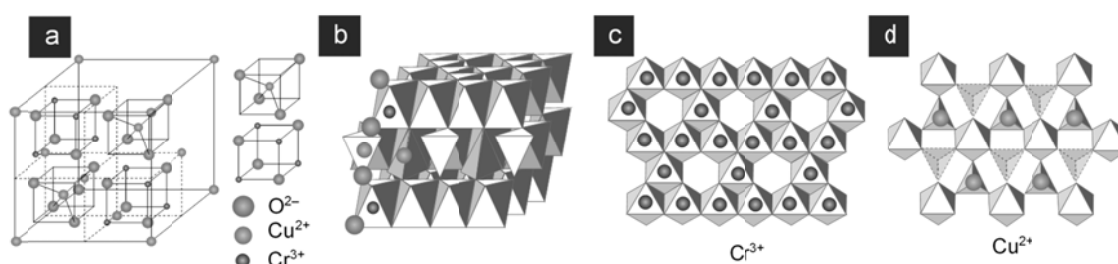
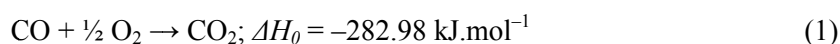


Figure 1. Models of spinel CuCr_2O_4 unit cells structure (a, b), distribution of Cu^{2+} and Cr^{3+} cations in tetrahedral (c) and octahedral (d) cavities of the lattice.

Spinel CuCr_2O_4 materials can be synthesized by various routes such as, co-precipitation [5, 6], impregnation; oxalate method using ammonium oxalate salts of copper and chromium [7]; solid phase method using a mixture of copper oxides and chromium pure dispersion in acetone [8]. Sol-gel method is considered as one of the promising routes for synthesis of nanoparticles catalyst materials; scalable ability; controllable chemical compositions; high purity and specific surface area; products forms in particles, thin films and rod.

Pd has high activity and widely used in CO oxidation due to its good selective adsorption capacity for reactants. When dispersed on the surface of spinel $\text{CuCr}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ catalytic system Pd nanoparticles play as a promoter in CO oxidation that operating under two mechanisms. First, focusing the interaction between CO and O_2 by adsorption mechanism. Meanwhile, O_2 adsorbed in strong chemical active form such as O^{2-} , O^- , and O_s^- that easy to interact with CO. Second, reducing total activation energy addition by receiving energy (ΔE) produced from CO oxidizing reaction takes place at low temperature on Pd surface described as equation (1):



This energy facilitates the subsequent interactive process on spinel CuCr_2O_4 crystals. Mechanism of CO adsorption on Pd nanoparticles surface primarily through the formation of terminal or bridge complex structures between CO and Pd [8]. Impregnation method is commonly used to attach Pd nanoparticles to the composition of catalyst. In this method, aqueous of solution Palladium such as $\text{Pd}(\text{OCOCH}_3)_2$ is used as precursors of Pd. Structure of the original catalysts system is not affected by impregnating palladium precursor but affect the dispersion of Pd particles on the catalytic surface.

This paper presents the experimental results of synthesis and evaluation of the promoting aspect of Pd nanoparticles on catalytic activity of spinel CuCr₂O₄.Pd/γ-Al₂O₃ materials in approach of CO containing exhaust treatment at low temperature.

2. MATERIALS AND METHODS

2.1. Synthesis of spinel CuCr₂O₄.Pd/γ-Al₂O₃

In this study, copper chromite nanoparticles synthesized via modified sol-gel method with the assist of polyvinyl alcohol. The chemicals (from Sigma Aldrich) include Cu(NO₃)₂.3H₂O (99.0 %), Cr(NO₃)₃.9H₂O (99.0 %), Pd(OCOCH₃)₂ (99.8 %), PVA (M = 11,000 g.mol⁻¹, 99.0%), sucrose, γ-Al₂O₃ (~200 m².g⁻¹, 99.8 %, Merck). Aqueous nitrate solution of copper (II) and chromium (III) with a molar ratio Cu²⁺/Cr³⁺ = 0.5; pH = 3 stirred in the presence of PVA and dispersed γ-Al₂O₃ particles forming viscous gel mixture. Gel was dried and calcined at 550 °C for 5 h, then impregnated in Palladium(II) acetate solution and heated to 280 °C for 2 h. The as-prepared materials were analyzed by XRD (MANAR Center-VNUHCM); FE-SEM methods (Institute of Chemical Technology-VAST), specific surface area and porous structure on the Nova 1000E (MANAR Center-VNUHCM); chemical composition analysis by SEM-EDS, SMEWW Pd-3500: 2012 (ISO 5502: 2003) (Institute of Chemical Technology-VAST).

2.2. Evaluating catalysis aspect of spinel CuCr₂O₄.Pd/γ-Al₂O₃ materials

The catalytic activity of spinel CuCr₂O₄.Pd/γ-Al₂O₃ for CO oxidation is conducted on the experimental system by Temperature programmed surface reaction (TPSR) method with gas flow of 15 L.h⁻¹ include (vol%) 1 % CO, 79 % N₂ and 21 % O₂. Temperature range of 30 ÷ 450 °C with heating rates 600 °C.h⁻¹. Schematic of experimental set up for investigating catalytic aspects of the as-prepared materials is shown in Figure 2.

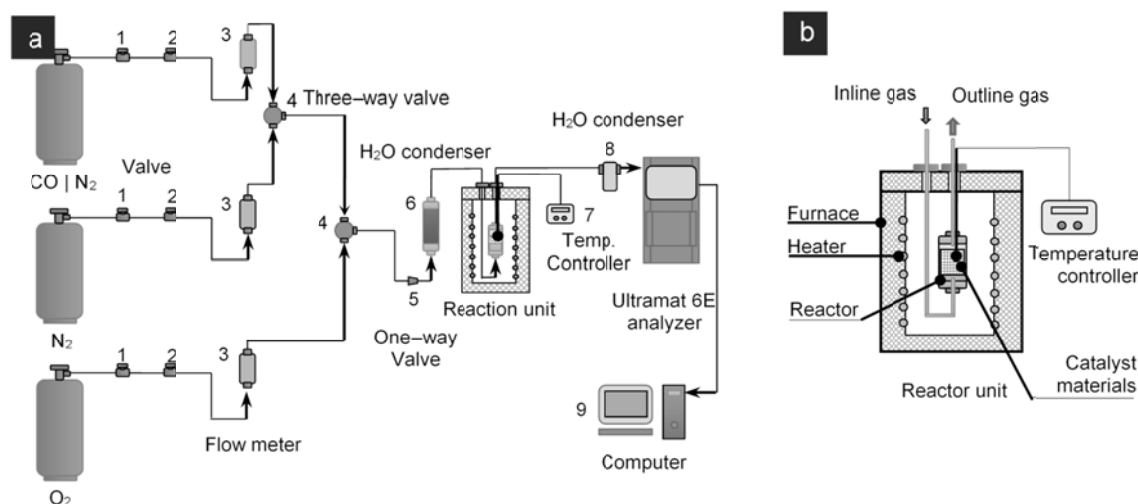


Figure 2. Catalytic aspect of spinel CuCr₂O₄.Pd/γ-Al₂O₃ materials investigating schematic set up (a) and details on reactor unit (b). Photographs of Ultramat 6E CO, CO₂ analyzer (c), experimental set up (d), reaction unit (d) and reactor (f).

An amount of 0.01 g catalysts is activated in O₂ (99.0 %) flow 3.0 L.h⁻¹ at 500 °C for 2 h. before the reaction. CO and CO₂ concentrations are continuously determined by Ultramat 6E instrument connected directly through Virtual Bench Logger 2.1 software. CO conversion ratio is calculated by equation (2):

$$\chi_{CO} = \frac{C_{CO}^o - C_{CO}^t}{C_{CO}^o} \cdot 100, \% \quad (2)$$

where C_{CO}^o, C_{CO}^t are the average CO concentration in the gas mixture before and after the reaction, respectively, ppm.

3. RESULTS AND DISCUSSION

3.1. Crystal structure and chemical properties

3.1.1. Crystal structure

The XRD crystalline phase qualitative analysis results of spinel CuCr₂O₄.Pd/γ-Al₂O₃ catalyst materials are shown on Figure 3a. XRD pattern of spinel CuCr₂O₄/γ-Al₂O₃ have a characteristic diffraction peak of (211) crystal plane at $2\theta = 35^\circ$ and other peaks matched with diffraction peaks of pure spinel CuCr₂O₄ ($2\theta = 18^\circ, 28^\circ, 29^\circ, 31^\circ, 36^\circ, 38^\circ, 42^\circ \dots$) (JCPDF card No. 05–0657). XRD results also show the presence of Pd nanoparticles in components of spinel CuCr₂O₄ catalytic systems the diffraction peak at $2\theta = 40, 46^\circ$ of (111) and (200) Pd lattice plane (JCPDF card No. 88–2335). Thereby indicating that the spinel CuCr₂O₄.Pd mixed catalytic system on γ-Al₂O₃ support successfully synthesized by modified the sol–gel and impregnation methods.

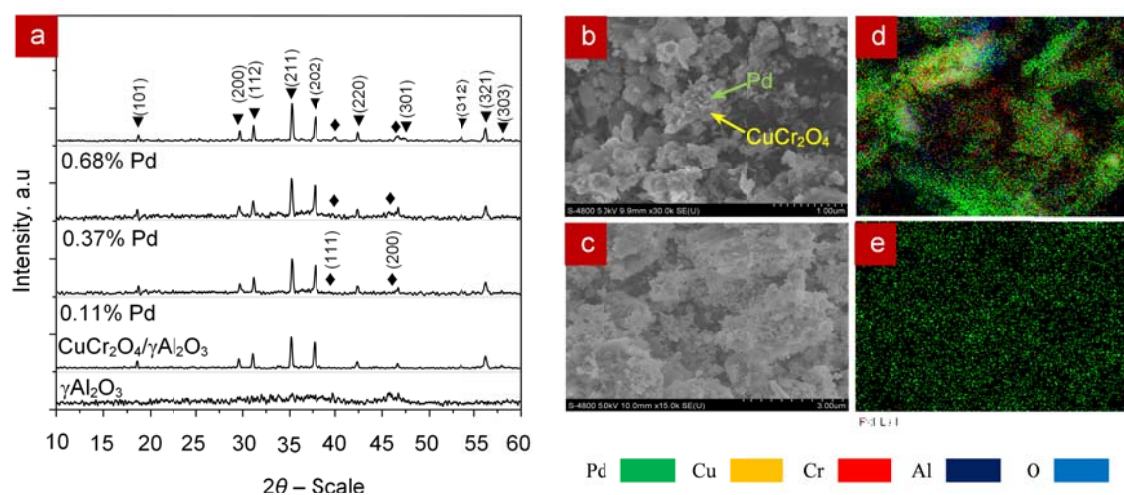


Figure 3. XRD (a) SEM images of spinel CuCr₂O₄.Pd/γ-Al₂O₃ with 0.11% (b) and 0.68% (c) Pd and SEM–EDS mapping of elements in (d) and Pd dispersion on catalysts (e).

3.1.2. Chemical composition

EDS results of catalytic chemical compositions of spinel 10% CuCr₂O₄ and (0.1 ÷ 0.7 %)

Pd on γ-Al₂O₃ support indicate that the molar ratio of Cu/Cr = 0.51 and other components are as shown in Table 1. SEM-EDS mapping of distribution of Cu, Cr, O and separately distribution Pd on catalyst surface are shown in Figure 3d, e. Pd is finely distributes on spinel surface that can be expressed by the size and position of the green points on the entire analysis surface. It also shows that Pd nanoparticles are successfully attached to the catalyst system.

Table 1. Chemical composition (wt%) of as-prepared spinel CuCr₂O₄.Pd/γ-Al₂O₃ analyzed by SMEWW Pd-3500: 2012 (ISO 5502: 2003) methods.

Catalyst	Pd calculate, %	Pd detected, %	SSA, m ² .g ⁻¹
10% CuCr ₂ O ₄ /γ-Al ₂ O ₃	0	0	55.56
0.1% Pd@ 10% CuCr ₂ O ₄ /γ-Al ₂ O ₃	0.10	0.11	56.49
0.2% Pd@ 10% CuCr ₂ O ₄ /γ-Al ₂ O ₃	0.20	0.21	63.19
0.35% Pd@ 10% CuCr ₂ O ₄ /γ-Al ₂ O ₃	0.35	0.37	116.68
0.7% Pd@ 10% CuCr ₂ O ₄ /γ-Al ₂ O ₃	0.70	0.68	117.04

3.1.3. Surface morphology and physical properties

Surface morphology structure of spinel CuCr₂O₄ is determined by FE-SEM as shown in the Figure 3 b, c reveal that the surface morphological characteristics of the catalyst systems have porous structure with the dispersion of the phase on the surface of the rod shaped polyhedron phases in clusters with small size. The difference in shape between phase and contrast on the SEM images allows conclude that Pd nanoparticles in rod-shaped dispersed on the surface of the spinel CuCr₂O₄ crystal as the result of the decomposition of Palladium (II) acetate after the impregnation and heat treatment. The specific surface area by BET method on 1000E Nova instrument of spinel 10 % CuCr₂O₄.Pd/γ-Al₂O₃ catalysts are shown in the Table 1. The increasing in the specific surface of the catalytic activity phase will significantly increase overall system activity.

3.2 Catalytic activity

The results of the catalytic activity of spinel CuCr₂O₄ for CO oxidation is shown in Figure 4b shows the starting oxidation temperature of reactions is from 90 °C. Conversion ratio is relatively slow in 90 ÷ 175 °C, but started rapidly in temperature range of 270 ÷ 180 °C indicating by a steep slope of the tangent to the CO conversion curves. CO conversion is approximately 50 % at 225 °C and about 99 % at 350 °C and maintain stable activity during treatment. Oxygen is adsorbed on the surface of spinel crystal CuCr₂O₄ according to reaction equations (3) and (4). In the presence of CO, the oxidizing reactions of CO are in accordance with the equations (5) and (6):



Reduce CO interacts with adsorbed oxygen ions at surface of spinel CuCr₂O₄ to form CO₂ and free electrons that return to the conduction band and recovery of the catalytic crystal structure according to equation (7).

3.3. Promoting effect of Pd nanoparticles on spinel CuCr_2O_4 .Pd/ $\gamma\text{-Al}_2\text{O}_3$ catalytic activity

The promoting effect of Pd nanoparticles to the activity of spinel CuCr_2O_4 .Pd in Figure 4a shows that the presence of dispersed Pd in spinel CuCr_2O_4 catalyst components enhance total activity of catalyst systems.

The experimental results above show that only about 0.11 % Pd content in spinel 10 % $\text{CuCr}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ mixed catalyst systems was able to completely converted all CO (1 % or 10000 ppm) in exhaust gas flow of 15 L.h^{-1} at temperatures from 260 °C. At the CO conversion reaches 50 % temperature has dropped nearly 30 °C (at 195 °C) or conversion ratio increases from 15 ÷ 30 % compared to individual spinel CuCr_2O_4 catalysts in the temperature from 260 ÷ 180 °C. On the surface of spinel CuCr_2O_4 , Pd particles active in a region surrounding adjacent spinel crystals [7] as shown in Figure 4a. At this zone, oxygen in the air adsorbed on the surface of Pd then diffused and transformed into forms of active ions; outside the adsorbed oxygen spillover on the surface. CO conversion ratio in this case (Figure 4b) increases with increasing Pd concentration from 0.11 ÷ 0.68 wt%.

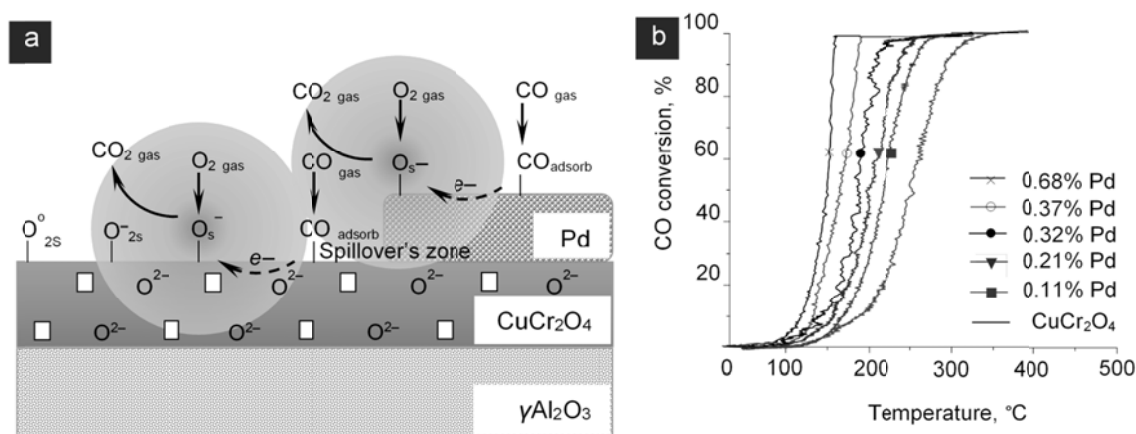


Figure 4. Promoting effect mechanism of Pd particles on catalytic activity of spinel CuCr_2O_4 .Pd/ $\gamma\text{-Al}_2\text{O}_3$ (a) and CO conversion testing results by TPSR method (b).

The Pd active sites dispersed on the surface of catalyst system will increase the overall activity of the catalyst system. In this case spinel CuCr_2O_4 crystals acted as the main active phases simultaneously served as the supporting material for Pd catalysts decorated. While surrounding region between Pd and spinel crystals CuCr_2O_4 bring superior catalytic effects of carbon monoxide oxidation. This conclusion again reinforces the basis for modeling of Pd dispersion spinel CuCr_2O_4 crystal surface which serves as the Pd promoting center that is capable to enhance activity for spinel CuCr_2O_4 .

4. CONCLUSIONS

The spinel CuCr_2O_4 .Pd/ $\gamma\text{-Al}_2\text{O}_3$ catalyst mixture was successfully synthesized by modified sol-gel and impregnation method. These catalyst systems have been able to completely converse carbon monoxide at temperatures below 200 °C for 0.11% Pd and 140 °C for 0.68 % Pd with GHSV of $1500 \text{ L.h}^{-1}.\text{g}^{-1}$. Spinel CuCr_2O_4 .Pd catalysts system have high potential and promise applications in the treatment of exhaust gases containing CO at temperatures below 140 °C.

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