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Ru/CeO_2 catalysts for combustion of mixture of light hydrocarbons: Effect of preparation method and metal salt precursors

Janina Okal*, Mirosław Zawadzki, Piotr Kraszkiewicz, Katarzyna Adamska

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław, Poland

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ABSTRACT

Two preparation methods and two metal salt precursors (chlorine containing and chlorine-free) were used to synthesize Ru/CeO_2 catalysts and their catalytic behaviour has been evaluated in combustion of propane, *n*-butane and isobutane mixture. In the first method, Ru nanoparticles (Ru NPs) deposited on CeO_2 were synthesized by a microwave-assisted polyol method using $RuCl_3$ as a metal precursor and ethylene glycol as a reducing agent. In the second, Ru/CeO_2 catalysts were prepared by traditional incipient wetness impregnation method using $RuCl_3$ or $Ru(NO)(NO_3)_3$. ICP-AES, N_2 adsorption-desorption, H_2-TPR, XRD, HRTEM and SEM-EDS techniques were used to characterize the catalysts. In all the Ru/CeO_2 catalysts only highly dispersed Ru nanoparticles (1–2 nm) were present. The catalytic data show that the preparation method and the nature of the metal precursor have a significant influence on catalytic performance of the Ru/CeO_2 catalysts. The VOC reactivity order (iso-butane > *n*-butane > propane) show that propane is the most difficult to oxidize. The Ru(NPs)/CeO_2 and impregnated Ru(N)/CeO_2 catalyst exhibited much higher activity and stability than that of impregnated Ru(Cl)/CeO_2. It was found that the Ru(NPs)/CeO_2 nano-catalyst was free of chlorine species although it had been prepared from $RuCl_3$. The differences in the activity have been ascribed to the presence of Cl^- ions on the Ru(Cl)/CeO_2 catalyst and to much better reducibility of the chlorine-free Ru(NPs) and Ru(N) catalysts. The Cl species have a negative impact on the redox properties of CeO_2, they have some influence on Ru agglomeration during long-term activity tests (50 h), and consequently, the chlorinated catalyst exhibited a poorer activity and stability compared with those of the Cl-free catalysts.

1. Introduction

Volatile organic compounds (VOCs) are recognized as major components of air pollution because of their toxicity to human health and their involvement in the formation of photochemical smog. Among the different techniques available to reduce VOCs emission, catalytic combustion appears to be one of the most efficient [1] since it can operate with dilute VOCs effluent streams and at much lower temperature (100–400 °C) than conventional thermal combustion (> 800 °C). The development of noble metals (mainly Pt, Pd, Rh and Au) and metal oxides (for example CeO_2, MnO_x, CoO_x, CrO_x, CuO) as catalysts for VOCs oxidation has been widely reported in the literature and the research field continues to be very active [2,3]. Particularly ceria has been found to be a promising catalyst in the total oxidation of VOCs, either pure or in combination with noble metals or other metal oxides [4,5]. The promoting effect of cerium oxide is mainly related to its ability to a facile shift between Ce^{4+} and Ce^{3+} states under oxidative and reductive conditions and its high oxygen storage capacity (OSC) [6,7]. Additionally, when CeO_2 is used as high surface area support for noble metals such as Pt, Pd and Au, the catalytic systems are particularly active for VOCs oxidation at low temperature, due to the increased metal dispersion and to CeO_2 participation in the reaction [3,8]. Redox properties are substantially enhanced by formation of metal-ceria contacts, although significant differences can be produced if counter-anions of the metal salt precursor are partially retained on the surface of the catalysts during its preparation [4,9]. Especially, the presence of residual chloride decreases the extent of reduction/oxidation effects modifying the OSC capacity of ceria [10,11] and affecting VOC combustion in metal-supported catalysts. Bernal et al. [12] found that in the Rh/CeO_2 catalysts prepared from chlorinated metal precursor, a highly stable cerium oxychloride at the temperature as low as 300 °C was formed, which limits the spillover of hydrogen responsible for the reduction of ceria. Kępiński and Okal [13] studied the mechanism of the CeOCl formation in the Pd/CeO_2 catalysts prepared using a chlorinated precursor, $PdCl_2$, and found that at low reduction temperature Cl^- ions remain strongly chemisorbed on ceria which cause changes in the

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* Corresponding author.
E-mail address: J.Okal@int.pan.wroc.pl (J. Okal).

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textural, structural and chemical properties of the support. Recently, Abdelouahab-Reddam et al. [14] observed a much higher catalytic activity of chlorinated $Pt/CeO_2/C$ catalysts for the complete oxidation of ethanol comparing to those of the Cl-free catalysts. This behaviour was correlated with a high platinum dispersion and a strong metal-CeO_2 interaction in these catalysts, which promotes their redox properties. The effect of CeO_2 on the combustion activity of noble metal catalysts is also largely dependent on catalysts pre-treatments and the employed reaction conditions [15,16].

Previously, we investigated the effect of chlorine and the pretreatment procedure (reduction-oxidation) on the performance of the Ru/γ-Al_2O_3 catalysts for combustion of butane [17] and propane [18]. It was found that the presence of chloride on the catalyst surface as well as oxidation of the catalysts at high temperature leads to much lower activity of the Ru phase. We suppose that ceria as a support can be a promising candidate to improve the catalytic performance and especially stability of the ruthenium phase in the total oxidation of light alkanes, not only by its well-known redox properties, but also because the properties of the metals deposited on the support can be modified by strong metal-support interaction (SMSI) [9,19]. The strong metal-support interaction prevents metal particle from sintering, which also contributes to catalyst deactivation. Aouad et al. [20] reported a strong metal-ceria interaction with ruthenium *via* the formation of Ru—O—Ce bonds in the well-dispersed Ru species which are highly fragile and its mobile oxygen is the active species in the carbon and VOCs oxidation.

At present catalytic materials based on Ru and ceria or ceria-zirconia are being thoroughly investigated for several oxidation reactions, for example oxidation of organic pollutants in waste water [6,21–23], liquid-phase oxidation of benzyl alcohols [24], simultaneous oxidation of carbon black and VOCs like propene and toluene [20,25], oxidation of ethyl acetate [26], CO oxidation [27] and, more recently, soot oxidation [27–30]. Mitsui et al. [26] compared the catalytic performance of CeO_2-supported noble metals such as Ru, Pt, Pd and Rh, in oxidation of ethyl acetate and found that the Ru-containing catalyst demonstrated the highest catalytic activity. Recently, Matarrese et al. [31] investigated ceria/zirconia catalysts doped with Pt, Au, Ru or Fe for simultaneous removal of NO_x and soot and found that the Ru-based system was more active than the reference Pt-K/Al_2O_3 catalyst in both soot combustion and NO_x storage capacity. Moreover, in the past few years, a considerable effort was focused on the studies on the catalytic combustion of chlorinated hydrocarbons (like chlorobenzene) over Ru-doped ceria catalysts [32,33]. However, it can be noted that complete catalytic oxidation of light alkanes/alkenes over Ru/CeO_2 catalysts has received relatively little attention.

Currently available studies were primarily focused on the catalytic oxidation of a single VOC pollutant, and catalytic evaluation and stability test were commonly reported. In the present study, the catalytic performance of Ru/CeO_2 catalysts for total oxidation of propane, *n*-butane and isobutane mixture was investigated for the first time with respect to the preparation methods (microwave-polyol or incipient wetness impregnation) and the nature of metal salt precursors, $RuCl_3 \times 3H_2O$ or $Ru(NO)(NO_3)_3$. Microwave-assisted synthesis of metal nanoparticles (NPs) represents a sustainable and green approach to preparation of supported nanostructured catalysts using environmentally friendly and less energy-demanding conditions, compared with those involved in conventional methods. The preparation of ceria supported Ru NPs under microwave-solvothermal conditions using ethylene glycol as a reducing agent has not been reported in the literature. This synthesis technique is very attractive as it allows obtaining a heterogeneous catalyst with well-defined metal particle morphology (shape and size). At present, the studied VOCs compounds are released to the atmosphere in increasing amounts since liquefied petroleum gas (LPG), composed of primarily propane and butane, is used even more as a substitute for gasoline and diesel in transport vehicles. These light alkanes, emitted also from stationary power sources, have much larger detrimental greenhouse effect than carbon dioxide. The nature of the used metal precursor is important because it can yield chemical and structural differences visible particularly in the catalysts prepared from a Cl-containing precursor. The presence of residual chlorine ions on the catalyst promotes stability of cerium in a low oxidation state with possible formation of cerium oxychloride and can affect the adsorption and catalytic properties of the catalyst in oxidation of light alkanes. The experiments were conducted with the use of Ru/CeO_2 catalysts of the same metal loading (5 wt.%). Structural studies were also performed to correlate the intrinsic properties of the catalyst materials to their catalytic performance.

2. Experimental

2.1. Preparation of the Ru/CeO_2 catalysts

$RuCl_3 \times 3H_2O$ (Alfa-Aesar) and $Ru(NO)(NO_3)_3$ (Sigma-Aldrich) were used as metal salt precursors. A commercial CeO_2 oxide (Aldrich, nanopowder, 544,841) was calcined in static air at 600 °C for 3 h prior to use for catalysts preparation.

Ruthenium deposition (5 wt.%) on the ceria support was carried out by two different preparation methods. The first one − the polyol reduction method − involved *in situ* deposition of Ru nanoparticles (NPs), i.e., reduction of $RuCl_3$ with ethylene glycol (EG) in the presence of the ceria support. First, 0.27 g $RuCl_3$ was dissolved in 50 ml of ethylene glycol and then 2 g of CeO_2 was added to form a suspension. The mixture was magnetically stirred for 15 min at room temperature (RT) and next put in a Teflon vessel placed in an autoclave with microwave heating (MW Reactor, Ertec, Poland). The synthesis time was set up to 20 min and reaction proceeded at 180 °C under autogenic pressure of ~20 atm. After the reaction was completed the vessel was rapidly cooled down in an ice-water bath. A grey solid was filtered off, washed several times using aq. (0.3 M) $NaNO_3$ solution, next with distilled water to remove the chlorine and sodium ions and finally dried under vacuum at room temperature (RT). The sample was stored in a closed container until using it and it was designated as Ru(NPs)/CeO_2. We also studied the reactivity of the bare CeO_2 support in EG under the same conditions as the ones used for preparation of the Ru(NPs)/CeO_2 nanocatalyst.

In the second method, Ru/CeO_2 catalysts were prepared by incipient wetness impregnation technique using an aqueous solution of $RuCl_3$·or $Ru(NO)(NO_3)_3$ as a metal precursor. After impregnation, the samples were stirred for 4 h at room temperature, next dried overnight at 110 °C and finally activated by reduction under hydrogen flow (30 cm^3/min) at 400 °C for 5 h (3 °C/min). After reduction, the catalyst samples were cooled to RT in H_2 flow and then were slowly exposed to air. The samples prepared by this method were designated as Ru(Cl)/CeO_2 and Ru(N)/CeO_2, respectively. Since some catalysts were obtained from Ru chloride we also prepared a Cl/CeO_2 sample by impregnation of ceria with sufficient amount of HCl aq. solution to yield a similar content of chlorine (5.5 wt.%) as in the Ru(Cl)/CeO_2 catalyst. Next, after drying the Cl/CeO_2 sample at 110 °C, it was treated in H_2 flow at 400 °C for 5 h.

2.2. Catalysts characterization

The ruthenium content in the catalysts was determined by ICP-AES method (Thermo Scientific ICAP 7000). Chemical composition of the samples was checked with a FEI NovaNanoSEM 230 FE-SEM microscope equipped with EDS (EDAX Genesis XM4). The crystalline structure of the catalysts was analysed by X-ray powder diffraction (XRD) using PANanalytical X'Pert PRO diffractometer with CuKα radiation (λ = 0.15406 nm). The data were recorded in the 10 − 80° 2Θ range with an angular step of 0.017° and a counting time of 0.26 s per step. Diffraction peaks of crystalline phases were compared with those of standard compounds reported in the JCPDS Data File. Microstructure characterization and dispersion measurements of the catalyst samples