



Light alkane oxidation over Ru supported on ZnAl_2O_4 , CeO_2 and Al_2O_3

Janina Okal*, Mirosław Zawadzki, Ludwina Krajczyk

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

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ABSTRACT

Zinc aluminate, alumina and ceria supported ruthenium catalysts were tested in the total oxidation of propane, *n*-butane and iso-butane. Structure of the catalysts was characterized by means of XRD, TEM, BET and H_2 chemisorption techniques. The Ru dispersion changes from 0.67 for 5% Ru/ CeO_2 , 0.56 for 4.5% Ru/ ZnAl_2O_4 and to 0.28 for 4.7% Ru/ γ - Al_2O_3 catalyst. TEM and XRD results confirmed high dispersion of the samples. All oxidation reactions occur at much lower temperatures over Ru/ CeO_2 compared to those over Ru/ γ - Al_2O_3 and Ru/ ZnAl_2O_4 . Also, the site-time yields of all catalysed oxidation reactions follows the order Ru/ CeO_2 > Ru/ γ - Al_2O_3 > Ru/ ZnAl_2O_4 . Activity results cannot be explained by the differences in the Ru dispersion. The redox species of ruthenium on CeO_2 oxide, easily reacted with the lattice oxygen of CeO_2 , are responsible for the enhanced activity of the Ru/ CeO_2 catalyst in the VOCs oxidation.

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1. Introduction

Deep catalytic oxidation of volatile organic compounds (VOCs) is frequently used method to remove VOCs from industrial waste gases. Catalytic oxidation of light alkanes, alkenes and aromatics were widely investigated over metal catalysts such as platinum, palladium and rhodium [1,2] and numerous studies have shown that short-chain hydrocarbons are amongst the most difficult to destroy [3,4]. It is well known that both the metal and the support play a essential role in the combustion reaction [5]. For this reason, a number of recent studies have focused on new combustion catalysts based on noble metals, including Pt, Pd and Au, supported on different metal oxides or mixed oxide supports [6,7]. Supported ruthenium catalysts have received also much interest over the past years, because of their high combustion activity at low temperatures [8–13]. The combustion activity for the oxidation of ethyl acetate, acetaldehyde, and toluene was investigated over Ru-based catalysts deposited on supports such as γ - Al_2O_3 , CeO_2 , ZrO_2 and SnO_2 [10,11]. Recently, reactivity of Ru supported on CeO_2 and Al_2O_3 in the oxidation of propene, toluene and carbon black was studied by Aouad et al. [9,13]. In our recent studies, the performance of Ru/ γ - Al_2O_3 catalysts (from RuCl_3 precursor) for the oxidation of *n*-butane/iso-butane mixture [14] and propane [15] has been investigated. Generally, amongst the supports examined in bibliography, the CeO_2 and TiO_2 materials are two of the most promising candidates for combustion of light alkanes much likely due to their

good redox properties and their crucial role as a source of oxygen. Ceria also promotes stabilization of precious metals and prevents sintering of particles [16].

In this work the structure and activity of ruthenium catalysts supported on ZnAl_2O_4 and CeO_2 is compared to that supported on γ - Al_2O_3 material. Zinc aluminate, with spinel structure and high surface area, was never used as support for ruthenium catalysts. Recently, spinel materials, like ZnAl_2O_4 , have gained considerable interest since they may be used as supports for noble metals to substitute more traditional materials, such as γ -alumina [17–19]. The effect of support on the structural and surface catalyst properties were determined by N_2 adsorption, H_2 chemisorption, X-ray diffraction (XRD) and transmission electron microscopy (TEM) methods and related to the activity results in the oxidation of mixture of propane, *n*-butane and iso-butane. To the best of our knowledge, oxidation of light alkanes over Ru/ CeO_2 and Ru/ ZnAl_2O_4 catalysts has not been studied yet.

2. Experimental

The ZnAl_2O_4 support was prepared by the unconventional coprecipitation method using aqueous solutions of $\text{Zn}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$, with molar ratio Al:Zn = 2:1. The precipitate was filtered off, washed with water, then air-dried and finally calcined at 550 °C for 3 h. Such prepared nanocrystalline ZnAl_2O_4 support had a BET surface area of 205 m^2/g and pore volume of 0.38 cm^3/g . CeO_2 oxide (Aldrich) was calcined at 600 °C for 3 h before catalyst preparation. The γ - Al_2O_3 support was used as previously in Refs. [14,15]. The catalysts with ruthenium loading of about 5 wt.%, were prepared by the incipient wetness impregnation method using $\text{Ru}(\text{NO})(\text{NO}_3)_3$

* Corresponding author. Tel.: +48 71 34 350 20; fax: +48 71 34 410 29.
E-mail address: J.Okal@int.pan.wroc.pl (J. Okal).

Table 1
Main physicochemical characteristics of the supported Ru catalysts and catalytic activity data expressed as $T_{50\%}$ ($^{\circ}\text{C}$).

Sample	S_{BET} (m^2/g)	Dispersion ($\text{H}_{\text{irr}}/\text{Ru}_{\text{total}}$)	$d_{\text{av}}(\text{TEM})$ (nm)	$T_{50\%}$ ($^{\circ}\text{C}$) ^b		
				Iso-butane	<i>n</i> -Butane	Propane
ZnAl ₂ O ₄	205.0	–	–	550	555	570
4.5%Ru/ZnAl ₂ O ₄	198.0	0.56	1.7	180	188	196
γ -Al ₂ O ₃	245.9	–	–	473	485	512
4.7%Ru/ γ -Al ₂ O ₃	215.3	0.28	2.6	168	174	178
CeO ₂	108.0	–	–	453	474	490
5.0%Ru/CeO ₂	82.9	0.67 ^a	1.5	150	153	158

^a The dispersion calculated on the basis of TEM studies.

^b Temperatures required for 50% conversion of a given hydrocarbon.

as a metal precursor. The impregnated materials were air-dried at 120 $^{\circ}\text{C}$ for 20 h and finally reduced in hydrogen flow at 500 or 400 $^{\circ}\text{C}$ for 5 h.

The Ru content in the catalysts was estimated by ICP-AES method. The morphology of the samples was investigated by TEM method with Philips CM 20 Super-Twin microscope operated at 200 kV. XRD patterns were obtained employing a DRON-3 diffractometer using Ni-filtered Cu K α radiation. The dispersion of the Ru catalysts was determined by the volumetric hydrogen chemisorption method at 100 $^{\circ}\text{C}$ using glass apparatus employed earlier [14,15]. The same apparatus was used to perform N₂ adsorption measurements. Catalytic tests were performed at atmospheric pressure in a fixed-bed flow reactor using 400 mg of Ru catalyst. A gaseous mixture of hydrocarbons/air, with the volumetric ratio of 1:500, was maintained with a flow rate of 15 l/h (gas hourly space velocity (GHSV) = 21,000 h⁻¹) [14,15]. Reaction products were analysed by gas chromatography.

3. Results and discussion

3.1. Characterization of the supported Ru catalysts

BET surface area of the catalysts and the ruthenium dispersions are given in Table 1. All catalysts possess the BET surface area somewhat lower than that of bare supports. Chemisorption results show that kind of the support have a significant influence on the metal dispersion and ruthenium deposited on the ZnAl₂O₄ material possesses much higher dispersion than on γ -Al₂O₃. Fig. 1 shows the XRD patterns of the 4.5% Ru/ZnAl₂O₄, 4.7% Ru/ γ -Al₂O₃ and 5% Ru/CeO₂ catalysts. The patterns contain only reflections consisted with those of ZnAl₂O₄ (at 2θ of 31.2, 36.8, 44.8, 49.1, 55.6, 59.3 and 65.2 $^{\circ}$), γ -Al₂O₃ (at 2θ of 38, 45 and 67 $^{\circ}$) and CeO₂ (at 2θ 28.6, 33.1, 47.5 and 56.5 $^{\circ}$), indicating that the size of the Ru crystallites was too small to be detected. A typical TEM micrographs and

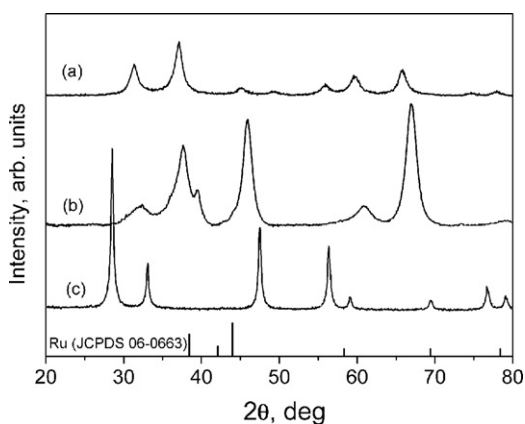


Fig. 1. X-ray diffraction patterns of the Ru/ZnAl₂O₄ (a), Ru/ γ -Al₂O₃ (b), and Ru/CeO₂ catalysts (c).

SAED patterns (insets) for all catalysts are shown in Fig. 2. For the Ru/ZnAl₂O₄ and Ru/CeO₂ catalysts, metal particles could be identify only by HRTEM images (Fig. 2a and c, respectively) and the fast Fourier transform (FFT) pattern (inset in Fig. 2a). These results indicate on good dispersion of Ru particles evidenced also by XRD and H₂ chemisorption experiments (Table 1). Only in the SAED pattern of the Ru/ γ -Al₂O₃ catalyst (inset in Fig. 2b) weak diffraction spots from the Ru metal phase are present. The mean particle size of 1.7 and 1.5 nm was obtained for the Ru/ZnAl₂O₄ and Ru/CeO₂ catalyst, respectively, while for the Ru/Al₂O₃ catalyst much broader distribution of particle sizes was observed (1–9 nm) with mean size of 2.6 nm.

3.2. Catalytic activity

Fig. 3 shows the propane, *n*-butane and iso-butane conversions over Ru/ZnAl₂O₄, Ru/ γ -Al₂O₃ and Ru/CeO₂ catalysts as a function of the reaction temperature. The only detectable products are carbon dioxide and water, indicating that C₃–C₄ hydrocarbons were completely oxidized during the progress of the reaction. Independent of the catalyst used, the activity with respect to the VOC molecule was observed to follow the sequence: iso-butane > *n*-butane > propane, indicating that propane is less combustible. This result agrees with the data of other authors according to which the alkane oxidation rate on platinum rises with increasing the hydrocarbon chain length [4,20], and is consistent with the concept that alkane oxidation is limited by the initial H abstraction, because the easy of breaking the C–H bond increases in the same order. Fig. 3 shows also that at a given reaction temperature, the CeO₂ supported Ru catalyst exhibits higher C₃–C₄ conversions than the γ -Al₂O₃ or ZnAl₂O₄ supported Ru catalysts. The evolution of the catalytic activity as a function of the time on stream, at constant temperature was also measured for all samples (results not shown). It was found that irrespective of Ru catalysts, conversion of light alkanes has not changed after 8 h time on line indicating on high stability of all catalysts under used reaction conditions.

To compare the oxidation activity, we measured from light-off curves the value of the temperature for conversion of 50%. The obtained $T_{50\%}$ values for the Ru catalysts are given in Table 1. For comparative purposes, $T_{50\%}$ values for the supports are also included. Catalytic effect of ruthenium phase on oxidation activity is clearly seen. Moreover, $T_{50\%}$ values greatly depend on the nature of the support used, as well as kind of VOC oxidation. For

Table 2
Specific catalytic activity of the supported Ru catalysts.

Catalyst	d (nm)	Site-time yield (h ⁻¹)		
		Iso-butane	<i>n</i> -Butane	Propane
5.0%Ru/CeO ₂		7.48	6.67	5.35
4.7%Ru/ γ -Al ₂ O ₃	2.6	7.26	4.11	2.84
4.5%Ru/ZnAl ₂ O ₄	1.7	2.16	0.95	0.54

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