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

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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.

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 co-precipitation method using aqueous solutions of $Zn(NO_3)_2$ and $Al(NO_3)_3$, 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 $Ru(NO)(NO_3)_3$

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

Sample	S_{BET}	Dispersion	d_{av}(TEM)	$T_{50\%}$ (°C)[b]		
	(m^2/g)	(H_{irr}/Ru_{tatal})	(nm)	Iso-butane	*n*-Butane	Propane
$ZnAl_2O_4$	205.0	–	–	550	555	570
4.5%Ru/$ZnAl_2O_4$	198.0	0.56	1.7	180	188	196
γ-Al_2O_3	245.9	–	–	473	485	512
4.7%Ru/γ-Al_2O_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 °C for 20 h and finally reduced in hydrogen flow at 500 or 400 °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-filltered Cu Kα radiation. The dispersion of the Ru catalysts was determined by the volumetric hydrogen chemisorption method at 100 °C using glass apparatus employed earlier [14,15]. The same apparatus was used to perform N_2 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 $ZnAl_2O_4$ material possesses much higher dispersion than on γ-Al_2O_3. Fig. 1 shows the XRD patterns of the 4.5% Ru/$ZnAl_2O_4$, 4.7% Ru/γ-Al_2O_3 and 5% Ru/CeO_2 catalysts. The patterns contain only reflections consisted with those of $ZnAl_2O_4$ (at 2Θ of 31.2, 36.8, 44.8, 49.1, 55.6, 59,3 and 65.2°), γ-Al_2O_3 (at 2Θ of 38, 45 and 67°) and CeO_2 (at 2Θ 28.6, 33.1, 47.5 and 56.5°), indicating that the size of the Ru crystallites was too small to be detected. A typical TEM micrographs and SAED patterns (insets) for all catalysts are shown in Fig. 2. For the Ru/$ZnAl_2O_4$ and Ru/CeO_2 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 H_2 chemisorption experiments (Table 1). Only in the SAED pattern of the Ru/γ-Al_2O_3 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/$ZnAl_2O_4$ and Ru/CeO_2 catalyst, respectively, while for the Ru/Al_2O_3 catalyst much broader distribution of particle sizes was observed (1–9 nm) with mean size of 2.6 nm.

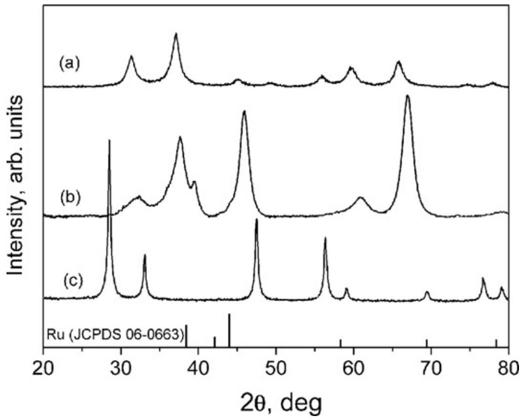

Fig. 1. X-ray diffraction patterns of the Ru/$ZnAl_2O_4$ (a), Ru/γ-Al_2O_3 (b), and Ru/CeO_2 catalysts (c).

3.2. Catalytic activity

Fig. 3 shows the propane, *n*-butane and iso-butane conversions over Ru/$ZnAl_2O_4$, Ru/γ-Al_2O_3 and Ru/CeO_2 catalysts as a function of the reaction temperature. The only detectable products are carbon dioxide and water, indicating that C_3–C_4 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 CeO_2 supported Ru catalyst exhibits higher C_3–C_4 conversions than the γ-Al_2O_3 or $ZnAl_2O_4$ 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	*n*-Butane	Propane
5.0%Ru/CeO_2		7.48	6.67	5.35
4.7%Ru/γ-Al_2O_3	2.6	7.26	4.11	2.84
4.5%Ru/$ZnAl_2O_4$	1.7	2.16	0.95	0.54

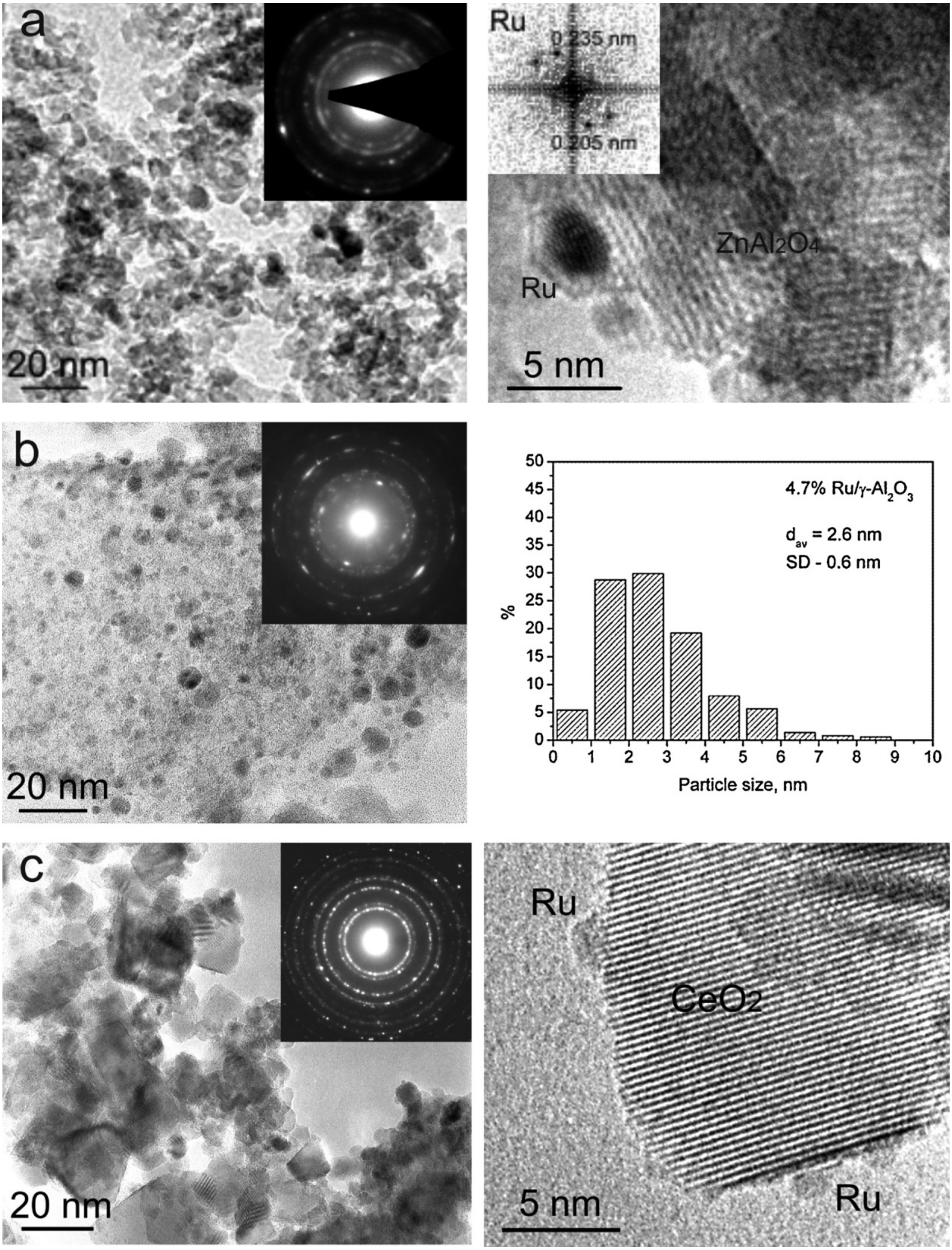

Fig. 2. TEM micrograph with SAED pattern (inset) of the Ru/$ZnAl_2O_4$ (a), Ru/γ-Al_2O_3 (b), and Ru/CeO_2 catalysts (c). Corresponding HRTEM images are shown in (a) and (c) (right side). FFT pattern obtained from one Ru particle is shown as inset to (a), and particle size distribution as inset to (b) (right side).

example, $T_{50\%}$ for oxidation of propane increased from 158 °C to 178 °C and to 196 °C for the Ru/CeO_2, Ru/γ-Al_2O_3 and Ru/$ZnAl_2O_4$ catalyst, respectively. However, according to Table 1, the Ru catalyst samples display different metal dispersion, thus the effect of support cannot be claimed by comparison of $T_{50\%}$ values because the number of Ru sites accessible to the reaction, is not the same for all catalysts. Since in the present work no detailed kinetic studies have been performed, to facilitate the qualitative interpretation of the catalytic data, we estimate a catalytic rate as a site-time yield (STY), i.e., a rate referring to the number of catalytic sites

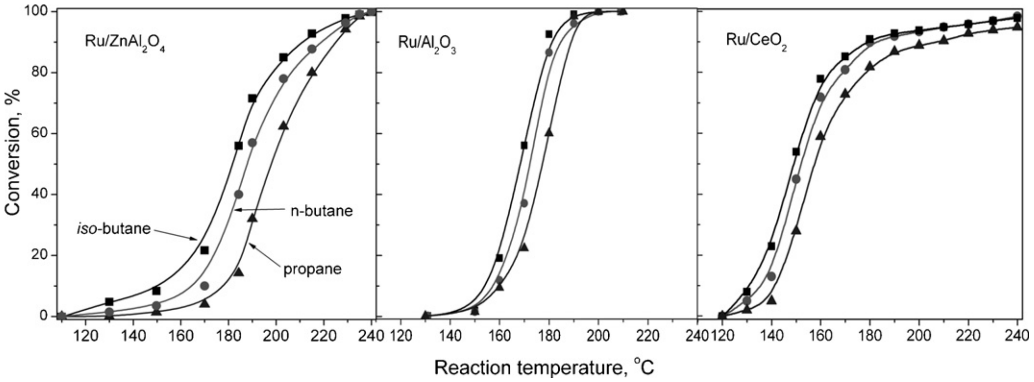

Fig. 3. Conversion of iso-butane (■), *n*-butane (●), and propane (▲) over supported Ru catalysts as a function of the reaction temperature.

[21]. At a given temperature, the site-time yield (in h^{-1}) was calculated by dividing the number of moles C_3–C_4 reacted by hour per the number of moles actives sites in the reactor determined by H_2 chemisorption measurements. The site-time yield values for oxidation of all hydrocarbons, at reaction temperature of 160 °C, are reported in Table 2. As can be seen the most active catalyst is Ru/CeO_2, while Ru/$ZnAl_2O_4$ system remains the less active for all the oxidation reactions. Thus, STY values decreased following the same catalyst trend as estimated from light-off curves in Fig. 3. Additionally, differences in the site-time yield values depend on the kind of VOC oxidation. As shown in Table 2, in the case of oxidation of iso-butane, the support effect is much smaller than for the oxidation of propane. In the oxidation of propane, the Ru/CeO_2 catalyst is five times more reactive than the Ru/Al_2O_3 catalyst and about ten times as compared to the Ru/$ZnAl_2O_4$ catalyst. As the particle size of Ru for the latter catalyst (1.7 nm) is nearly the same as for the former catalyst (1.5 nm) it is clear that this cannot be the only parameter influencing the activity. In accord with literature data [9,10,13], the redox species of ruthenium on CeO_2 oxide, easily reacted with the lattice oxygen of CeO_2, should be responsible for the higher activity in the C_3–C_4 alkane oxidation. Moreover, as the oxidation reaction occurs at a higher temperature (as in the case of oxidation of propane), the superiority of CeO_2 over the two other supports is better visible, which may result from the fact that ceria generally serves as a reservoir for oxygen in the oxidation reaction. For the Ru/γ-Al_2O_3 and Ru/$ZnAl_2O_4$ catalysts, the differences in the site-time yields could be explained by the different the acidity of the supports and/or by the differences in the size of metal particles. In line with literature data [5], the catalyst on the more acidic support, like γ-Al_2O_3, shows higher activity in the VOC oxidation (see Table 2). It can be noted that complete oxidation of iso-butane, *n*-butane and propane was observed for the Ru/CeO_2 and Ru/$ZnAl_2O_4$ catalyst at similar temperature of 240 °C, while for the Ru/γ-Al_2O_3 catalyst already at 200–210 °C (Fig. 3). We found previously [14,15] that under O_2-rich reaction conditions at temperature below 250 °C, the small Ru_xO_y clusters without well-defined stoichiometry, are catalytically active phase responsible for the high activity of Ru/Al_2O_3 catalysts. In this study, the post reaction characterization by XRD shows no diffraction peaks due to ruthenium oxide for the Ru/CeO_2 and Ru/$ZnAl_2O_4$ samples, indicating on high stability of the well-dispersed ruthenium species. However, for the used Ru/Al_2O_3 catalyst, RuO_2 phase was observed suggesting some aggregation of the ruthenium species under the reaction conditions. These results may indicate that partly oxidized Ru species are more stable on the surface of ceria and zinc aluminate than on the alumina surface.

4. Conclusions

These preliminary catalytic data show that all synthesized Ru catalysts are active in the low temperature alkane oxidation. A remarkable effect of the support was observed, and when CeO_2 was used catalytic activity was improved.

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