Electronic state of ruthenium deposited onto oxide supports: An XPS study taking into account the final state effects

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ABSTRACT

The electronic state of ruthenium in the supported Ru/EO$_x$ (EO$_x$ = MgO, Al$_2$O$_3$ or SiO$_2$) catalysts prepared by with the use of Ru(OH)Cl$_3$ or Ru(acac)$_3$ (acac = acetylacetonate) and reduced with H$_2$ at 723 K is characterized by X-ray photoelectron spectroscopy (XPS) in the Ru 3d, Cl 2p and O 1s regions. The influence of the final state effects (the differential charging and variation of the relaxation energy) on the binding energy (BE) of Ru 3d$_{5/2}$ core level measured for supported Ru nanoparticles is estimated by comparison of the Fermi levels and the modified Auger parameters determined for the Ru/EO$_x$ samples with the corresponding characteristics of the bulk Ru metal. It is found that the negative shift of the Ru 3d$_{5/2}$ peak which is observed in the spectrum of ruthenium deposited onto MgO (BE = 279.5–279.7 eV) with respect to that of Ru black (BE = 280.2 eV) or ruthenium supported on γ-Al$_2$O$_3$ and SiO$_2$ (BE = 280.4 eV) is caused not by the transfer of electron density from basic sites of MgO, as considered earlier, but by the differential charging of the supported Ru particles compared with the support surface. Correction for the differential charging value reveals that the initial state energies of ruthenium in the Ru/EO$_x$ systems are almost identical (BE = 280.5 ± 0.1 eV) irrespectively of acid–base properties of the support, the mean size of supported Ru crystallites (within the range of 2–10 nm) and the surface Cl content. The results obtained suggest that the difference in ammonia synthesis activity between the Ru catalysts supported on MgO and on the acidic supports is accounted for by not different electronic state of ruthenium on the surface of these oxides but by some other reasons.

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1. Introduction

Supported catalysts containing metallic ruthenium are utilized for many reactions including the Fischer–Tropsch synthesis [1,2] and synthesis of ammonia [3–6]. The electronic state of ruthenium is among important factors affecting the catalytic activity and selectivity; it can be modified through the metal-support interaction. Thereby catalytic properties of the supported ruthenium may depend on donor/acceptor properties of the support surface. As an example, the correlation between the chemical nature of the oxide support (EO$_x$) and the activity of supported Ru catalysts for ammonia synthesis is often mentioned: the stronger the support basicity, the higher the catalyst activity [7–11]. Indeed, the catalysts prepared by depositing ruthenium on MgO or CaO show considerable activity to ammonia synthesis even at 573–673 K and under the pressure of a N$_2$/H$_2$ mixture close to ambient. The substitution of

acidic oxides (Al$_2$O$_3$ and, in particular, SiO$_2$) for MgO leads to a sharp decrease in the catalytic activity of the supported ruthenium.

X-ray photoelectron spectroscopy was used to characterize the electronic state of ruthenium on the acidic and basic supports in order to identify the reason for the observed differences in catalytic behavior of Ru/EO$_x$ systems [7,8,12–17]. The experimentally determined binding energy (BE) of the Ru 3d$_{5/2}$ core level was ranged between 279.5 and 280.0 eV for ruthenium supported on MgO or CaO [7,8,12], but between 280.2 and 280.6 eV for ruthenium supported on Al$_2$O$_3$ or SiO$_2$ [13–17]. For comparison, the reported BE(Ru 3d$_{5/2}$) values for bulk Ru metal vary from 279.9 to 280.2 eV depending on the instrument calibration [18]. The fact that the BE(Ru 3d$_{5/2}$) values are lower for the Ru/MgO and Ru/CaO catalysts than for bulk Ru metal gave Aika et al. an impetus to explain the promoting effect of basic supports on the activity of ruthenium catalysts for ammonia synthesis by their ability to donate electrons to surface Ru atoms [7,19,20]. The shift of the Ru 3d core level spectrum of supported ruthenium towards lower BEs with respect to that of the bulk metal indicates the excess electron density, which can be transferred from the d orbitals of Ru atoms to the antibonding orbitals of N$_2$ molecules upon their adsorption on the surface of Ru crystallites. This transfer weakens the N–N bonds

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and therefore facilitates the dissociation of dinitrogen, which is the rate-determining step of ammonia synthesis.

The said hypothesis was accepted by other researchers (see, e.g., Refs [21,22]), but the mechanism of the electron density transfer from basic sites of the support to supported Ru particles still remains unclear. Examination of Ru/EO$_x$ catalysts with alternative research techniques such as infrared spectroscopy of adsorbed CO did not reveal any dependence of the electronic state of supported ruthenium on acid-base properties of the support surface [23]. Eventually, it should be kept in mind that the negative shift of the core level spectra from supported metal particles compared to the bulk metal can reflect not only the presence of a negative charge on metal particles due to their interaction with the support, but may also be caused by the so-called *final state effects* appearing as a result of photoelectron emission [24,25]. Among these are *the relaxation effect* representing a change in the relaxation energy due to reorganization of electrons of the solid that provides the screening of the photoelectron holes remaining after electron emission, and *the differential charging effect*, i.e., appearance of a potential difference between the surface of supported metal particles and the support surface. The latter phenomenon originates from that the supported metallic nanocrystallites due to their internal conductivity can provide easier compensation of the surface positive charge accumulated as a result of photoelectron emission than the dielectric support. Neither relaxation nor differential charging effects in the heterogeneous systems like low-loaded supported metal catalysts can be eliminated using the internal reference method, since the positions of XPS peaks in their spectra are usually referenced to the selected peak of an element contained in the dielectric support.

Our earlier studies [26,27] revealed that namely the differential charging effect is responsible for variations of the binding energy of Ag 3d$_{5/2}$ core level measured for supported silver in the Ag/α-Al$_2$O$_3$ catalysts for ethylene epoxidation. Later, it has been assumed [28,29] that differential charging may also account for shifting the Ru 3d core level spectrum of the catalyst prepared by reduction of deposited ruthenium chloride on the MgO surface with respect to the spectrum of the bulk metal. The present paper reports the results of comparative XPS study on the chemical state of ruthenium deposited on oxides with different acid–base properties (MgO, γ-Al$_2$O$_3$, and SiO$_2$). The samples under study were prepared using various Ru precursors (ruthenium hydroxychloride, Ru(OH)Cl$_3$, or ruthenium(III) acetylacetonate, Ru(acac)$_3$) and differed by the mean size of the metal particles, as was confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis. When inspecting the XPS data obtained, we took into consideration a probable influence of the final state effects such as differential charging of the metallic Ru crystallites supported on a dielectric support and the relaxation effect on observed BE values. It was revealed that differential charging is considerable if the metallic ruthenium is supported on MgO but negligible when γ-Al$_2$O$_3$ and SiO$_2$ are used as the supports. Taking this into account, we found that the energies of the initial state of supported Ru on all the examined supports are approximately identical that differs from previous conclusions.

2. Experimental

2.1. Materials

"Ruthenium hydroxychloride" (Ru(OH)Cl$_3$, 44.8 wt% Ru), aqueous formaldehyde (40 wt%) and acetone were of analytical grade and used as received without further purification. Ruthenium(III) acetylacetonate, Ru(acac)$_3$ was synthesized as described elsewhere [30].

Table 1
Textural properties of supports.

Support	S (m^2/g)	V_{pore} (cm^3/g)	R_{pore} (nm)[a]
MgO	228	0.80	4 and 20–30
γ-Al$_2$O$_3$	220	0.50	7.5
SiO$_2$	160	0.95	30

As determined by N$_2$ adsorption at 77 K using a Micromeritics ASAP-2400 instrument (before measuring, all samples were heated in vacuum at 423 K for 4 h).
  [a] Corresponding to the maxima of the pore-size distribution.

Magnesia prepared in G.K. Boreskov Institute of Catalysis by precipitation from an aqueous solution of Mg(NO$_3$)$_2$, γ-alumina supplied by Ryazan Oil Refinery Company (Russia) and Silochrom-2 silica purchased from Siberian Catalyst Co. (Novosibirsk) were used as the supports in the form of 0.2–0.5 mm granules. Textural properties of the supports are given in Table 1. Prior the impregnation with Ru compound, MgO and γ-Al$_2$O$_3$ were evacuated at 523 K for 3 h, while SiO$_2$ was calcined in air at the same temperature for 3 h.

2.2. Sample preparation and characterization

Ruthenium deposition was carried out by incipient-wetness impregnation of the support with an acetone solution of Ru(OH)Cl$_3$ or Ru(acac)$_3$, followed by drying in an airflow at room temperature. Then the samples were evacuated at 293 K for 2 h and at 323 K for another 2 h. Due to the low solubility of Ru(OH)Cl$_3$ and Ru(acac)$_3$ in acetone, the impregnation procedure was twice repeated. After the last portion of a Ru precursor was deposited, the samples were evacuated at 323 K for 6 h, heated in flowing hydrogen to 723 K for 2.5 h and reduced under these conditions for another 6 h. After reduction, they were cooled in a H$_2$ flow to room temperature, transferred from the reactor to a glass ampoule without atmospheric exposure and stored in the ampoule filled with argon. As a reference sample, ruthenium black was synthesized by reaction of Ru(OH)Cl$_3$ with alkaline formaldehyde solution at 353 K, washed with distilled water, dried and reduced again by heating in flowing hydrogen at 623 K for 5 h [31].

The Ru content of the Ru/EO$_x$ samples was measured using X-ray fluorescence technique on a VRA-30 instrument equipped with a W-anode. TEM (JEOL JEM-2010 microscope with a lattice resolution of 0.14 nm operating at 200 kV) and XRD (HZG-4 diffractometer with Cu K$_\alpha$ radiation and a graphite monochromator) analyses were performed to determine the size of Ru crystallites. Diffractograms were collected at a scanning rate of 0.60 K/min with a 0.05° step size in the 2θ range between 30° and 90°. Prior to XRD analysis, a sample was quickly ground in air and wrapped in an organic polymer film to prevent it partly from contacting air during the XRD pattern acquiring.

2.3. Catalytic tests

The catalytic activity of the Ru/EO$_x$ samples for ammonia synthesis was tested under continuous flow conditions at 300–400 °C under 101 kPa using a stoichiometric (1:3) N$_2$/H$_2$ mixture at the flow rate of 170 mL/min. The reaction feed was deoxidized (to the level <0.1 ppm O$_2$) and dried (<0.5 ppm H$_2$O) by passing successively through the columns filled with active alumina, a reduced Ni-Cr catalyst and molecular sieves NaA and NaX. A catalyst sample (2.0–2.4 g) was transferred to a glass plug-flow reactor under synthesis gas (1:3 N$_2$/H$_2$) atmosphere (without contact with air) and heated to 300 °C. As soon as the outlet NH$_3$ concentration ceased to change noticeably with time (pseudo-stationary state), the reaction temperature was risen by 50 °C, and the reaction again was carried out until reaching the pseudo-stationary state of the catalyst at the