XPS Study of Metal-Support Interaction in Ru/MgO Catalyst for Low-Temperature Ammonia Synthesis

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Abstract

The catalytic system Ru/MgO has been characterized by TEM and XPS in the Ru 3*d*, Cl 2*p* and O1*s* regions. It was shown, that the treatment of the sample with H_2 at 450 °C leads to reduction of supported Ru (III, IV) chloride complexes to Ru metal crystallites of 2–5 nm in size (the surface atomic ratio Ru : Cl of reduced sample is 6.2). The shift of Ru 3*d* peak (279.5 eV) to lower bond energy (BE) found for Ru/MgO sample as compared with bulk Ru metal (280.2 eV) is proved to be due to the differential charging effect. The value of this effect was estimated by a comparison of the valence band spectrum of supported Ru particles with that of bulk Ru. Taking the differential charging into account, the "true" value BE of Ru $3d_{5/2}$ (280.5 eV) was determined. The shift of Ru 3*d* peak towards the higher BE values may indicate the electron-withdrawing effect of MgO surface to supported Ru particles.

INTRODUCTION

Metallic ruthenium catalysts has proved to permit milder operating conditions in ammonia synthesis compared with the magnetite-based systems, such as low synthesis temperatures and pressure (70–105 bars *vs.* 150–300 bars), while maintaining higher conversion than a conventional $Fe-K_2O-Al_2O_3$ catalyst [1]. The activity of Ru/*support* catalysts in ammonia synthesis strongly depends on the support nature and increases in the following order: *support* = carbon $< TiO_2 < Nb_2O_5 << Al_2O_3 <<$ MgO [2]. It has been suggested [3] that dissociative chemisorption of N_2 on Ru metal, which is the rate-determining step of ammonia synthesis, is promoted by electron donation from basic MgO surface to Ru particles. However, the experimental data, which have been published yet [4], look insufficient for making the strong conclusions on the type of electronic effect of MgO to supported Ru particles. Here we report the data of further characterization of Ru/MgO system by XPS and high-resolution transmission electron microscopy (HRTEM) techniques.

EXPERIMENTAL

Magnesium oxide (prepared in BIC; surface area, 135 m^2/g; fraction 0.25–0.50 mm) calcined in a dry airflow at 450 °C and stored under Ar was used as a support. The weighted amount of MgO was incipient wetness impregnated with an acetone solution of $Ru(OH)Cl_3$ at room temperature (RT) for 10–15 min. The sample was dried by blowing air at RT, than by outgassing at RT for 2 h and at 60 °C and 0.02 Torr for 6 h. To attain the desirable content of Ru in the sample the impregnation run was repeated 3 times due to low solubility of Ru complex in acetone. The reduction of $Ru(OH)Cl_3/MgO$ precursor was carried out in a tube fixed-bed glass reactor in flowing H_2 (80 ml/min) by heating the sample up to 450 °C during 2 h and keeping at this temperature in a H_2 flow for another 6 h. The reduced Ru/MgO sample was cooled to RT, unloaded in an argon flow and stored in sealed glass ampoules under Ar or *in vacuo*. The resulting sample contains 4.2 % mass of Ru, as determined by X-ray fluorescence spectroscopy.

For XPS studies the samples were pressed into a Ni grid immediately after unsealing the storage ampoules and transferred to a test chamber (the duration of sample stay in air during these manipulations was ≤5 min). The vacuum in the test chamber was maintained at 10^{-6} mbar. H_2 was then admitted at a pressure of 1 bar, and the samples were re-reduced under static conditions at 350 °C for 1.5 h, followed by outgassing ($1-5 \cdot 10^{-8}$ mbars) the samples at RT. The XPS spectra were recorded on a VG ESCALAB HP spectrometer using the non-monochromatic radiation of AlK_α ($E_{h\nu}$ = 1486.6 eV, 200 W power). The binding energy (BE) scale was calibrated relative to the peaks of Au $4f_{7/2}$ (84.0 eV) and Cu $2p_{3/2}$ (932.6 eV). Charging was corrected using the Mg 2*s* peak (88.1 eV) as internal standard. The charging factor was determined as the difference between the measured and tabulated values of BE.

The HRTEM measurements were performed on a JEM2010 electron microscope operated at 200 kV. Prior the examination, the sample powder was ground and suspended in ethanol. A drop of suspension was then mounted on a copper grid covered by carbon film, and the solvent was allowed to evaporate. Maximal resolution was 0.14 nm at 180 000 magnifaction. From each sample about 250 particles were measured to determine a statistically justified averaged particle size and particle size distribution.

RESULTS AND DISCUSSION

Figure 1, *a* compares XPS spectra, in the Ru 3*d* region, performed on the $Ru(OH)Cl_3/MgO$ and Ru/MgO samples. In this region Ru species show two peaks due to the Ru $3d_{5/2}$ and Ru $3d_{3/2}$ transitions. In the following the values of BE will be referred to the Ru $3d_{5/2}$ peak. The BE of the peak at 282.1 eV for the $Ru(OH)Cl_3/MgO$ sample before reduction (see Fig. 1, *a*, curve *1*) coincides with the BE of Ru $3d_{5/2}$ measured for the native bulk $Ru(OH)Cl_3$. Another peak around 285 eV assigned to be Ru $3d_{3/2}$ is considered to contain the C 1*s* component; the appearance of C 1*s* peak is presumably caused by carbon impurity in the apparatus. After the reduction of Ru/MgO sample (see Fig. 1, *a* curve *2*), the Ru 3*d* peak shifts to lower BE value (279.5 eV) indicating the presence of ruthenium in the metallic state. It should be noted that the BE value of 279.5 eV is by 0.6–0.8 eV lower than that is observed

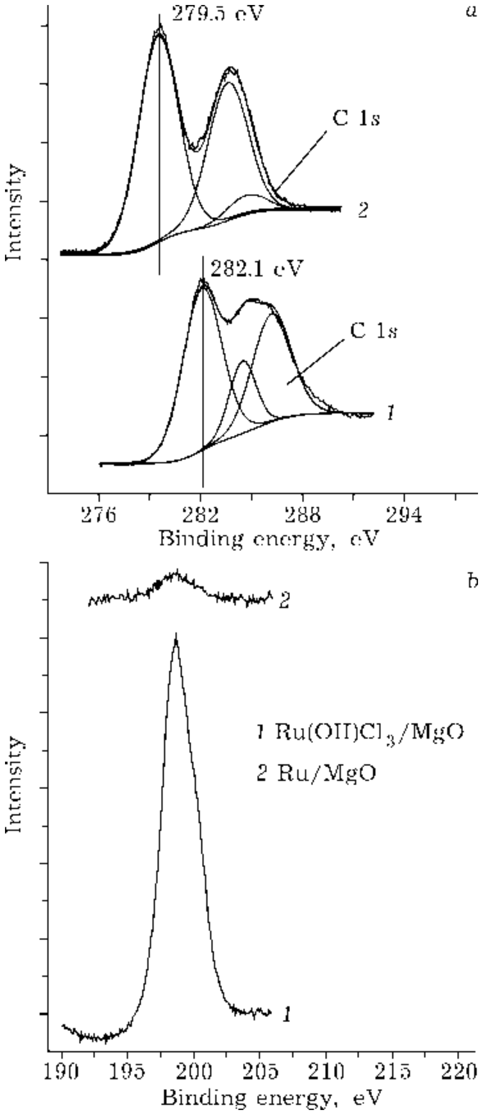

Fig. 1. Ru 3*d* (*a*) and Cl 2*p* (*b*) spectra of Ru/MgO sample before (*1*) and after (*2*) reduction.

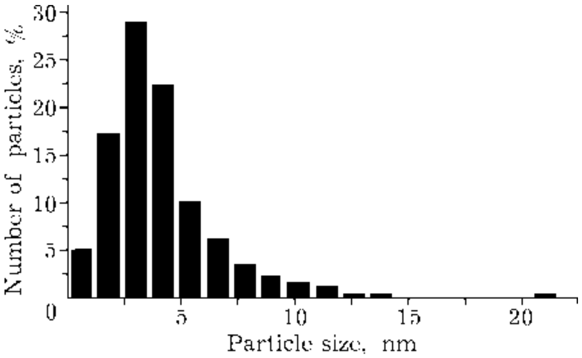

Fig. 2. Size distribution of Ru particles supported on MgO.

for bulk Ru metal (E_b = 280.2 eV). This shift of the Ru 3*d* peak is often interpreted as a result of electron transfer from a support to supported Ru metal particles [3].

To obtain information on the Ru particle size and size distribution, the reduced Ru/MgO sample was subjected to a HRTEM study. The electron micrographs demonstrate the contrast images of Ru particles of spherical shape, which are uniformly distributed over the support.

The Ru crystallites having diameters d_i less than 10 nm constitute the majority of the metal particles. Besides, few larger Ru crystallites (d_i ~ 10–18 nm) were also present. The average diameter of Ru particles, $<d>$ defined as $<d>= \Sigma(n_i d_i)/\Sigma n_i$, is (4.08 ± 0.26) nm, as determined from the histogram (Fig. 2).

Figure 1, *b* exhibits XPS spectra, in the Cl 2*p* region, recorded for the Ru(OH)Cl_3/MgO and Ru/MgO samples. The surface Ru/Cl atomic ratio of Ru(OH)Cl_3/MgO sample, as determined from the integral intensities of Ru 3*d* and Cl 2*p* peaks (see Fig. 1, *a* and *b*, curves *1*) was 0.65, *i. e. ca.* 2 times higher than the Ru/Cl ratio of 0.36 found for native Ru(OH)Cl_3 in agreement with the stoichiometric ratio. This increase in the Ru/Cl ratio may be caused by hydrolysis of Ru(OH)Cl_3 under H_2O traces containing in acetone and/or by partial substitution of Cl ligands of native compound for OH groups on MgO surface during the impregnation. Upon reducing the Ru(OH)Cl_3/MgO sample, the Cl 2*p* spectrum (see Fig. 1, *b* curve *2*) shows a further sharp decrease in the peak intensity. The surface Ru/Cl ratio was increased by a factor of about 10 (Ru/Cl = 6.2) obviously due to conversion of hydroxychloride complexes of Ru into metallic Ru. An insignificant amount of chlorine still remains after reduction on the sample surface presumably as $MgCl_2$ formed due to the reactions of Ru(OH)Cl_3 and/or HCl with MgO [5].

Figure 3 presents XPS spectra of MgO and Ru/MgO samples in the O 1*s* region. The both spectra contain a peak of asymmetric shape suggesting the presence of different surface states of oxygen. Deconvolution of this peak fits very well by using a pair of components, respectively, at 529.9 and 532.2 eV in the case of MgO bulk or at 529.8 and 531.7 eV in the case of Ru/MgO. The component at higher BE (about 530 eV for the both samples) is related to O^{-2} ions of MgO lattice, whereas the second

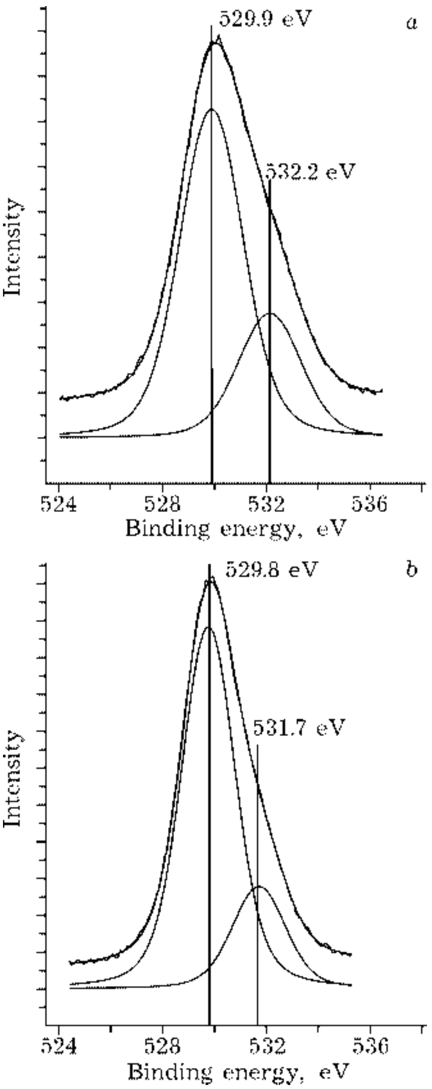

Fig. 3. O 1*s* spectra of MgO (*a*) and Ru/MgO (*b*).

component can be assigned to OH groups on MgO surface [6]. The shift of the second component by 0.5 eV to lower BE observed in the spectrum of Ru/MgO as compared with the spectrum of pure MgO may derive from interaction of surface OH groups with supported Ru particles leading to the appearance of a negative charge on oxygen atoms. However, this assumption is in contradiction with the fact that the Ru 3*d* peak observed in the spectrum of Ru/MgO sample is shifted to lower BE values; this shift may show that Ru metal particles, when supported on MgO, also are negatively charged.

Meanwhile, the appearance of a negative charge on metal atoms may not be the only reason for the shift of corresponding XPS features towards lower BE values. Another possible reason is the differential charging effect observed, as it has been shown previously [7], for the non-conducting samples which consist of several phases significantly differing by their conductivity (for example, Ru metal and MgO support). This effect can not be corrected by using an internal standard. Indeed, the uniform shift of all peaks observed may result in underestimation of BE value for the phase possessing the higher conductivity, since its surface positive charge generated due to electron loss under photoemission would be less than that for the phase having the lower conductivity. Evidently, if the differential charging phenomenon be taken into account for the case of Ru/MgO system, the aforementioned contradiction may prove to be apparent.

To check the presence of differential charging phenomenon, we recorded the Ru 3*d* and Auger Ru MNN spectra (Fig. 4) for the samples of bulk Ru metal and Ru/MgO and calculated the corresponding values of Auger parameter, α by the formula α = KE (RuMNN) + BE (Ru 3*d*), where KE is the kinetic energy of Auger electrons and BE is the binding energy of Ru 3*d* core level spectra. As a first approximation, the *a* value is supposed to be independent of the charging. Figure 4 demonstrates that the values of Auger factor found for Ru bulk (554.7 eV) and Ru/MgO (554.8 eV) samples coincide confirming that the Ru/MgO sample contains metallic ruthenium. Therefore, the shift of Ru 3*d* peak in the spectrum of Ru/MgO to lower BE is caused by the differential charging effect and not related to the presence of a negative charge on Ru particles.

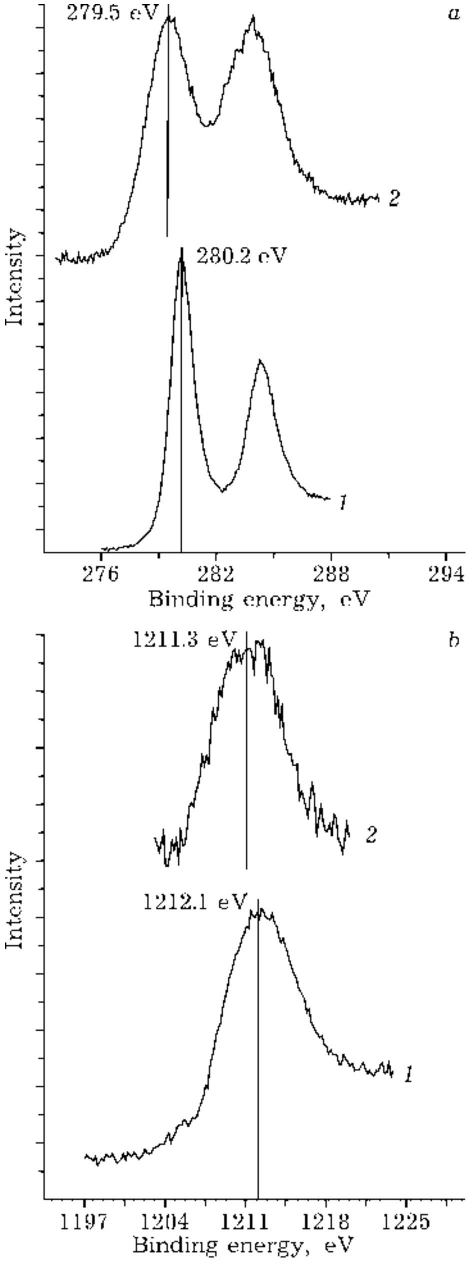

Fig. 4. Ru 3*d* (*a*) and Auger RuMNN (*b*) spectra for of bulk Ru (*1*) and Ru/MgO (*2*).

The value of the differential charging effect can be estimated by a comparison of the valence band spectrum of supported metal particles with that of bulk metal [8]. It should be noted that this comparison gives a reliable result only if any changes of the valence band spectrum caused by the small sizes of supported metal particles may not observed, *i. e.* if

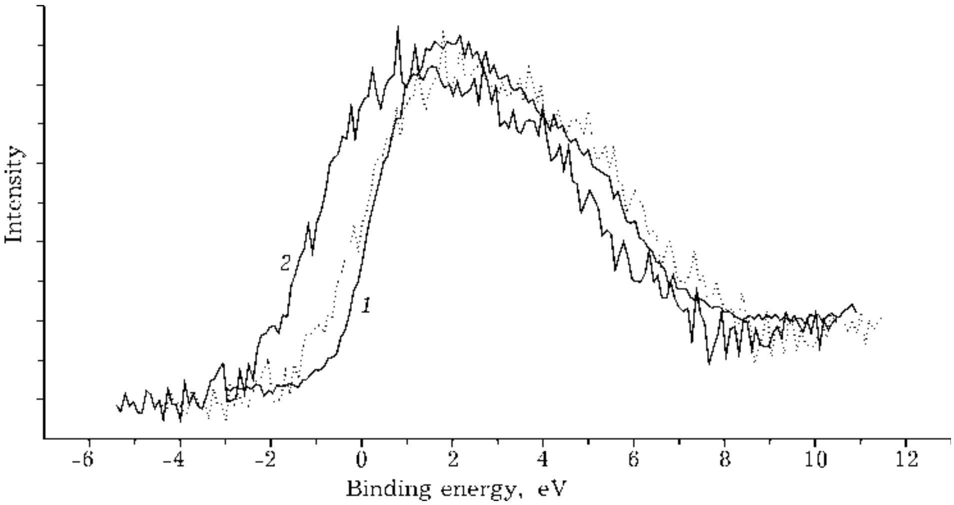

Fig. 5. Valence band spectra for bulk Ru (*1*) and Ru/MgO (*2*). The dotted curve was obtained after the shift curve *2* by 1.0 eV towards higher binding energy values.

the mean diameter of these particles is higher than 2 nm [9]. Figure 5 comprises the difference valence band spectrum of supported Ru particles (obtained by subtraction the spectrum of MgO support from the spectrum of Ru/MgO sample) with the valence band spectrum of bulk Ru. The both spectra exhibit the lines of similar widths, but the line in the spectrum of supported Ru metal is shifted by 1.0 eV to lower BE values relatively to the line for bulk Ru. Since, according to HRTEM data, the mean diameter of supported Ru crystallites containing in the Ru/MgO sample is as large as 4.0 nm, it is reasonable to attribute this shift to the differential charging effect. Correspondingly, the value of differential charging can be estimated as equal to +1.0 eV. After the correction of the Ru 3*d* spectrum of Ru/MgO (see Fig. 1, *a*, curve *2*) by this value, the BE of Ru $3d_{5/2}$ is changed to 280.5 eV and becomes by 0.3 eV higher than the BE of Ru $3d_{5/2}$ for bulk Ru. Based on this result, we assume the supported Ru particles are positively charged in fact. The last conclusion along with the observation of a negative shift of O 1*s* peak at 532.2 eV allows to suppose that Ru metal particles interact with the acidic OH groups of MgO surface, and this interaction is accompanied by transfer of electronic density from metal particles to oxygen atoms.

Thus, unlike that was suggested early [3, 4, 10], we found that the resulting electronic effect of MgO surface to supported Ru particles is the electron-withdrawing one. We did not observe any evidences for the electron-donating effect of lattice O^{-2} ions of MgO lattice to supported Ru metal, which may be manifested in a positive shift of O 1*s* peak at 530 eV, possibly due to the weakness of this effect or the considerably higher surface content of O^{-2} ions as compared with the atomic content of Ru. The increased electron-withdrawing properties of MgO support observed here may be caused by the presence of Cl^{-} impurity, which usually increases the acidity of a support [11]. In order to confirm or reject this assumption we are planning to study the Ru/MgO sample prepared by use of Cl-free Ru precursor.

CONCLUSION

Here, we have demonstrated that the negative shift of Ru 3*d* peak (279.5 eV) as compared with bulk Ru (280.2 eV), which was observed in the XPS spectrum of Ru/MgO sample, is caused by the differential charging effect and not related to the presence of a negative charge on Ru particles. The value of BE Ru 3*d* determined for supported Ru taking the differential charging effect into consideration is equal to 280.5 eV. The shift of Ru 3*d* peak towards the higher BE values may be explained by electron-withdrawing effect of OH groups located on MgO surface to supported Ru metal particles. This suggestion is supported by the observation of a negative shift of O 1*s* peak at 532.2 eV. The positive charging of Ru particles on MgO surface may be a reason for insufficiently high activity of unpromoted Ru/MgO catalyst in ammonia synthesis. As it is well known, for increasing the activity of Ru/MgO catalyst the addition of basic promoters ($CsNO_3$, Cs_2CO_3, potassium metal *etc.*) is necessary.

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REFERENCES

1 M. Muhler, F. Rosowski, O. Hinrichsen, A. Hornung and G. Ertl, Stud. Surf. Sci. Catal., vol. 101; in J. W. Hightower, W. N. Delgass, E. Iglesia and A. T. Bell (Eds.), Elsevier, Berlin 1996, p. 101.
2 M. S. Khaja, R. K. S Rama, R. P. Kanta, *Indian J. Chem.* A, 32(1993) 383.
3 K. Aika, A. Ohya, A. Ozaki, Y. Inoue and Y. Yasumori, *J. Catal.*, 92 (1985) 305
4 K. Aika and K. Tamary, Ammonia: Catalysis and Manifacture, in A. Nielsen (Ed.), Springer, Berlin, 1995, p. 104 and references therein.
5 S. Murata and K. Aika, *Appl. Catal.*, 82 (1992) 1.
6 V. I. Nefedov, D. Gati, B. F. Dzhurinskii, N. P. Serguhin and Ya.V. Salyn, *Zhurn. neorgan. khimii*, 20 (1975) 2307.
7 V. I. Bukhtiyarov, I. P. Prosvirin, and R. I. Kvon, *J. Electron Spectrosc. Relat. Phenom.*, 77 (1996) 7.
8 G. K. Wertheim, *Z. Phys. B-Condensed Matter.*, 66 (1987) 53.
9 R. C. Bartzold, *Surface Sci., 106* (1981) 243.
10 K. Aika, T. Takano, and S. Murata, *J. Catal.*, 136 (1992) 126.
11 K. Tanabe, Catalysis: Science and Technology, in J. R. Anderson and M. Boudart (Eds.), Springer, Berlin, 1981, vol. 2, p. 231.