

# XPS Study of Ru/Fe<sub>2</sub>O<sub>3</sub> Catalysts for the Water-Gas Shift Reaction

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*Received: 2 October, 2002*

*Accepted: 10 October, 2002*

## Abstract

The water-gas shift reaction performance of Fe<sub>2</sub>O<sub>3</sub>, Ru/Fe<sub>2</sub>O<sub>3</sub> catalysts and the same compounds doped with sodium ions was studied. An addition of sodium was found to result in an increase of the ruthenium catalyst activity and stabilization of its surface area during the reduction with the reaction mixture. This series of catalysts was examined by XPS method. The addition of sodium and ruthenium causes an increase in the ionicity of the Fe<sub>2</sub>O<sub>3</sub> lattice, manifested as changes in intensity of peaks of the Fe 2p band.

**Keywords:** Ru/Fe<sub>2</sub>O<sub>3</sub> catalysts, water-gas shift reaction, sodium doped Ru/Fe<sub>2</sub>O<sub>3</sub> catalysts, XPS studies of Ru/Fe<sub>2</sub>O<sub>3</sub> catalysts

## Introduction

It has been established that ruthenium deposited on alkali-promoted supports makes catalysts for ammonia synthesis so active that they have been accepted as alternatives to the commercially used iron catalysts [1]. The catalysts obtained by deposition of ruthenium on iron oxides proved very attractive in water-gas shift reaction [2-5]. Moreover, a modification of the iron support with sodium was found to improve significantly the activity of these catalysts [5]. A particular improvement in the catalyst activity was obtained when the iron oxide was prepared through the  $\delta$ -FeOOH stage. It is necessary to characterise the active centres of the catalysts responsible for such a reaction run.

In studies of a catalyst structure the need very often arises to know chemical states of elements and their relative content and, if possible, to determine the interaction

of surface atoms with their neighbours. Under some circumstances the XPS analysis is able to provide all these required data. Yet in the studies of iron, precise XPS analysis is difficult. Because of the common use of iron oxides in a great number of industrial catalysts, an improvement of their surface analysis is of special importance.

In this work an attempt was made to characterise the changes in the surface state caused by doping of the catalysts with sodium mainly with the use of XPS. Subtle variations in the structure of "shake-up" satellites in the Fe2p<sub>3/2</sub> band have been connected to the surface properties.

## Experimental Catalyst Preparation

The catalyst support, labelled as D, was obtained from  $\delta$ -FeOOH by calcination for 3 h at 600°C in air. The support was doped with 0.45% of sodium irrespective of the ruthenium amount, using aqueous solution of NaNO<sub>3</sub> and calcined at 600°C. The unmodified support (D) and

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the Na-containing one (Na-D) were impregnated with acetone solution of  $\text{RuCl}_3$  (incipient wetness impregnation), dried and calcined in air at  $400^\circ\text{C}$  for 3h. Only the catalyst 2%Ru/D-Na in whose preparation sodium was introduced after ruthenium, was calcined at  $400^\circ\text{C}$  at both stages, i.e. after deposition of ruthenium and after deposition of sodium on  $\text{Ru/Fe}_2\text{O}_3$ . Beside the catalyst, also simple compounds: Fe, FeO,  $\text{Fe}_3\text{O}_4$ ,  $\text{RuO}_2$  and RuO of analytical grade or spectral purity were examined by XPS to get the band parameters, used then in analysis of the XPS spectra of the catalyst.

### Catalyst Characterisation

**Surface area** was obtained by low temperature nitrogen adsorption according to the BET method using a Micromeritics sorptometer ASAP2010 (USA).

**X-ray diffraction** (XRD) studies were carried out on an automatic Philips PW 1710 diffractometer using  $\text{FeK}_\alpha$  radiation.

**Catalytic activity** in the water-gas shift reaction (WGS) was measured in a flow reactor at atmospheric pressure in the reaction conditions which were as follows: catalyst amount 0.25 g, reaction temperature  $350^\circ\text{C}$  or  $300^\circ\text{C}$ , CO flow rate  $3.5 \text{ dm}^3/\text{h}$ , the molar ratio of  $\text{H}_2\text{O}:\text{CO}=2.5$ . Carbon monoxide 99.97% of BOC Ltd. Special Gases Company was used. The conditions for running the reaction and product analysis were discussed before [2]. The catalytic activities presented are means of three measurements performed after 3h on stream.

**The XPS measurements** were performed with a VG Scientific ESCA-3 photoelectron spectrometer using  $\text{Al K}\alpha_{1,2}$  radiation (1486.6 eV) from an X-ray source operating at 13 kV and 10 mA. Working pressure was higher than  $2 \times 10^{-8}$  Torr ( $2.7 \times 10^{-6}$  Pa). All spectra were recorded at a photoelectron take-off angle of  $45^\circ$ . Binding energies were referred to the C1s peak from the carbon surface deposit at 284.8 eV. Data processing consisted of the basic operations of calibration of the peak position against the C1s line, background of Shirley's type and  $\text{K}\alpha_{3,4}$  peaks removal together with routines for the analysis of composite spectra by their fitting with single peaks or doublets. The spectra were decomposed into symmetric gaussian-20%-lorentzian peaks. The relative element content (N) was calculated from the formula including carbon deposit influence [6, 8]:

$$N = F \cdot I_A \cdot E_A^{0.25} \cdot \sigma_A^{-1} \cdot \exp(d_C \cdot \lambda_{A,C}^{-1})$$

where: F contains all instrumental factors (including transmission function T) and is assumed to be constant for the measurements,  $I_A$  is intensity of the line A measured,  $E_A$  is kinetic energy of the A level,  $\sigma_A$  is elemental cross-section for photoionization [7],  $\lambda_A$  is A-level electrons' inelastic mean free path in the adventitious carbon deposit [8] and  $d_{C,A}$  is the thickness of the carbon deposit [8]. The  $\lambda$  and T values were obtained according to [8].

Scofield's cross-sections were used in this study only for C1s ( $\sigma_C = 1.0$ ) and O1s ( $\sigma_O = 2.93$ ) lines. In the case of  $\text{Ru}3d_{3/2}$ ,  $\text{Fe}2p_{3/2}$  and Na1s lines, the sensitivity factors obtained from the element-oxygen intensity ratio in simple oxides were determined and applied, instead of  $\sigma_A$ , in the element content calculations.

### Results

As was shown by XRD, the iron oxide carrier always was in the form of the low-crystalline  $\alpha\text{-Fe}_2\text{O}_3$  phase [9]. In samples containing ruthenium neither ruthenium compounds nor metal were detected. During the CO water-gas shift reaction the carrier was reduced and a mixture of  $\text{Fe}_3\text{O}_4$  with  $\gamma\text{-Fe}_2\text{O}_3$  phases was observed.

The surface area of the catalysts, like that of the support, was low, about  $20 \text{ m}^2/\text{g}$ . It was not stable under the reaction conditions and after time on stream it was significantly reduced (Table 1). In the case of the support free of metal additions, the surface area decreased more, by about 40% as compared to about 30% in samples containing sodium only and less than 20% in the case of  $\text{Ru/Fe}_2\text{O}_3$  (without sodium). This is the evidence of the stabilising effect of ruthenium and sodium on the support.

According to expectations the pure support (D) and that doped with sodium (Na-D) do not show catalytic activity in WGS at  $300^\circ\text{C}$  (Table 1). At  $350^\circ\text{C}$  (the temperature for a high-temperature conversion), these carriers catalyse the conversion reaction at the level of 13%. Under these conditions the  $\text{Ru/Fe}_2\text{O}_3$  catalysts reach productivities above 90% near the maximum, which follows from the thermodynamic equilibrium. This is the reason why the conversion data at  $300^\circ\text{C}$  seems more representative. The activity of the  $\text{Ru/Fe}_2\text{O}_3$  catalysts varied, and was the highest in the case of  $\text{Ru/Na-D}$  catalyst with the lower ruthenium content (2wt.%). Since a distinct correlation between the catalytic activity and the surface area was not found, it can be concluded that the activity is sensitive to local changes in the vicinity of Ru active centres.

As follows from Table 1, ruthenium is the only element introducing high catalytic activity to the system. However, sodium enhanced it by about 13% at  $300^\circ\text{C}$  (2%Ru/Na-D vs. 2%Ru/D). The lower activity of the sample containing more ruthenium (5 wt.%) can be due to a formation of larger structural forms of ruthenium, likely islands or crystallites. On the other hand, it turns out, that ruthenium is highly active if it is better dispersed [10], perhaps partially incorporated to the support lattice. Crystal growth, expectedly more effective in 5%Ru/Na-D, can cause a decrease of the amount of metal accessible to reactants.

XPS measurements were performed on samples as received. In this study, determination of the chemical state of the main elements: ruthenium and iron was difficult because of a complex character of their most intense, analytical  $\text{Ru}3d$  and  $\text{Fe}2p$  bands. Sodium was introduced into some of the catalysts; however, low intense Na1s lines were detected also in other samples.

Table 1. Characterization of composition, surface area and catalytic activity of studied samples.

Catalyst	Ru content	Na content	Surface area [m <sup>2</sup> /g]		Catalytic activity (CO conversion)			
					350°C		300°C	
	[wt.%]	[wt.%]	as prepared	after WGSR	[%mol]	micromole CO/g s	[%mol]	micromole CO/g s
D	-	-	18.8	11.1	12.9	22.4	-	-
Na-D	-	0.45	17.7	12.2	13.3	23.1	-	-
2%Ru/Na-D	2.0	0.44	19.0	17.1	93.4	162.1	95.6	166.0
5%Ru/Na-D	5.0	0.43	19.1	19.0	92.8	161.1	89.9	156.1
2%Ru/D-Na	2.0	0.44	-	-	91.5	145.4	84.7	134.6
2%Ru/D	2.0	-	19.5	15.4	90.6	157.3	82.7	143.6

All samples contained some amount of carbon on the surface, which was deposited during their synthesis and storage. The XPS spectrum of the pure support (D) reveals the main peak at 284.8 eV, corresponding to a mixture of hydrocarbons and two other peaks at about 287 and 289 eV assigned to products of their oxidation. Since the 3d band of Ru superimposes the carbon C1s band, the experimental spectral envelope of this region was decomposed by fitting with C1s and Ru3d “synthetic” bands produced with the use of experimentally determined parameters. The Fe2p band, composed of the doublet corresponding to Fe2p<sub>3/2</sub> and Fe2p<sub>1/2</sub> is of complex character. Besides the main peaks and the Fe2p band envelope from the K $\alpha_{3,4}$  excitation it contains structures of “shake up” multiplets. It is believed that this structure arises from a splitting of the Fe2p line due to a coupling between the core hole and the unfilled shell [11] or is a result of local charge compensation of the core hole by a population of 3d or 4s-p orbitals with the electron charge drawn from the  $\pi$  band of the hybridized ligand [12]. The band corresponding to Fe 2p spreads over 30 eV, from 705 to 735 eV. The Shirley’s background [13, 14] was removed from the whole Fe2p band by iteration in such a way that the ratio R=H1:H2 of the spectrum height at its local maximum, corresponding to the main peaks Fe2p<sub>3/2</sub> and Fe2p<sub>1/2</sub> was 1.65. Then, the resulting Fe2p band was fitted with multiplets in the range including the main photoelectron peaks and the satellite structure. The obtained structure of the Fe2p<sub>3/2</sub> sub-band in pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (D) is given in Fig.1.

The shape of the band and the quality of the fit obtained for other samples were similar. The multiplet for the fitting was composed of the main, peak (1) and five (2-6) component peaks, all with the same full width at half maximum (FWHM). The distances from the main peak ( $\Delta$ BE-binding energy) and intensities ( $I_x$ ) were varied to get the best fitting. Initially the peaks S2 ( $\Delta$ BE = 1.1 eV,  $I/I_1 = 0.18$ ) and S5 ( $\Delta$ BE = 7.4 eV) were introduced somehow arbitrarily, following the calculated structure [11,12]. Then other component peak positions and intensities were added to achieve good fitting.

Ruthenium in the catalysts was sprayed over the D support forming possibly a one or few monolayer depos-

its. XPS spectra of Ru were strong enough to analyse this spectral region and to determine the position of Ru3d<sub>5/2</sub> peaks maxima. Parameters used in the fitting of the Ru3d doublet were obtained from the spectrum of pure RuCl<sub>3</sub>. In the spectra of all samples the ruthenium 3d band was well fitted with two doublets. The first one (about 281 eV) can be assigned to RuO<sub>2</sub> and the second (about 282 eV) to RuO<sub>3</sub> in good agreement with reference data [14-17]. Metal ruthenium (280 eV) has not been detected.

The introduction of ruthenium and sodium induced some changes in the electronic structure of the support surface, as revealed by changes in the Fe2p band. Thus, the conclusion on the influence of Ru and Na ion incorporation into the iron oxide matrix on the chemical nature of the interaction between Fe, Ru and Na ions is justified. Table 2 contains the data on binding energies (BE) of electrons in surface atoms and relative contents of elements. The observed changes in BE Fe2p and Ru3d are significant, pointing to considerable interactions between the carrier and the active component. The presence of sodium causes a decrease in the binding energy of Fe2p<sub>3/2</sub> electrons (Na-D vs D), while that of ruthenium has the opposite effect (2%Ru/D vs D). The two contributions to some extent can cancel each other, as it has been observed for other catalysts. In the catalyst with a low content of ruthenium (less than 5 wt %), the interaction between sodium and ruthenium 4+ distinctly decreased the binding energy of Ru3d electrons. Surface atomic ratios of ruthenium and iron correspond to the introduced amount, with the exception of 2%Ru/D-Na in which sodium was deposited on the Ru-catalyst already formed. Such a sequence of the catalyst preparation, unprofitable for catalysis, results in the surface enrichment in sodium, manifested as a decrease of Ru/Na and an increase of Na/Fe ratios. Small changes of the Na/Fe ratio caused by a considerably increasing content of ruthenium (2%Ru/Na-D and 5%Ru/Na-D) can be connected to the growth of ruthenium oxide crystallites.

Veal and Paulikas [12] reported a linear dependence of the satellite separation versus ligand electronegativity for a series of Fe, Sc, Zr and Ti oxides with equal

Table 2. Binding energies (eV) of Ru3d5/2, Fe2p3/2 and Na1s photoelectrons and the element content.

Samples	D	Na-D	2%Ru/D	2%Ru/Na-D	5%Ru/Na-D	2%Ru/D-Na
Fe2p <sub>3/2</sub>	710.4	710.1	710.8	710.5	710.3	710.2
Na1s		1071.6		1071.6	1072.2	1071.6
Ru3d <sub>5/2</sub> (Ru <sup>4+</sup> )			281.0	280.8	281.0	280.9
Ru3d <sub>5/2</sub> (Ru <sup>6+</sup> )			282.5	282.4	282.4	282.5
Ru/Fe			0.17	0.15	0.46	0.11
Ru <sup>4+</sup> /Ru <sup>6+</sup>			3.0	2.1	2.4	1.8
Na/Fe(tot)		0.24	-	0.13	0.16	0.36
Ru/Na			-	1.15	2.88	0.31

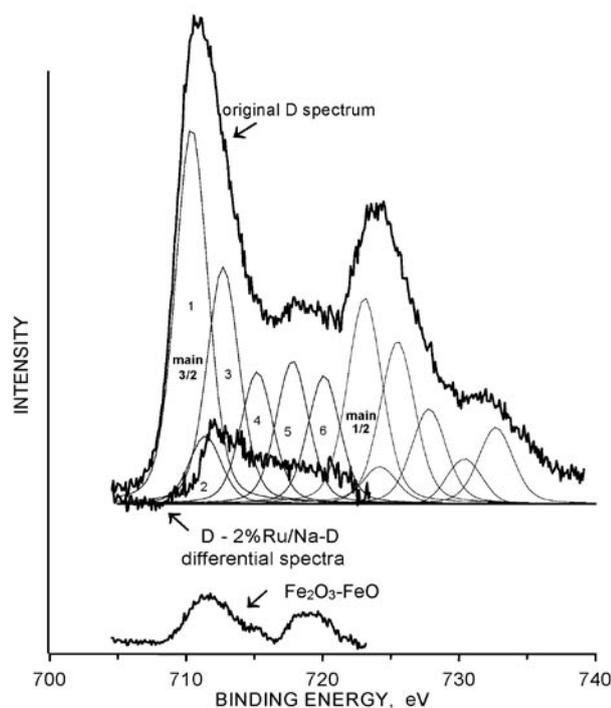


Fig.1. Fe2p spectrum of the carrier (D). The spectrum is fitted with the main Fe2p<sub>3/2</sub> and Fe2p<sub>1/2</sub> peaks and the set of relative peaks (2-6) substituting the satellite bands (thin solid lines). Subtraction of the spectrum of 2% Ru/Na-D from the spectrum of the pure support gives differential spectrum (broken line) shown inside the bottom part of the latter. The difference between Fe2p bands in pure Fe<sub>2</sub>O<sub>3</sub> and FeO oxides is presented below.

cation valence. Since in all sodium doped samples the separation of the most prominent peak S3 was better and in the ruthenium doped sample (2%Ru/Na-D) it was the best, the two metals seem to react with iron oxide, causing an increase in the ionicity of the lattice. This observation is confirmed by the effect of quenching of the satellites (Fig.2).

The contributions of the main peak (uniform filling) and the S3 peak (shaded) to the Fe2p<sub>3/2</sub> band are shown in Fig.2. The lowest contribution of the all-satellite band to the spectrum and smallest of S3 peak (most sensitive region) are observed for the 2%Ru/Na-D sample. The changes in the intensity of the S3 peak can be related to the catalytic activity of Ru/Fe<sub>2</sub>O<sub>3</sub> catalysts in the water-gas shift reaction. Fig. 3 shows the S3 peak intensity versus the catalyst activity in WGS at 300°C, illustrating the influence of doping on the electronic state of the support and the activity of the Ru/Fe<sub>2</sub>O<sub>3</sub> catalysts.

## Discussion

The activity of Ru/Fe<sub>2</sub>O<sub>3</sub> catalysts in the water-gas shift reaction depends on the kind of support used [2-4], and it is not directly affected by the surface texture of iron oxide supports. The most important feature seems to be the susceptibility of Fe<sub>2</sub>O<sub>3</sub> to reduction by CO [18]. The active phase was made of ruthenium compounds since in reaction conditions the catalytic activity of the support is very small and at 300°C it is practically non-existent. Preliminary studies have shown that the presence of the sodium promoter leads to an improvement in the properties of Fe<sub>2</sub>O<sub>3</sub> as the support [5].

So far little is known about the surface reactions taking place in the system (Na,Ru)Ox-Fe<sub>2</sub>O<sub>3</sub> and XPS studies of Ru/Fe<sub>2</sub>O<sub>3</sub> catalysts could bring some relevant information. Analysis of the Fe2p band in the XPS spectrum of Ru/Fe<sub>2</sub>O<sub>3</sub> catalyst was performed with the method proposed in [13]. The method is based on the fitting with a multiplet and allows an accurate reproduction of the band and, consequently, an accurate determination of the differences between the spectra of two surfaces of different electronic state. A comparison of the Fe2p spectra for Fe<sub>2</sub>O<sub>3</sub> and FeO (Fig. 1), irrespective of the differences in the electron binding energy, shows that the electronic state significantly affects the structure of the band satellites. Particularly important changes take place in the area of the peak S3. This fragment of the band is particularly

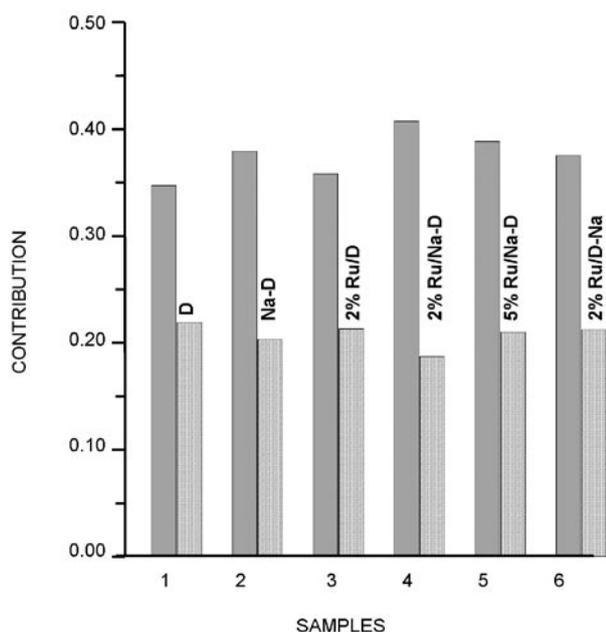


Fig.2. Main Fe2p<sub>3/2</sub> peak (bars with uniform filling) and peak S3 (shaded bars) contributions to the Fe2p<sub>3/2</sub> band.

intensive for Fe(III). This observation has been used in analysis of the catalysts samples studied. For the most active sample of 2%Ru/Na-D, despite a high binding energy of 710.5 eV, similar to that in the pure support (Fe<sub>2</sub>O<sub>3</sub> (710.4 eV), which indicated the presence of Fe(III), the electronic structure of the surface atoms became closer to the state established for FeO [19,20]. Thus, we may conclude that the admixture of Na and Ru caused an increase in the ionic character of the surface atoms. This conclusion supported by the results of EPR measurements [21], indicates a strong interaction between the supported atoms of the active phase and the iron oxide support leading to an increase in the ionic character of the surface of the system. From the two kinds of ruthenium oxide (Ru<sup>4+</sup> and Ru<sup>6+</sup>) occurring on the surface of the as-prepared catalysts, a more stable is RuO<sub>2</sub> [22, 23], which explains its greater contribution in the ruthenium phase. The less stable RuO<sub>3</sub> is stabilised in the presence of sodium ions. As suggested by the shift of the binding energy of iron and Ru<sup>4+</sup> electrons, the interactions between RuO<sub>2</sub> and the surface iron cations of the support are stronger than in RuO<sub>3</sub> case.

The changes in the binding energy of Fe2p<sub>3/2</sub> electrons under the influence of sodium and ruthenium and those in the binding energy of Ru3d<sub>5/2</sub> electrons under the influence of sodium, bring the information on the reactions taking place on the surface of the support. A decrease in the iron electron binding energy as a result of sodium ions influence (the effect similar to that caused by an introduction of Na<sup>+</sup> ions to SiO<sub>2</sub> [20]) in the Na-D sample suggests an increase in the electronegativity of the surrounding of Fe<sup>3+</sup> ions, so the appearance of ferrite structures. Such structures were found in the systems with Fe<sub>2</sub>O<sub>3</sub> doped with potassium cations [24]. The shift of the binding energy of iron elec-

trons towards higher values in the Ru/D sample leads to the inverse situation and then iron plays the role of the cation. If so, the electronegativity of the surrounding of ruthenium increases leading to formation of complexes iron ruthenate type. Similar changes in the energy of Ru<sup>(4+)</sup>3d<sub>5/2</sub> in the presence of sodium ions suggest the formation of sodium ruthenate type complexes.

The lack of changes in the binding energy of Ru<sup>(6+)</sup>3d<sub>3/2</sub> electrons under the effect of iron and sodium cations, can be interpreted as a consequence of the lack of interactions or (which is more probable) the interactions with both kinds of cations leading to the formation of complexes with ruthenium playing the role of the anion. Such an interpretation of the acid-base interactions in the system (Na,Ru)Ox-Fe<sub>2</sub>O<sub>3</sub> can explain the promoting properties of the sodium cations. The part of ruthenium, which has not been sufficiently strongly bonded with the cations of the support becomes bonded and stabilised on the surface by the sodium cations. This enhances the dispersion of the ruthenium phase. The increased dispersion of ruthenium oxides occurring as a result of the introduction of sodium to Fe<sub>2</sub>O<sub>3</sub> is suggested by the results of temperature programmed reduction by hydrogen [25]. In the water-gas shift reaction the crystallites of ruthenium compounds are reduced to strongly dispersed metal, which is the actual active phase of the Ru/Fe<sub>2</sub>O<sub>3</sub> catalysts. As indicated by the results of high-resolution electron microscopy measurements [10], the increased dispersion of ruthenium favours a great activity of the catalysts in the water-gas shift reaction.

In conclusion we are of the opinion that the high activity of the catalysts tested is related to the role of ruthenium introduced into multiatomic active centres formed by iron ions responsible for the proper structure of the centres and ruthenium bonding. The presence of sodium atoms enhance the ionic character, which decreases the

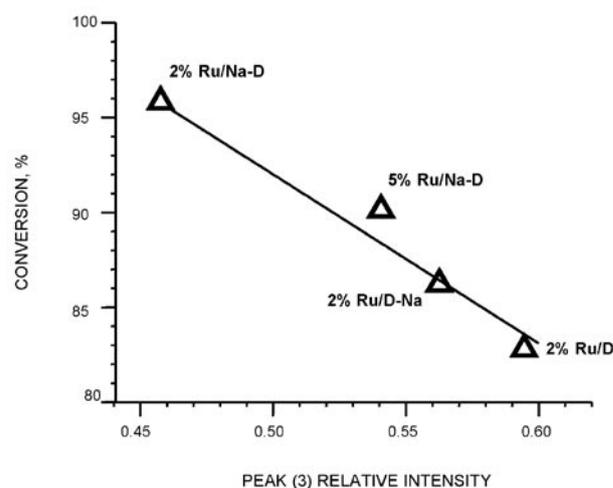


Fig.3. Relationship between CO conversion (% mol.) at 300°C and the structure of the Fe2p<sub>3/2</sub> band represented by the relative intensity of the S3 peak (S3/S1).

electronegativity of ruthenium and increases the mobility of its valence electrons.

### References

1. HINRICHSSEN O., ROSOWSKI F., HORNING A., MUHLER M., ERTL G., *J.Catal.*, **165**, 33, **1997**.
2. BASIŃSKA A., DOMKA F., *Catal. Lett.*, **17**, 327, **1993**.
3. BASIŃSKA A., DOMKA F., *Catal. Lett.*, **22**, 327, **1993**.
4. BASIŃSKA A., *React. Kinet. Catal. Lett.*, **60**, 49, **1997**.
5. BASIŃSKA A., DOMKA F., *Catal. Lett.*, **43**, 59, **1997**.
6. SZAJMAN J., LIESEGANG J., JENKIN J.G. and LECKEY R.C.G., *J. Electron Spectrosc. Relat. Phenom.*, **23**, 97, **1981**.
7. SCOFIELD J.H., *J. Electron Spectrosc.*, **8**, 129, **1976**.
8. PENN D.R., *J. Electron Spectrosc.*, **9**, 29, **1976**.
9. BASIŃSKA A., NOWACKI A., DOMKA F., *React. Kinet. Catal. Lett.*, **66**(1), 3, **1999**.
10. BASIŃSKA A., KĘPIŃSKI L., DOMKA F., *Appl. Catal. A*, **183**, 143, **1999**.
11. GUPTA R.P. and SEN S.K., *Phys. Rev. B*, **10**, 71, **1974**; *Phys. Rev. B*, **12**, 15, **1975**.
12. VEAL B.V. and PAULIKAS A.P., *Phys. Rev., B*, **31**, 5399, **1985**.
13. STOCH J., CAPECKI A., *Surf. Interface Anal.*, **15**, 206, **1990**.
14. *Practical Surface Analysis*, 2nd ed., Vol.1. Ed. by D.Briggs and M.P.Seah, J.Wiley&Sons, **1990**, Appendix 5, p.595.
15. KIM K.S., BAITINGER W.E., AMY J.W., WINOGRAD N., *J. Electron Spectrosc. Relat. Phenom.*, **5**, 351, **1974**.
16. KIM K.S., WINOGRAD N., *J. Catal.*, **35**, 66, **1974**.
17. MITCHELL P.C.H., SCOTT C.E., BONNELLE J.P., GRIMBLOT J.G., *J. Catal.*, **107**, 482, **1978**.
18. BASIŃSKA A., JÓŹWIAK W.K., GÓRALSKI J., DOMKA F., *Appl. Catal. A*, **190**, 107, **2000**.
19. BARR T.L., *J. Phys. Chem.*, **82**, 1801, **1978**.
20. BRUNDLE C.R., CHUANG T.J. and WANDEL T., *Surf. Sci.*, **68**, 459, **1977**.
21. BASIŃSKA A., WÓJTOWICZ W., WIĘCKOWSKI A.B., DOMKA F., *React. Kinet. Catal. Lett.*, **69**(1), 47, **2000**.
22. SEDDON E.A., SEDDON K.R., *The Chemistry of Ruthenium*, Elsevier Science, New York **1984**.
23. *Chemistry of the Platinum Group Metals: Studies in Inorganic Chemistry 11 Recent Developments*, edited by Frank R. Hartley, Elsevier Science Publishers B.V. **1991**.
24. MUHLER M., SCHÜTZE J., WESEMANN M., RAYMENT T., DENT A., SCHLÖGL R., ERTL G., *J. Catal.*, **126**, 339, **1990**.
25. A.BASIŃSKA, F.DOMKA (to be published).