

Effect of rhenium on copper supported on activated carbon catalysts for methanol decomposition

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Abstract

Rhenium modified copper supported on activated carbon materials with different Re/Cu ratio are prepared by various methods. XRD, EPR, XPS and magnetic measurements are used for their characterization. Their behaviour in the catalytic methanol decomposition to CO and H₂ is also studied and compared. The nature of the catalytic active complex is also discussed.

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1. Introduction

In the last decades methanol gains a considerable interest as a renewable energy carrier for hydrogen storage and transportation [1–5]. In this aspect, methanol synthesis or its transformation into various enriched with hydrogen gaseous mixtures, are of a great importance for the industry. It was reported, that the catalytic methanol decomposition to CO and hydrogen is one of the promising ways in this aspect. For the purpose of its usage, such as automotive fuel or fuel cells, the catalysts must be active at low temperature, selective over a wide range of temperatures and stable during the reaction [1,3,4]. Several types of catalysts have been reported to be suitable for the methanol decomposition [1,3,4,6–9], the main class being the copper based materials [4,10–33]. They are usually commercial catalysts for methanol synthesis, but their selectivity below 500 K as well as their stability at higher temperatures is not sufficient. Nowadays, various methods are

used to improve their catalytic behaviour, and among them the active phase loading on suitable supports [21–24,27] and the addition of different promoters [4,12,34,35] are usually applied. It is known that activated carbon is one of the best catalysts carriers because of its well developed porous structure, high specific surface area, a large number of different functional surface groups and also its catalytic inertness [36–40]. In our previous investigations we observed that copper based activated carbon materials, obtained by the corresponding ammonia precursor are suitable catalysts for methanol decomposition at approximately lower temperatures [41–43]. On the other hand, bimetallic systems reveal unusual possibilities for expansion of the catalysts family [44,45]. In principle, the second metal could be a major source of electron interaction effects and changes in the electron structure of a given metal could occur. The promoter effect, with respect to the additional interaction with the reacting molecule, the blocking mechanism, where the migration of the active metal is prevented, or the formation of bimetallic particles with different catalytic properties are the main mechanisms of the second metal action [44]. For copper supported on activated carbon

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catalysts for methanol decomposition the influence of various metals, such as Cr, Mn, Zn, etc. is studied [4,12,34,35]. However, no information on the effect of rhenium additives into this type of catalysts has been given in the literature yet. The property of rhenium species, which are capable of adopting a variety of oxidation states, may provide rich and interesting chemistry. In this aspect, rhenium based materials are known to be good catalysts for metathesis of functionally substituted olefins [46], oxidation of methanol [47] or alcohols dehydrogenation [48]. Re is also known as a promoter for number of catalysts for refining industry, CO hydrogenation, etc. [49–51].

The aim of the present paper is to study the effect of rhenium additives to copper supported on activated carbon catalysts for methanol decomposition. Special attention is paid on the nature of the catalytic active sites of the modified materials.

2. Experimental

2.1. Materials

An activated carbon (commercial product, obtained from apricot shells) with specific surface area of 910 m²/g and pore volume of 0.64 cm³/g was used as a support [52]. Three various methods were applied for metals deposition.

Method 1. The 2.0 g of activated carbon (AC) was impregnated for 24 h with 6.8% solution of copper ammonium hydroxy carbonate (pH 9.9). After drying at 303 K for 2 h, the samples were heated at 573 K for 6 h (heating rate was 0.6 K/min) in vacuum. As prepared material was denoted as 5Cu/AC and it was used as a reference sample in the paper [42]. After that, the obtained material was spraying with 1% aqueous solution of NH₄ReO₄ (the number of the sprayings depends on the desired Re content). The sample was drying at 303 K for 2 h and after that treated at 573 K for 6 h (heating rate was 0.6 K/min). The samples were denoted as *x*Re5Cu/AC-1, where *x* is the rhenium content (wt.%).

Method 2. The 2.0 g of AC was spraying with 1% aqueous solution of NH₄ReO₄. The sample was drying at 303 K for 2 h and after that treated at 573 K for 6 h (heating rate was 0.6 K/min). As prepared material was denoted as 1.5Re/AC and it was used as a reference sample in the paper. After that, the obtained material was impregnated for 24 h with 6.8% solution of copper ammonium hydroxy carbonate (pH 9.9). After drying at 303 K for 2 h, the sample was heated at 573 K for 6 h (heating rate was 0.6 K/min) in vacuum. The obtained material was denoted as 1.5Re5Cu/AC-2.

Method 3. The 2.0 g of AC was four-fold spraying by mixture of aqueous solutions of NH₄ReO₄ and copper ammonium hydroxy carbonate (Re:Cu = 0.3). After drying at 303 K for 2 h, the sample was heated at 573 K for 6 h (heating rate

Table 1
Composition and specific surface area of Cu and Re supported on activated carbon materials

Samples	Chemical composition			<i>S</i> _{BET} (m ² /g)
	Re (wt.%)	Cu (wt.%)	Re/Cu atomic ratio	
0.5Re5Cu/AC-1	0.5	5.0	0.03	422
0.7Re5Cu/AC-1	0.7	5.0	0.05	668
1.0Re5Cu/AC-1	1.0	5.0	0.07	686
1.5Re5Cu/AC-1	1.5	5.0	0.10	454
1.5Re5Cu/AC-2	1.5	5.0	0.10	910
1.5Re5Cu/AC-3	1.5	5.0	0.10	350

was 0.6 K/min) in vacuum. The obtained material was denoted as 1.5Re5Cu/AC-3.

Some characteristics of the initial copper and rhenium-modified materials are presented in Table 1.

2.2. Methods of investigation

Textural characteristics were determined by low-temperature (77.4 K) nitrogen adsorption. The specific surface area was estimated by BET method. Cu content in the samples was determined by atomic absorption technique with Pye Unicam SP90V. Re content in the samples was determined by vacuum thermal extraction and following quantitative kinetic analysis, based on the catalytic activity of Re(IV) to the *N,N*-dimethyldithiooxamide (DMDTO) reduction with SnCl₂ in alkaline medium. An alkaline extraction of rhenium from the activated carbon, followed by the quantitative kinetic determination was also done [53,54]. The magnetic measurements were performed with Faraday type magnetic balance in the temperature range of 298–473 K. The EPR spectra were done with ERS 22Q spectrometer at 100–400 K. XP spectra were registered using an ESCALAB MkII (VG Scientific). X-ray diffraction powder patterns were obtained on Philips APD-15 diffractometer equipped with Cu K α radiation source and graphite monochromator.

2.3. Catalytic test

The catalytic experiments were carried out in a flow reactor (0.1 g of catalyst, three times diluted with grounded glass), Ar being used as a carrier gas (50 ml/min). The methanol partial pressure was 1.57 kPa. The catalysts were tested under conditions of a thermo-programmed regime of heating rate 2 K/min within the temperature range of 400–670 K. Some experiments with selected samples under isothermal conditions at 585 and 630 K were also done. The gas chromatographic analysis was performed on-line by use of a Porapak Q and molecular sieve columns. The results were calculated using the method of absolute calibration. A carbon-based material balance was done. Before the catalytic test, the samples were pre-treated for an hour at 373 K in argon.

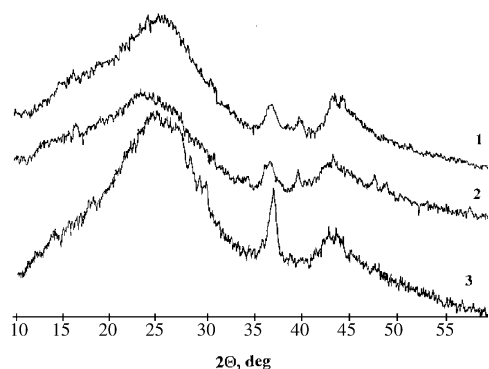


Fig. 1. XRD spectra of selected samples prepared by various methods: 1.5Re5Cu/AC-1 (1), 1.5Re5Cu/AC-2 (2) and 1.5Re5Cu/AC-3 (3).

3. Results

3.1. Physicochemical characterization of rhenium modified materials

3.1.1. XRD spectra

Powder X-ray diffraction patterns of selected samples, obtained by different preparation procedures are given in Fig. 1. They are almost similar for all the samples prepared by consecutive metals deposition (curves 1 and 2). Here, only reflections, typical of CuO are observed. However, new types of reflections, belonging to Cu₂O are found for the sample obtained by Method 3 (curve 3). At the same time, no reflections of copper or rhenium containing phases are registered for the reference 5Cu/AC and 1.5Re/AC samples (not shown).

3.1.2. Magnetic measurements

In Table 2 data on the specific magnetic susceptibility (χ) and the effective magnetic moments (μ_{eff}) for the studied bimetallic materials are presented. Taking into account the diamagnetism of Re(VII), Re(0), Cu(I) and Cu(0) species, and also the data from the spectral experiments (see Section 3.1.3), the observed results could be ascribed mainly to the presence of paramagnetic Cu(II) and Re(IV) ions. So, the theoretical values of magnetic moments (μ_{t}) were calculated only on the base of the corresponding content of Re(IV) and Cu(II) ions for each sample (Table 2). According to [55], μ_{t} for Cu(II) and Re(IV) is 2.08 and 3.87 BM, respectively. The observed essential differences in the specific magnetic susceptibility (Table 2) could be associated mainly to the changes

Table 2
Magnetic susceptibility (χ), effective magnetic moments (μ_{eff}) and theoretic magnetic moments (μ_{t}) of Cu and Re supported on activated carbon materials

Samples	χ ($\times 10^{-6}$)	μ_{eff} (BM)	μ_{t} (BM)
0.5Re5Cu/AC-1	0.410	2.01	2.21
0.7Re5Cu/AC-1	1.400	2.81	2.26
1.0Re5Cu/AC-1	-0.201	1.24	2.32
1.5Re5Cu/AC-1	-0.412	0.81	2.44
1.5Re5Cu/AC-2	0.262	1.61	2.44
1.5Re5Cu/AC-3	0.856	2.20	2.44

of the Cu(II) and Re(IV) ions amount. However, the similar values of μ_{eff} and μ_{t} which are observed for the samples with lower Re/Cu ratio (0.03 and 0.05), and also for 1.5Re5Cu/AC-3, could be an indication for the predominantly presence of Cu(II) and Re(IV) in them. At the same time, the lower values of μ_{eff} in comparison with the corresponding μ_{t} which are obtained for the samples with higher Re content (prepared by Methods 1 and 2) could be an evidence for the increase of the relative part of diamagnetic species in these materials.

3.1.3. EPR spectra

Additional information for the copper and rhenium state in the studied samples is obtained by EPR spectroscopy (Fig. 2). Data for selected materials are presented only. It is worth noting that Cu(II) in CuO phase as well as Cu(I) ions do not give EPR signals. Two types of copper ions could be distinguished in the spectra of the corresponding monocomponent sample [42]. The first one, giving a single line width of 25 mT is more probably from magnetically coupled Cu(II) ions. The second one, characterized with $g_{\parallel} = 2.3$, $g_{\perp} = 2.04$, $A_{\parallel} = 15.9$ mT and $A_{\perp} = 2$ mT belongs to the single Cu(II) ions, bonded only to the support. At the same time, a very broad and low signal, with high value of A constant of fine interaction, probably belonging to Re(IV), is detected for 1.5Re/AC (Fig. 2). Two types of signals are registered in all bimetallic samples. The first sharp signal could be ascribed to the presence of single Cu(II) ions. Its intensity essentially decreases when a simultaneous deposition of metals is applied (Fig. 2). The second, broader EPR signal, could be due to the presence of Re(IV) ions, probably magnetically interacted with the copper ions. Its intensity decreases with the temperature increase, but even then it remains larger for 1.5Re5Cu/AC-3 in comparison with the other bimetallic samples. The presence of isolated Re(IV) ions is not excluded in this case as well.

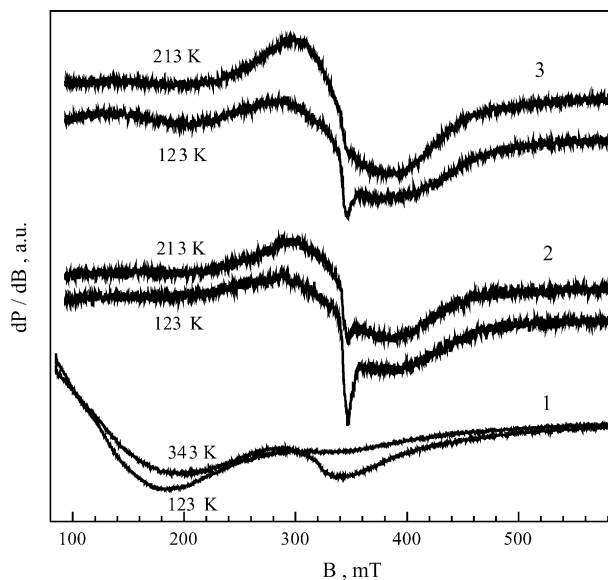


Fig. 2. EPR spectra of selected samples: 1.5 Re/AC (1), 1.5Re5Cu/AC-1 (2), 1.5Re5Cu/AC-3 (3).

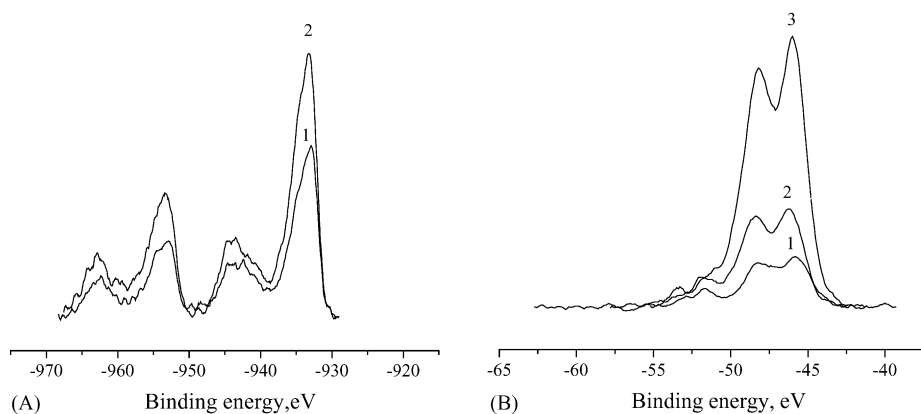


Fig. 3. XPS of selected samples: (A) Cu $2p_{2/3}$ photoelectron lines for 1.5Re5Cu/AC-1 (1) and 1.5Re5Cu/AC-3 (2) and (B) Re 4f photoelectron lines for 1.5Re5Cu/AC-1 (1), 1.5Re/AC (2) and 1.5Re5Cu/AC-3 (3).

3.1.4. XPS analysis

In Fig. 3 and Table 3 are presented Cu $2p_{2/3}$ (Fig. 3A) and Re 4f (Fig. 3B) photoelectron lines for selected samples. According to the spectra, CuO, Cu₂O and Re₂O₇ are the main observed phases for all the samples [41]. However, the main line of Re 4f for the bimetallic samples exhibits higher value of binding energy as compared to that one of the reference sample (1.5Re/AC), which could be an indication for the presence of different types of rhenium oxides in them. Different values of Re/Cu surface ratio are also calculated for both bimetallic materials (Table 3), the latter being about 3 times higher for the sample prepared by Method 3.

3.2. Catalytic study

In Figs. 4 and 5 are presented the temperature dependencies of methanol decomposition for various copper–rhenium supported on activated carbon materials. For comparison, catalytic data for the corresponding monocomponent metal systems are also shown (Fig. 4). All bicomponent materials exhibit a catalytic activity just above 500 K and the main registered carbon containing product is CO. Only small amounts of methyl formate (FM) (below 2%) at lower temperatures and methane (4–8%) above 600 K are observed. The conversion curves are significantly shifted to the higher temperatures with the increase of the Re loading in the samples, which could be an evidence for the corresponding catalysts activity decrease (Fig. 5). A complex character of the conversion curves, which are characterized with a maximum at 550–600 K is observed as well (Fig. 5). The catalytic activity of the samples with similar Re/Cu ratio is not affected

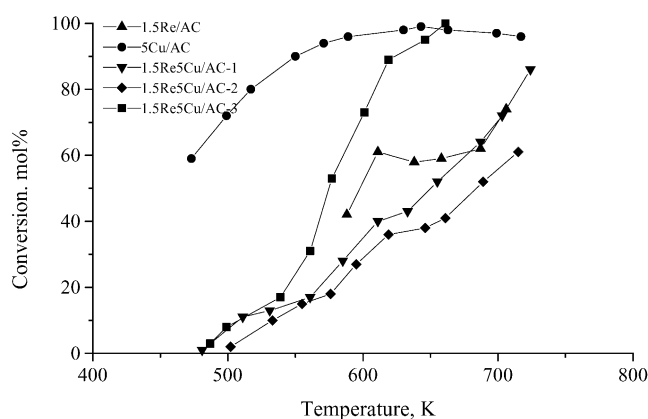


Fig. 4. Methanol conversion vs. temperature for copper and/or rhenium modified by various methods and materials.

significantly with the changes of the metals deposition sequence (Fig. 4) but it is essentially improved when a preparation method with a simultaneous metals loading is applied (1.5ReCu/AC-3). At the same time, 5Cu/AC exhibits much higher catalytic activity and selectivity to MF (about 22%) in comparison with all rhenium modified materials (Fig. 4). On the contrary, lower catalytic activity and no MF are registered for 1.5Re/AC, but similarly to the bicomponent materials, up to 6% methane are found above 600 K. In order to clear the observed results (Figs. 4 and 5), some isothermal experiments at selected temperatures were carried out (Figs. 6 and 7) as well. The catalytic activity for 5Cu/AC and 1.5Re5Cu/AC-3 at 585 K remains almost unchanged for 1 h, while a well defined tendency for its decrease is found for 1.5Re 5Cu/AC-1 and 1.5Re 5Cu/AC-2 (Fig. 6). The later effect is significantly

Table 3
Energies of Cu $2p_{3/2}$, O 1s and Re 4f lines of selected samples

Samples	Ratio of Re/Cu	Cu $2p_{3/2}$			Re 4f			O 1s		
		CuO	Cu ₂ O	Cu	Re ₂ O ₇	ReO ₂	Re	CuO	Cu ₂ O	Cu
1.5Re/AC	–	–	–	–	45.7	–	–	–	–	–
1.5Re5Cu/AC-1	0.109	934.2	933.0	–	46.1	–	–	531.8	532.9	–
1.5Re5Cu/AC-3	0.326	934.5	933.0	–	46.0	–	–	533.0	532.0	–

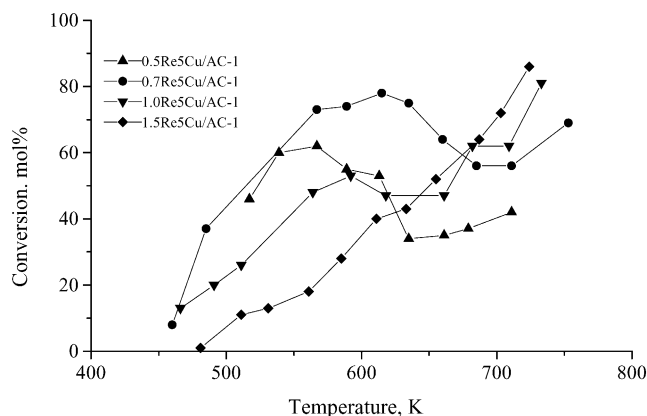


Fig. 5. Methanol conversion vs. temperature for samples with different Re/Cu ratio prepared by Method 1.

higher with the temperature increase (Fig. 7) and about four-fold decrease of the catalytic activity during 40 min time on stream is registered for 1.5Re/AC and also for all bimetallic samples obtained by Methods 1 and 2. It is worth mentioning as well, that 5Cu/AC also exhibits a significant reduction of its catalytic stability with the temperature increase (Fig. 7).

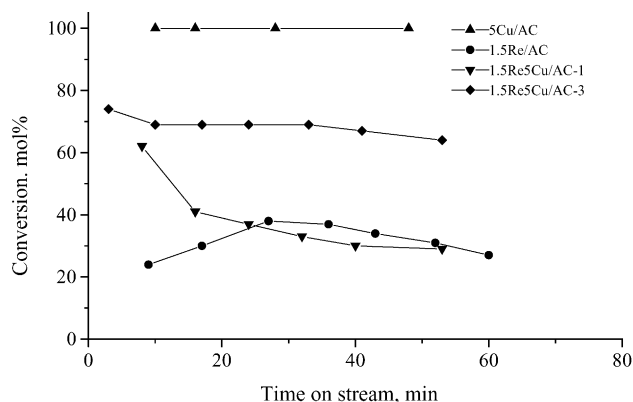


Fig. 6. Methanol conversion at 585 K for selected copper and/or rhenium modified samples.

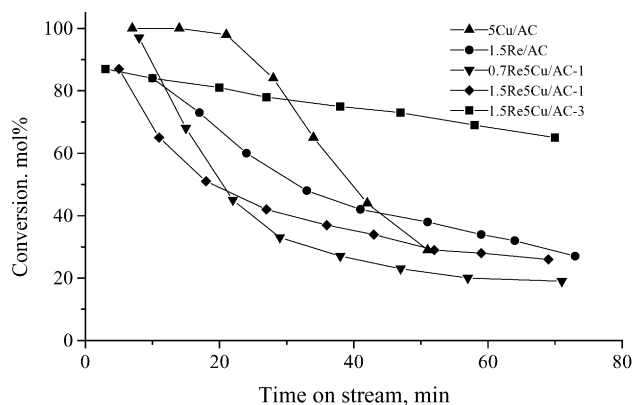


Fig. 7. Methanol conversion at 630 K for selected copper and/or rhenium modified samples.

On the contrary, under the same conditions, essentially lower changes in the methanol conversion for 1.5Re5Cu/AC-3 are observed.

4. Discussion

Three general catalytic effects in methanol decomposition with rhenium addition to copper based materials could be established. First, a well-defined tendency of methanol conversion decrease in comparison with 5Cu/AC is observed for all bimetallic samples (Figs. 4 and 5). The magnitude of this effect depends not only on the rhenium content of the samples but also on the procedure of the metals deposition used. As a whole, the increase in the Re/Cu ratio of the samples prepared by consecutive metals deposition reduces their catalytic activity (Fig. 5). However, the conversion decrease is considerably lower for the sample prepared by simultaneous metals loading, despite the higher rhenium content in it (Fig. 4). The second effect concerns the catalysts stability (Figs. 6 and 7). All bicomponent samples rapidly lose their catalytic activity even at lower temperatures, which is in contrast with 5Cu/AC (Fig. 6). Only in the case of the sample prepared by Method 3, a significant increase of the catalytic stability is observed even at 630 K, where a deactivation for all other copper loaded samples occurs (Fig. 7). Finally, an essential decrease in the MF formation and also the appearance of small amounts of methane are found for all studied bimetallic materials.

According to the nitrogen adsorption (Table 1) and XRD data (Fig. 1), some specific structural changes with Re modified copper based materials occur. A significant decrease of BET surface area, which could be an indication for the support structure collapse is established for some bicomponent samples. On the other hand, the appearance of copper oxides phase for all rhenium-containing samples is found by XRD spectra (Fig. 1), which is in contrast with 5Cu/AC, where no reflections typical of copper oxides are registered [42]. Obviously, the observed structural effects could not explain the catalytic peculiarities of the samples and the problem seems to be closely related to the nature of the catalytic active sites. Number of papers dealing the state of copper on carbon supports is known [56–65], but no data for rhenium influence on it have been reported yet. On the other hand, the data on the role of different copper species in methanol decomposition are usually rather different [12,16,20,28]. In our previous study, the formation of catalytic active complex (CAC) for various copper based porous materials was discussed [34,35,41–43,66,67]. For AC based materials, the participation of copper species in various oxidative state, one of them being Cu(I) in CAC formation was assumed [34,35,41–43]. Here, the observed catalytic effects clearly indicate that some essential changes in CAC with rhenium modification occur. According to data obtained by EPR, XPS and magnetic measurements (Section 3.1) one can be concluded that Cu and Re species in different oxidative state are formed during the

process of catalysts preparation. Simultaneous presence of Cu(I), Cu(II), Re(IV) and Re(VII) species is found in all bimetallic samples, but their distribution depends on the rhenium loading and also on the preparation procedure used. The magnetic measurements show that the relative part of Cu(II) and Re(IV) ions increases with the decrease of Re/Cu ratio or when the simultaneous procedure of metals deposition is applied (Table 2). At the same time, higher catalytic activity is achieved for these samples. More over the existence of strong interaction between Cu(II) and Re(IV) species could be assumed according to the corresponding EPR spectra (Fig. 2). This effect gradually increases for 1.5Re5Cu/AC-3 where more stable catalytic activity with time on stream is observed. In addition, higher Re/Cu surface ratio (1:3) for the later material is found by XPS analysis. So, the formation of CAC, containing strongly interacted between themselves both copper for rhenium species in different oxidative state, could be assumed. An intensive electron transfer of a type Re(VII) \rightarrow Re(IV) as well as Cu(0) \rightarrow Cu(I) \rightarrow Cu(II) during the catalysts preparation, and also due to the influence of the reaction medium could be proposed. As a result, two general effects on CAC characteristics could be considered. First, the stabilisation of Cu ions in various oxidative state, which probably improves the catalysts stability even at higher temperatures, occurs. More over, it is not excluded the catalytic stability of the samples to be favourite only by the formation of CAC with defined structure and composition, as it was approximately achieved for 1.Re5Cu/AC-3. Second, the electronic properties of CAC seems to be essentially changed in comparison with the monocomponent copper based materials. As a result, changes in the methanol adsorption ability and also in the –O–H bond polarisation of the methanol molecule, leading to the changes of the reaction mechanism [10,68,69] could be suggested as well.

5. Conclusions

Rhenium modified copper supported on activated carbon materials exhibit lower catalytic activity and changes of the methanol decomposition selectivity in comparison with the their monocomponent copper analogues. The simultaneous metals deposition significantly improves the catalysts stability at higher temperatures, but it seems that a defined Re/Cu ratio is also required. The formation of CAC with a complex composition is assumed to be responsible for the observed results.

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