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Report on the PhD Thesis
of Mrs. Sylwia TURCZYNIAK

The manuscript of the Thesis of Mrs Sylwia Turczyniak is entitled « Surface composition of cobalt catalysts for steam reforming of ethanol ». The subject of the thesis is indeed devoted to the fine characterization of new catalysts for steam reforming of ethanol (ESR) based on cobalt nanoparticles supported on ceria or zirconia powder oxides. Ethanol steam reforming is a promising way to produce hydrogen in a clean and renewable way. Indeed, ethanol can be produced easily in large quantity from biomass. The use of cobalt catalysts is an alternative to the use of expensive and rare precious metal catalysts like Rh, Pt, Pd or Ru supported mainly on alumina. However, Co on alumina catalysts are less active and rapidly become heavily contaminated by carbon deposits (coke). Recently, Co on ceria and Co on zirconia catalysts have shown high activity in ESR. Furthermore, carbon deposition can be strongly reduced by the presence of potassium. These new catalysts are now subject to many studies but a clear understanding of the ESR reaction on them is still lacking. The aim of the thesis was to clarify the relative role of the Co particles, the oxide support and the effect of K as a promoter. The chosen way is to characterize the surface state of the catalyst before, during and after the reaction by using as a main tool high resolution XPS. Additional characterization techniques like TEM, AFM provide more information about the dispersion of the metal particles and the oxide powders. In parallel to the surface state characterization, the performances of the catalysts are measured by gas phase chromatography or mass spectrometry for the in situ in operando experiments. Thanks to the use of ambient pressure XPS these two measurements have been possible in the low pressure range (0-0.2 mbar). From these measurements made carefully as a function of the reactions parameters (temperature, total pressure, ratio of the reactants, reaction time) and systematically performed on different catalysts (Co/ceria, Co/zirconia with two mean sizes of the oxide support particles and with or without K promoter). A detailed description of the role in ESR of the chemical state of the Co particles and oxide support and of the promoter has been obtained. Furthermore these results clarify some controversial points emerging from the abundant literature on the subject.

The manuscript is long (almost 280 pages) but always clearly written and well-illustrated that allows an easy reading. It is divided in 6 main chapters. It begins by an extended abstract in three languages (English, French, Polish) and it is followed by a general introduction of the subject. At the end of the manuscript a general conclusion summarizes in a comprehensive way the main results obtained during the thesis.

Chapter I present an extensive review of the literature on ESR. This chapter is really excellent it present a comprehensive view of the actual knowledge on ESR on Co based catalyst. The roles of Co dispersion and mainly of Co oxidation state are particularly detailed and show some contradictions in published results. The active role of the ceria support is also well discussed. Oxygen from the substrate take part on the oxidation of cobalt but this is also influenced by the reaction conditions (total pressure, reactant relative partial pressure, temperature) and justified the necessity of in situ – in operando measurements. Promoters (like alkali metals) have been widely used to improve the catalysts activity and stability but their role is not well understood.

Chapter II is the first chapter concerning the results obtained during the thesis. It concerns the relation between the surface state and the catalytic activity in ESR on Co/CeO₂ catalysts. The catalysts are prepared by impregnation and calcination. Before the reaction they are oxidized under oxygen or reduced under hydrogen. The size of the ceria particles is determined by XRD, STEM and AFM. The size of the cobalt particles are determined by hydrogen chemisorption. Despite the fact that that microscopic characterization have been made by a powerful TEM (TITAN G2, 300 kV) in STEM mode, the particle size has not been measured by TEM. The comparison with chemisorption measured would be interesting. The surface state of the catalysts has been studied in situ under reaction at 0.2 mbar by Ambient Pressure XPS (at the BESSY synchrotron). These kinds of measurements are very important to monitor the effect of the environment (reactant and products) during the reaction. The reaction rate is followed by mass spectrometry. During the reaction the Co particles are purely metallic whatever the initial state (reduced or oxidized) and the ceria support is partly reduced. Conversion of ethanol is observed but it gives more CO than CO₂. The conversion is larger when ceria is less reduced. These results are characteristic of ESR at low pressure. The effect of reactant pressures on the surface state has been tested by XPS under UHV after reaction. When the pressure increases from 0.2 to 20 mbar Co becomes partially oxidized while Ce becomes less reduced. The selectivity of the reaction changes from CO to CO₂ production. The results are followed by a very good discussion which takes into account the literature results. A detailed mechanism for ESR is proposed explaining low pressure and high pressure conditions which is very convincing. The explanation for the higher selectivity toward CO₂ at high pressure is that adsorbed acetaldehyde is not directly dissociated to form CO but it form acetate with oxygen at the cobalt-ceria interface which decomposes in CO₂ and adsorbed CH₃.

Chapter 3 is devoted to the effect of the size of cobalt and ceria particles and of the presence of potassium in the selectivity of ESR. Two types of ceria were used with average sizes of 87.1 nm (LS-ceria) or 26.5 nm (HS-ceria). These two supports give two different sizes of Co particles, 39.3 and 3.8 nm, respectively. On the HS-Co/CeO₂ catalyst the selectivity in CO₂ is larger and the carbon contamination is smaller in comparison to LS-Co/CeO₂ catalyst. In the better catalyst (HS-Co/CeO₂) Co is more oxidized than on the other. The larger oxidation of Co on HS-Co/CeO₂ sample is attributed to the higher oxidizability of small Co particles which should be also increased by smaller ceria particles. In fact it is difficult to separate the effect of particle size of cobalt and of ceria because they change simultaneously in the two samples. The effect of the H₂O/EtOH ratio has been also studied in detail. When it increases both Ce and Co become more oxidized but the proportion of cobalt oxide reaches a maximum value (34%) whatever the sample, this proves that both metallic and oxidized Co are always present during the reaction at high pressure. The increase of the oxidation state is explained by the high content of water; the fact that it reaches a maximum is probably due to the presence of hydrogen. When the H₂O content increases the selectivity towards CO₂ increases. To understand this increase of selectivity it has been correlated tentatively with the degree of the oxidation of Co particles, with the reduction of ceria or with the OH content. A good correlation is obtained with the content of OH. The higher selectivity of the HS-Co/CeO₂ is attributed to the smaller particle size (3.8 nm against 39 nm) which presents a higher density of low-coordinated sites.

The presence of K has a huge effect on the stability of the ESR catalyst: practically no coking appears even at low H₂O/EtOH ratio. This effect is correlated with the presence of a form of oxidized K (probably KO). The K promoter has another role which is to increase the selectivity up to almost the stoichiometric ratio of the reaction for all the H₂O/EtOH ratios studied. This important increase in the selectivity relatively to unpromoted samples is convincingly explained by the presence KO species which provide additional selective sites for the reaction.

Chapter 4 presents the effect of the reaction time (1 h to 7 h) on the catalysts performances. The same catalysts as in the previous chapter are used. The unpromoted highly dispersed sample is continuously oxidized by increasing the reaction time while the two other samples are continuously reduced. However all the samples present 100 % of conversion and after 3 hours the selectivity in CO₂ is stable and very high (more than 90%). For the three samples the ceria support is progressively reduced. The highly dispersed unpromoted sample becomes contaminated for long reaction times while the promoted one stays free of coke.

From chapter 5 a new support is investigated which is zirconia. As before two zirconia powders are used, one (HS) presents smaller ceria particles (25.7 nm) and the other (LS) has larger particles (86.9 nm). As in the case of ceria support the cobalt particles on HS-ZrO₂ are smaller (22.5 instead of 42.3 for LS-ZrO₂). For the K-promoted sample (HS-K/ZrO₂) the Co particles have about the size for the LS/ZrO₂ sample (43.5nm). The big difference between CeO₂ and ZrO₂ supports is that ZrO₂ is never reduced. This is probably the reason why the cobalt particles are less oxidized than in the case of ceria. The carbon contamination is higher than in the case of ceria support. By increasing the H₂O/EtOH ratio the oxidation of cobalt particles increases and the carbon contamination decreases like for Co/CeO₂ catalysts. On the K promoted sample no coking occurs. The selectivity in CO₂ is rather good but less than for Co/CeO₂. The selectivity increases from LC to HS samples and with the presence of K promoter. A good correlation is obtained between the increase of selectivity and the increase of the oxidation degree of Co but the correlation is not so good with the total amount of CoII. A correlation is also observed between selectivity and the amount of OH. Then it is concluded that the OH species is responsible for the selectivity in CO₂. However LS-Co/ZrO₂ sample is definitely less selective than the two other samples. This fact is explained by the lower dispersion of Co and zirconia particles. This argument was already invoked for the Co particles in ceria supported catalysts by the larger proportion of low coordinated sites on Co/HS-ceria where the particles are very small (3.8 nm against 39.3 nm in Co/LS-ceria). But in the present case the particles on HS-ZrO₂ have a diameter of 22.5 nm and the proportion of low coordinated sites is certainly low and not very different with the 42.3 nm in the LS-ZrO₂ sample. Thus it is rather difficult to attribute the selectivity to only one factor. The resistance to coking is clearly correlated with the amount of oxygen containing species (OH + KO). If the coverage of these species is at least 25% no coking occurs.

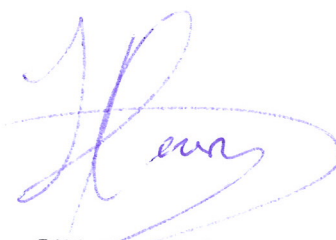
Chapter 6 presents the effect of the reaction time on the performances of the Co/ZrO₂ catalysts. The same experimental processes are used as for Co/CeO₂ catalysts. Severe coking appears which produces about 50% of the atomic concentration after two hours of reaction on the unpromoted catalysts, while no coking is observed on the K-promoted sample even after 7 hours of reaction. On the unpromoted samples the quantity of Co decreases as a function of the reaction time and not on the K-promoted catalysts. During the first hour of reaction the Co particles become more oxidized and reach an equilibrium value. During the first hour the quantity of OH increases and later it is stable on the unpromoted samples. The selectivity in CO₂ is constant as a function of the reaction time for the unpromoted HS sample while it slowly decreases for the LS sample. It is difficult to attribute the variation of selectivity for the two unpromoted samples either to the degree of oxidation of the Co which is constant after about 1 h, or to the quantity of OH which is larger on the LS sample. The measurements on the K promoted sample confirms that KO provides new sites responsible for the selectivity.

The last part of the manuscript summarizes the main results obtained during the thesis and gives a synthetic view of surface state of the studied catalyst during the ethanol steam reforming. In particular the role of the oxidation state of Co and Ce, the role of the reaction pressure, the role of the H₂O/EtOH ratio, the role of adsorbed OH and the role of K promoter are presented in a comprehensive way.

The work presented in this thesis is impressive by the quality and the quantity of the results. The striking point of the work is the methodologic approach which allows a direct comparison between the different catalysts studied which gives rise to a comprehensive view of the role of the various parameters like nature and dispersion of the support, reaction pressure, reactants composition, role of the precursors. Even if the role on the ESR reaction of some parameters is not completely clear (for example the relative proportion of metallic and oxidic cobalt) the precise measurements obtained in well-defined various conditions provides an accurate data base that will be useful for the large community of researchers working in the field.

It is absolutely clear that the work described in this manuscript largely deserves to be presented for a doctoral thesis in chemistry.

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