

STUDY OF CATALYSTS USED FOR OXIDIZING CARBON MONOXIDE AND HYDROCARBONS IN INDUSTRIAL EXHAUST GASES

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ABSTRACT: Starting from the requirement of an ecological way to reduce emissions in the exhaust gases of thermal power plants, the current paper analyzes the manner of obtaining specific catalysts for oxidizing CO and HC using different support materials (carbon molecular sieve, alumina, zeolite) and high catalytic activity metals (Cu, Co, Mg, Pd, Ni, Zr, Ti) and characterizes these from a physical-structural point of view. The characterization of the prepared catalysts was done by X-ray diffraction, optical microscopy, electronic transmission microscopy, atomic adsorption, textural studies with mercury porosimetry. It was noticed that the presence of palladium considerably improves the reduction degree of copper and cobalt oxides, increases the degree of dispersion and decreases the metal crystal size in the support mass, besides its role as an active catalytic component. These improvements lead to an increase in the catalysts' activity, aspect which will be considered in the next step of the research.

KEY WORDS: catalytic efficiency, catalytic reactor, catalysts, pollutant emissions, selective reduction.

1 INTRODUCTION

Catalysts are chemical substances which, in given reaction conditions, form chemical bonds with different stability grades with other atoms or groups of atoms. Selecting catalysts for a certain application is done after many tests and evaluations. (Gates, 1991)(Janssen, 1997)

A large variety of catalysts are used in technologies used for protecting the environment, according to the composition of exhaust gases.

Choosing a certain type of catalyst depends on many factors and, as such, it is difficult to make a decision because many conditions specific to each component in the process need to be met (Nenitescu, 1985):

- the catalyst needs to have high activity, selectivity and stability; its chemical nature of the components and the effect of additives need to be known;
- the support must have an active surface and high porosity, must be stable and bi-functional and its effect on the chemical activity must be known;
- the reactor must insure a good contact and control and a correct flow.

Correctly selecting these materials and preparation methods assures the obtaining of the right catalysts for the desired goal.

The catalytic action is produced by the chemical interaction of the catalyst with the reactant substances, which opens a new way of reaction, usually more complex as number of steps and composition of the active components, but with lower energy of forming the complexes.

According to the manufacturing technology, the particularities of the preparation method and their chemical nature, solid catalysts are divided into the following categories (Lox and Engler, 1997):

- catalysts obtained by precipitation;
- catalysts obtained by impregnation;
- catalysts obtained by melting;
- catalysts obtained by mixing;
- skeletal catalysts;
- natural catalysts (silicates, aluminum silicates, natural zeolites);
- organic catalysts (ion changing resins, polymers);
- synthetic zeolites catalysts;
- colloidal catalysts.

2 MATERIALS AND METHOD

The experimental research that was done had as objectives the obtaining of specific catalysts for oxidizing CO and HC in the exhaust gases from thermal power plants and calcination ovens. It is reckoned that by placing filters containing such catalysts in the path of exhaust gases, the CO concentration will drop below 0.25% and that of HC below 0.1%. These catalysts are composed of

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metals with high catalytic activity: Cu, Co, Mg, Pd, Ni, Zr, Ti and have as support molecular carbon mesh, alumina and zeolite.

The goal was to obtain catalysts with an active surface area of 5...350 m²/g, total volume of pores of 0.2...0.5 cm³/g, weight contents of active metal ingredient of 0.1...4 % and predominant metal particle dimension under 250Å.

Metallic catalysts always contain the metal in a dispersed state, insuring the maximum available surface area. The metal particles are distributed on a support in order to prevent their agglomeration and to offer mechanical properties necessary for the integration in technological process and to permit heat transfer.

2.1 Support materials used in preparing catalysts

During our research for this paper, zeolites, alumina, carbon and mixes based on metal oxides were used as support. These materials are indicated by the specialty literature as being optimal for obtaining catalysts with applications in diminishing noxious agents from stationary sources (Vielstich and Iwasita, 1997).

The active alumina obtained in a laboratory from aluminum chip has the following characteristics:

- spherical grains with a diameter of 3.5-5 mm;
- density: 0.65 g/cm³;
- specific surface: 280 m²/g;
- pores volume (5...300Å): 0.289 cm³/g;
- mechanical resistance at compression: min 12.36 MPa.

Active carbon was prepared in the laboratory from coal treated with sulfuric acid at 150°C and presents the following characteristics:

- cylindrical grains with a diameter of 3.5-4 mm;
- density: 0.45...0.55 g/cm³;
- specific surface: 10.87 m²/g;
- pores volume (5...300Å): 0.334 cm³/g;
- mechanical resistance at compression: min 11.57 MPa.

The zeolite used as catalytic support is of type 4A, obtained from the molecular mesh factory in Govora, Romania and is characterized by:

- cylindrical grains with a diameter of 3-3.4 mm;
- density: 500...700 g/cm³;
- specific surface: 293.7 m²/g;

- pores volume (5...300Å): 0,137 cm³/g;
- mechanical resistance at compression: 12.75 MPa.

The main characteristics determined for the materials used as catalytic support are presented in Table 1.

Table 1. Materials used as catalytic support and determined characteristics

Material	Porosity [%]	Specific surface [m ² /g]	Density [g/cm ³]	Strength [MPa]	Medium pore diameter [Å]
Alumina (Al ₂ O ₃)	38	280	0.90	12.36	45
Carbon (CMS)	55	10.97	0.51 – 0.55	11.57	30 – 280
Zeolite (Z4A)	30	293.7	1.28	12.75	4 – 6

2.2 Preparing catalysts with the impregnation method.

2.2.1. Copper/carbon (Cu/CMS-1, Cu/CMS-2) catalysts

Copper, as an active component, was introduced on the CMS coal support and two kinds of catalysts were prepared, which differ by the concentration of the active component: Cu/CMS-1 and Cu/CMS-2.

These catalysts were analyzed with the method of atomic adsorption and their main characteristics are presented in Table 2.

Table 2. Copper/carbon catalysts

Catalyst	Cu [%]	C [%]	Cupric compound as precursor	Content in CuO [%]	Specific surface [m ² /g]	Total volume of pores [cm ³ /g]
CMS (support)	-	96.29	-	-	10.97	0.513
Cu/CMS-1	2.26	88.85	Cu(NO ₃) ₂ · 3H ₂ O	8.226	7.93	0.535
Cu/CMS-2	1.4	91.38	Cu(NO ₃) ₂ · 3H ₂ O	5.264	9.22	0.412

2.2.2. Cobalt/alumina (Co/Al₂O₃) catalysts

The preparation of the catalyst consisted of the incorporation of Cobalt in the mass of active alumina. The alumina pearls were impregnated with 0.2 molar alcoholic solution of cobalt nitrate, with a volume 3 times higher than the total pore volume in the alumina. After the decantation of the excess solution, the material was dried for one hour at 140 °C.

The characteristics of Co/Al₂O₃ catalysts are presented in Table 3.

Table 3. Cobalt/alumina catalysts

Catalyst	Co [%]	Al ₂ O ₃ [%]	Cobalt compound as precursor	Content in CoO [%]	Specific surface [m ² /g]	Total volume of pores [cm ³ /g]
Co/Al ₂ O ₃	2.75	97.15	Co(NO ₃) ₂ · 6H ₂ O	3.5	142	0.41

2.3 Metal/zeolite 4A catalysts: Co/Z4A, CoPd/Z4A, Cu/Z4A, CuPd/Z4A, Mg/Z4A

The synthetic zeolite Z4A was used to prepare these catalysts because it is more mechanically resistant than natural zeolites.

In the first step, copper or cobalt were introduced, then half from each type was treated with 1% palladium chloride solution and the final catalytic materials were dried at 250°C.

Cu and Mg catalysts were reduced by heating to 200..300°C for 24 hours in a 4...30% H₂ mix in nitrogen, with a progressive increase of the H₂ concentration.

The catalysts containing cobalt were reduced in the same conditions but at 400...650°C.

The Mg/Z4A catalyst was obtained by impregnating the Z4A support with 10% magnesium acetate solution for 20 hours at room temperature and then 4 hours at 65°C.

The obtained material was heat-treated in air flow to decompose the magnesium acetate with the following cycle: 1 hour for t = 65°C; 100°C; 120°C and 150°C; 2 hours for t = 200°C and 250°C; 4 hours for t = 300°C and 350°C. The temperature gradient was 3...5° C/mm.

For the obtained Mg/Z4A, a hydrogen reduction (4...30% H₂) was then applied in nitrogen at t = 550...600°C for 12 hours.

The metal – active catalytic component – content was determined for all sorts of obtained catalysts with the method of atomic adsorption.

The most important characteristics of these catalysts are presented in Table 4.

Table 4. Catalysts based on copper, magnesium, cobalt, palladium; zeolite 4A support

Catalyst	Cu [%]	Co [%]	Mg [%]	Pd [%]	Chemical compound as precursor	Specific surface [m ² /g]	Total volume of pores [cm ³ /g]
Cu/Z4A	4.38	-	-	-	Cu (CH ₃ COO) ₂	361.82	0.289
CuPd/Z4A	4.38	-	-	0.1	Cu (CH ₃ COO) ₂	392.72	0.302
Co/Z4A	-	3.26	-	-		366.80	0.290
CoPd/Z4A	-	3.26	-	0.1		379.55	0.285
Mg/Z4A	-	-	4.28	-		116	0.410

3 EXPERIMENTAL DETERMINATIONS. CHARACTERIZATION OF THE PREPARED CATALYSTS

3.1 Physical-structural characterization of Cu/CMS catalysts

The physical-structural analyses of the prepared catalysts were done by: X-ray diffraction, optical microscopy, electronic transmission microscopy, atomic adsorption and textural study with a mercury porosimetry [2].

X-ray diffraction was used to determine the crystallization degree and system.

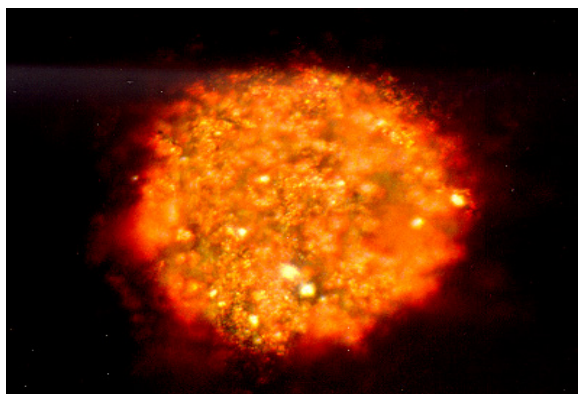
The Cu/CMS-1 catalyst has a crystallization degree of approximately 3% and the Cu/CMS-2 catalyst around 2% and the size of the elementary cell is a_c = 3.615Å.

Optical and electronic microscopy have highlighted the following aspects:

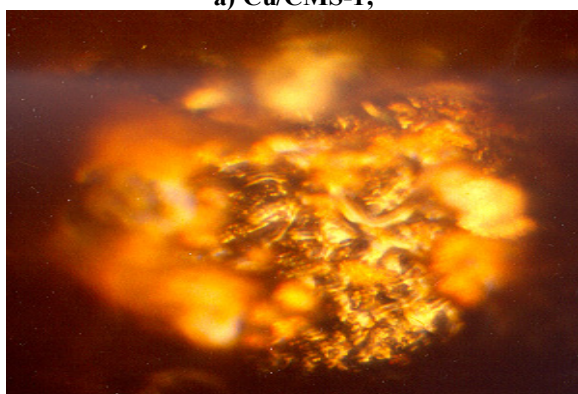
- Cu/CMS-1 catalysts present in polarized light clear deposits of crystals of reddish color with green inclusions; they have a spongy aspect and presents metal clusters as scales with dimensions of 5...10 μm on the granules' surface.
- Cu/CMS-2 catalysts have clear deposits of predominantly cooper-colored crystals with reddish inclusions and they present agglomerations of scales formed from metallic clusters with dimensions of 5...25 μm, but the surface is less rough than Cu/CMS-1.

3.2 The influence of palladium on the reduction process

It was noted that materials presented on Z4A zeolite support, when treated with reduction gas at t = 200...350°C for Cu/Z4A and t = 400...650°C for Co/Z4A for 16 hours, no noticeable changes of color in the zeolite support were obtained, these having a dark grey color for Cu and light grey for Co, which indicates a weak reduction of corresponding oxides.



a) Cu/CMS-1;



b) Cu/CMS-2;

Figure 1. Cu/CMS catalysts



a) CuZ4A



b) CoZ4A

Figure2. Catalysts with zeolite Z4A support

When the CuPd/Z4A and CoPd/Z4A catalysts were subjected to the reduction process under the same conditions, as with those that did not contain palladium,

the catalyst mass was colored black with copper reflexes for CuPd/Z4A and complete black for CoPd/Z4A. This modification of color indicates the strong reduction of copper and cobalt oxides in the presence of palladium.



a) CuPd/Z4A



b) CoPd/Z4A

Figure 3 CuPd/Z4A and CoPd/Z4A

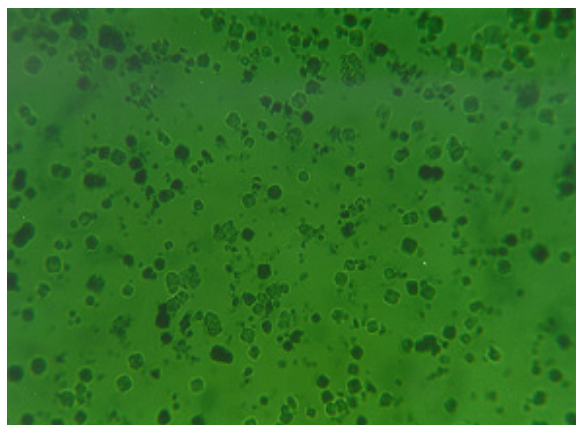
It was noted that palladium also has the role of improving the dispersion rate and decreasing the metal crystal dimensions.

The distribution of Cu or Co crystals in the zeolite mesh before and after reduction was studied by optic and electronic transmission microscopy.

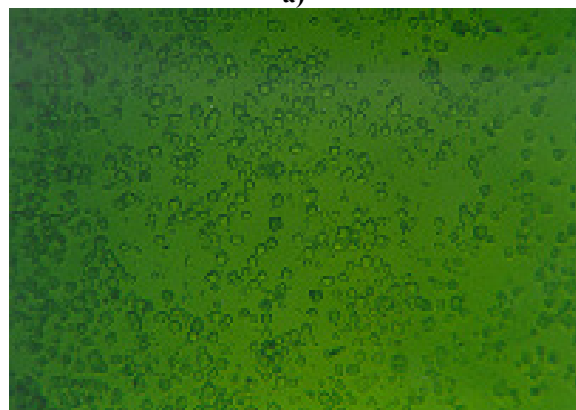
The images of metal crystals on the zeolite support are presented in Figure 4.

For the catalytic samples Co/Z4A and CoPd/Z4A, the microphotographs obtained through electronic microscopy are presented in Figure 5.

The size of all crystals for the CuPd/Z4A catalyst is 10...2800Å while for Cu/Z4A they are 180...4000Å, having also a reduced mobility. For CuPd/Z4A samples, the analyses were difficult to do because of the increased mobility of copper crystals, phenomenon attributed partially to the high oxidation speed of copper, favored by the presence of palladium.



a)



b)

Figure 4. Images obtained through electronic microscopy for a) Cu/Z4A and b) CuPd/Z4A (magnification 75x)

Similar effects were noticed in cobalt and palladium catalysts, where crystal dimensions are under 180\AA .

Without the addition of palladium, cobalt crystals are hard to spot because of the difficult reduction of cobalt oxide to metallic cobalt.

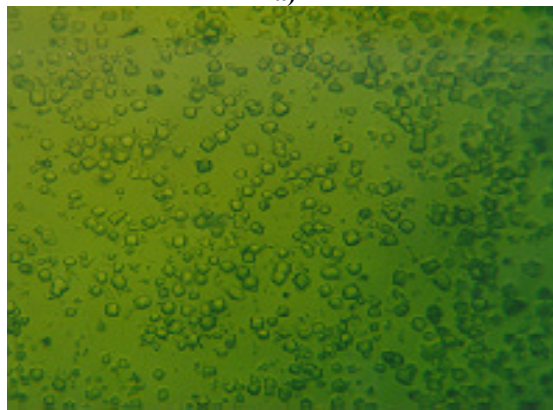
By analyzing the images presented in Figures 4 and 5, it is noted that the presence of palladium decreases cluster and metal crystal size and increases the dispersion and uniformity rates.

Catalysts obtained by impregnation with CuPd and CoPd have a modified structure opposed to that of the zeolite support and present an contracted grid. An opaque phase, the metallic phase, appears on the crystals' surface. In mono-metallic catalysts Cu-zeolite and Co-zeolite, the metal is unevenly distributed, both on large and small crystals.

By adding palladium, the metallic phase disappears from the surface of large particles, leaving them "clean", and it is found mostly on sub-micron particles in amorphous formations. Surfaces with mezopores also decrease by adding palladium.



a)



b)

Figure 5. Images obtained through electronic microscopy for a) Co/Z4A and b) CoPd/Z4A (magnification 75x)

The contraction of the crystal grid can be explained by the intrusion of metal atoms in the zeolite structure, keeping the structural skeleton and modifying only the inter-planar distances, phenomenon known as "grid epitaxy". These structural improvements lead to an increase of the catalysts' activity.

4 CONCLUSIONS

Results obtained by experimental research have highlighted many interesting aspects regarding the prepared catalysts:

- the mechanical resistance of the support materials increases in the following order: CMS > alumina > zeolite 4A;
- the highest thermal stability is obtained in catalysts with cobalt deposited on alumina and zeolite 4A;
- the optimum volume of metallic precursor solution used for impregnation is over 3 times higher than the pore volume of the support material;
- the drying and calcination temperature must be rigorously correlated with the physical

properties of the support material and the chemical compounds of the metallic precursor;

- catalysts obtained by impregnation with Cu and Co do not present significant modifications from the support sample;
- catalysts which also contain palladium have a modified structure from the support zeolite, with a contracted grid;
- the distribution and uniformity of the metallic component in the support material mass increase by adding small quantities of palladium, obtaining smaller particles;
- Research and experiments will continue because their final goal is obtaining catalysts which will be used in diminishing pollutant agents coming from stationary sources like thermal power plants or chalk calcination ovens.

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