

Preparation-Properties Relation of Mn-Cu Hopcalite Catalyst

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Abstract: Problem statement: The Mn-Cu hopcalite catalyst was used for the conversion of CO to CO₂ at low temperatures. It was the catalyst of choice in the gas masks for respiratory protection in mines, aircrafts, military, spatial laboratories. **Approach:** The efficiency of hopcalite catalyst depends on its surface parameters. Its surface characteristics can be influenced from the chosen way of the MnO₂ and CuO precipitation and from the pressure of pelletizing. **Results:** The hopcalite samples has been prepared by precipitation of MnO₂ and by adding CuSO₄ further in the solution the adsorption of Cu²⁺ ions on MnO₂ particles surface is achieved. After acidification of the solution up to pH = 3 the copper is precipitated in form of Cu (OH)₂CuCO₃ by adding NaHCO₃. Precipitate was washed, dried, pressed, crushed, sieved (1-2 mm) and calcined at 180°C for 3 h. MnO₂ and hopcalite samples were characterized by XRD. The activity was evaluated by determination of its protection time and it was 610 min, better than activity of a commercial catalyst. Specific surface area, pore volume and density were measured by nitrogen adsorption and mercury intrusion porosimetry. The X-Ray diffractograms shows that the only crystallinity of hopcalite comes from MnO₂, which is present mainly in amorphous form. By increasing the pressure in the pelletizing step, a significant decrease in the specific surface area (247.64-147.77 m² g⁻¹) and in the total pore volume (446-278 mm³ g⁻¹) is observed in the hopcalite samples. **Conclusion:** The obtained hopcalite catalyst by the two step precipitation method shows high catalytic activity. The increasing pressure increases the strength and reduces the specific surface area and pore volume. A pressure of 500 kg cm⁻² is recommended for the hopcalite production procedure.

Key words: Hopcalite, pelletizing pressure, protection time, porosity

INTRODUCTION

Carbon monoxide is highly toxic and causes human fatalities at concentrations more than 600 ppm in the air. The removal of CO is done by its conversion to CO₂ by using different type of catalysts. Among others, the low temperature oxidation of CO occurs on mixed oxides of manganese and copper, known as hopcalite catalyst (Hutchings *et al.*, 1998). In comparison with other transition metal compounds, manganese oxides are more effective for the low temperature oxidation of CO. On the other hand they are friendly towards environment (Alvarez-Galvan *et al.*, 2003; Sharma *et al.*, 1995; Spivey, 1987).

Hopcalite catalyst is often used for respiratory protection in the gas masks of mining industry, aircrafts, space labs, closed room burning activities (Trimble, 1996; Jagow *et al.*, 1977).

Combination of MnO_x with other metal oxides in specific conditions, exhibit significant higher catalytic activity for CO to CO₂ conversion in comparison to the MnO_x oxides alone (Jagow *et al.*, 1977).

The preparation of hopcalite catalyst is effectuated in different ways like the coprecipitation of manganese and copper oxides (Hutchings *et al.*, 1998; Li *et al.*, 2007; Morales *et al.*, 2006) controlled oxidation of Cu - Mn (30-50% Mn) alloys at temperatures 400-500°C (Yoon and Cocke, 1998), sol-gel synthesis (Kramer *et al.*, 2006) and the two step precipitation method where the manganese and copper are precipitated in two separate steps.

In the preparation of Mn-Cu hopcalite catalyst by precipitation the procedure includes also washing, drying, pelletizing and calcination of the samples. The parameters used in the process of calcination are proved to influence the efficiency of the hopcalite catalyst (Hutchings *et al.*, 1998), mainly due to the changes in its specific surface area. A special attention is given in this study to the pelletizing process since it influences the specific surface area of the prepared hopcalite catalyst as well.

The pelletizing step in the procedure of hopcalite preparation is necessary to give the needed strength to the catalyst pellets, in order to increase the resistance

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against possible pulverization inside the gas mask boxes, which works under mechanical stress. Different preparation steps have an influence on the strength of the hopcalite catalyst like the precipitation conditions, adding of binders, pelletizing pressure, drying and calcination conditions.

In this study the effect of changing the pelletizing pressure from 0-1700 kg cm⁻² on the surface parameters of hopcalite catalysts is measured. The catalytic efficiency of the produced hopcalite catalyst is compared to a commercial one from SIDACO and the changes in its crystalline structure after copper precipitation and after calcination are determined.

MATERIALS AND METHODS

Hopcalite preparation: For the preparation of the hopcalite catalyst were used the following chemicals: KMnO₄ (Peking's Reagent A.R.), NH₄HCO₃ (Peking's Reagent A.R.), CuSO₄ • 5 H₂O (Peking Reagent A.R.) and NaHCO₃ (Peking's Reagent A.R.), H₂SO₄ p.a. (96%, d = 1,83 g cm⁻³).

The two step precipitation method similar to that of, with slight changes is used to produce the hopcalite catalyst. The hopcalite preparation procedure is described schematically in the Fig. 1.

All the catalysts used in this study were prepared after the two step preparation method. In 200 cm³ distilled water at 50°C were added 30 g KMnO₄ and dissolved under continuous stirring. Than 24 g NH₄HCO₃ were added and the solution was heated up to 65°C. Than the precipitation of MnO₂ began, accompanied by a heat release which brought the solution up to the temperature 93 °C. Simultaneously the characteristic color of permanganate disappeared. The solution was cooled down to room temperature and added there H₂SO₄ until pH = 3. In this mixture of precipitated MnO₂ in contact with the solution, we added 26 g of finely grinded CuSO₄ • 5 H₂O and dissolved it under stirring. Afterwards 28 g of NaHCO₃ was added to precipitate the copper in the form of basic copper carbonate Cu(OH)₂CuCO₃. The precipitate was washed with warm distilled water until no further SO₄²⁻ was observed in the washings (BaCl₂ test). The precipitate was dried at 70°C until 14% humidity to give a material denoted as the catalyst precursor which is a fine powder. It was pressed to obtain pellets under 500, 800, 1400 and 1700 kg cm⁻². The pellets were crushed and their fraction of 1-2 mm was selected for further treatment by sieving. The grains were afterwards calcined for 3 h at 180°C. After calcination the hopcalite catalyst samples were kept in exicator under vacuum to protect from humidity.

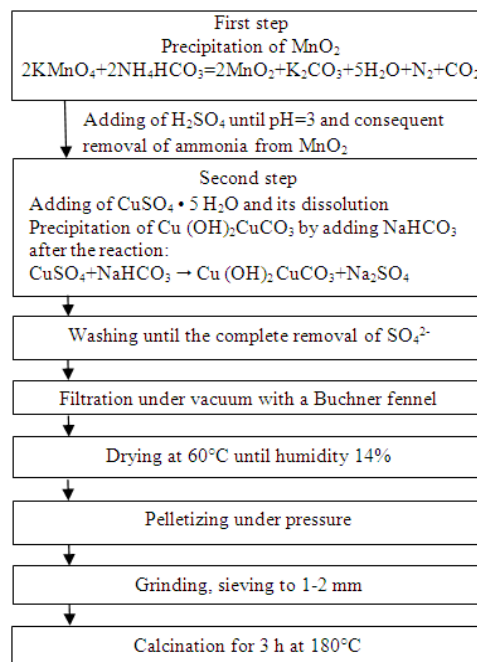


Fig. 1: Schematic procedure of the two step precipitation method used for the production of the hopcalite catalyst

Characterization methods: Samples were characterized by X-Ray diffraction in a Model D 5000 powder diffractometer from Siemens AG Muenchen (CuK_α source of wavelength 1.5406 Å). The measurements were carried out in the range of 2θ = 10-90°.

The specific surface area, the mesopore volume and the density of the hopcalite catalysts were determined by nitrogen adsorption-desorption isotherm at 77 K and Helium filling in a SORPTOMATIC 1900 apparatus of the producer Carlo Erba using the Volumetric Method (VM). The specific surface area was calculated in accordance with the BET method, the mesopore volume in accordance with the Calvin equation for pore diameters from 2-60 nm (Gregg and Sing, 1991), the cumulative mesopore volume after the Gurvich rule and the density by the helium pycnometer principle (Lowell, 2004). The liquid nitrogen (> 99%), nitrogen gas (99,996%) and helium gas (99,996 %) were products of Messer-Albagas. The macropore volume of the hopcalite samples were measured by means of Mercury Intrusion Porosimetry (MIP) in an apparatus Poremaster 60 of the producer Quantachrome Instruments, with the Software Poremaster Version 8. With the pressures applied from 0.138-24.92 MPa it determines the respective pore diameters of 10.85 μm to 60 nm. Calculation of the macropore diameter for a known pressure exerted on mercury is based on the Washburn's equation (Washburn, 1921).

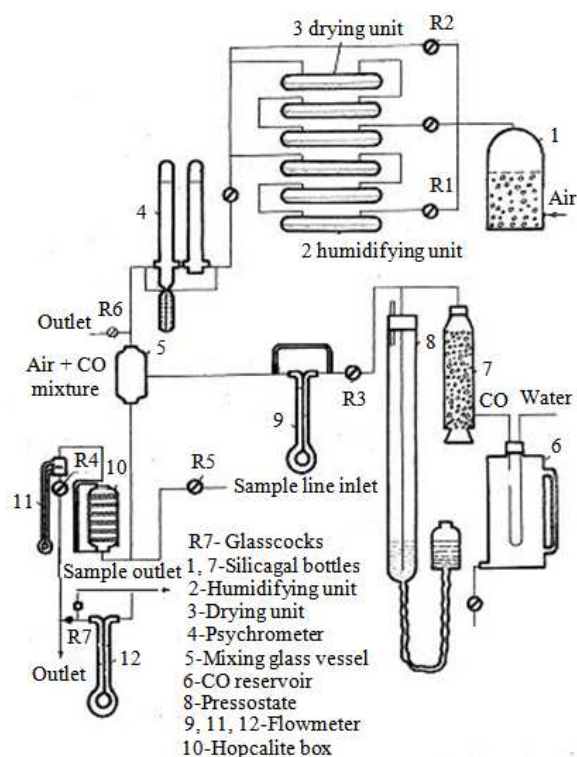


Fig. 2: The schematic construction of the laboratory equipment for determination of the protection time of hopcalite catalyst

Catalyst testing: The hopcalite sample, prepared using a pelletizing pressure of 500 kg cm^{-2} and a sample of commercial hopcalite catalyst of the producer SIDACO (Netherland B.V.) were tested for their catalytic efficiency, expressed in term of protection time. The protection time is determined following a standardized method (similar to standard EN 403) and is measured in the laboratory equipment showed in the Fig. 2.

The amount of 173.5 g of hopcalite sample is filled in the upper volume (135 cm^3) of the gas mask box 10 (cylindrical fixed bed reactor) in which a stream of controlled humidity air and carbon monoxide passes through. The humid air is produced by passing the air firstly through the silicagel bottle 1 in order to dry it after which it is divided in three streams, first one going directly to the psychrometer, second passing through the drying unit 3 (H_2SO_4 cc) and third one through the humidifying unit 2 (water). By controlling the air flow in the glass cocks R-1 and R-2 the humidity of the air is kept constant at 50%. The humidity is measured at the psychrometer 4. Carbon monoxide was produced separately in laboratory conditions by dropping HCOOH over boiling H_2SO_4 (cc) and was stored in

vessel 6, where it is diluted with dry air 3.3 times. CO is passed through the glass cock R-3 by adding water in the vessel 6 and its constant pressure is kept by the pressostat 8. Wet air (R.H. 50%) and carbon monoxide are mixed in the glass vessel 5. The flow rate of the wet air + CO mixture through the box 10 is measured by the flowmeter 11 and the flow rate of CO by the flowmeter 9. The flow rate of the wet air was kept 1800 L h^{-1} and the flow rate of CO was kept 30 L h^{-1} resulting in a concentration of 5000 ppm for CO before entering the box 10. CO concentration was measured after R-5 at the inlet of the box 10 using Draeger tubes of producer Draeger (CH29901) and after R-7 at the outlet of the box using a CO sensor. This sensor is the model MINI-CO of the producer A11 Airstest Technologies, Inc. can detect CO concentrations in the range 0-500 ppm and was calibrated before every measurement for concentration 100 and 300 ppm. The contact time of the hopcalite sample with the flowing gas mixture was 0.267 sec.

RESULTS

The X-Ray diffractograms of the MnO_2 (a), hopcalite sample pressed at 500 kg cm^{-2} before calcination (b) and after calcination (c) are given in the Fig. 3.

In Table 1 are summarized the results obtained by nitrogen sorption and helium filling of the hopcalite samples prepared using different pelletizing pressures. The BET specific surface area, cumulative mesopore volume and the mesopore average diameter are calculated from the nitrogen sorption data and the grain density of the samples is determined by helium filling at room temperature based on the gas pycnometer principle.

The adsorption-desorption isotherms of N_2 at 77 K on hopcalite samples are given in the Fig. 4.

The influence of the pelletizing pressure on cumulative mesopore volume and on the mesopore average diameter is given on the Fig. 5 and 6 respectively.

By the MIP method are determined the volume of the macropores, their pore size distribution as shown in Fig. 7 and 8 respectively and the average macropore diameter. The total volume of the pores and the sample porosity are calculated considering both nitrogen sorption and mercury intrusion experiments data for the hopcalite catalyst and are presented in Table 2 together with the macropore characterization data.

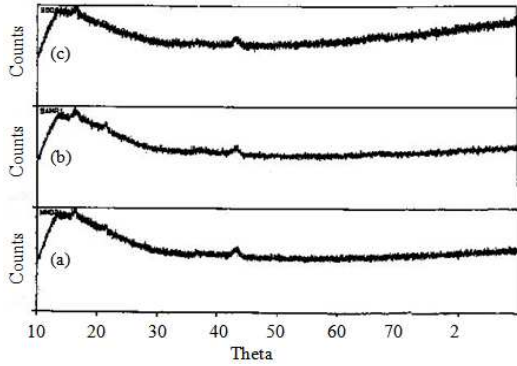


Fig. 3: Diffractograms of (a) in the first step precipitated MnO_2 ; (b) the catalyst $MnO_2 + Cu(OH)_2CuCO_3$ pressed at 500 kg cm^{-2} before calcination and (c) the catalyst prepared using pelletizing pressure 500 kg cm^{-2} and calcined at 180°C

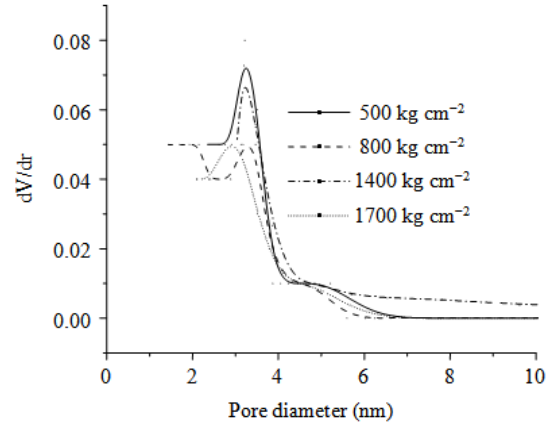


Fig. 6: Differential mesopore size distribution for all hopcalite samples (VM)

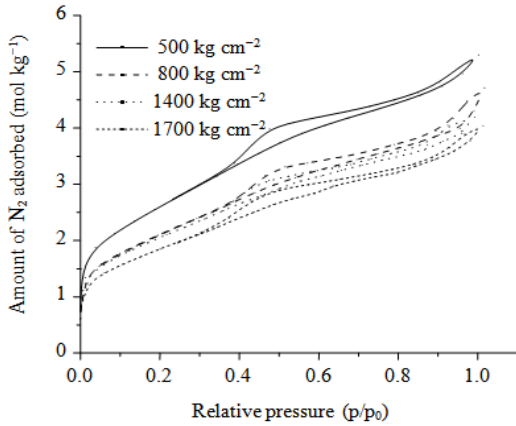


Fig. 4: Adsorption-desorption isotherms of N_2 at 77 K for the all hopcalite samples

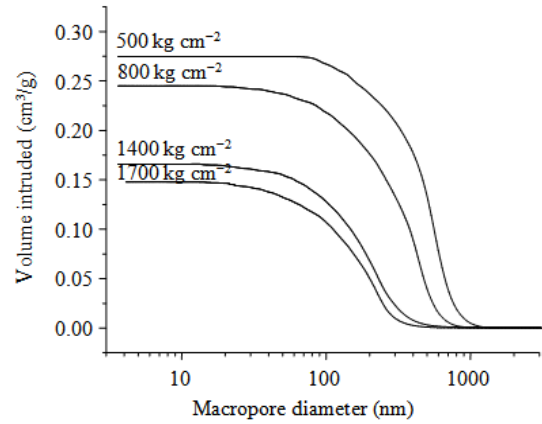


Fig. 7: Macropore volume of all hopcalite samples measured by MIP as function of pore size

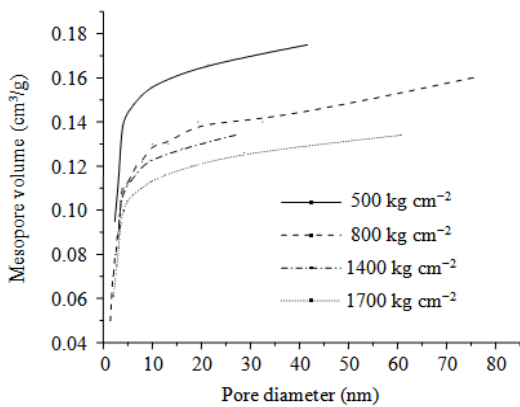


Fig. 5: Mesopore volume of hopcalite samples calculated from nitrogen desorption isotherms as function of the pore size

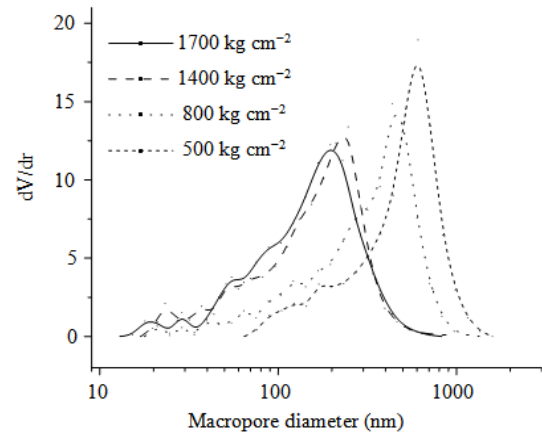


Fig. 8: Differential macropore size distribution of the hopcalite samples (MIP)

Table 1: Effect of the pelletizing pressure on pore structural parameters of hopcalite catalyst derived from nitrogen sorption

Pelletizing pressure /kg cm ⁻²	Specific surface area (BET)/m ² g ⁻¹	V _p (nitrogen)/cm ³ g ⁻¹	Mesopore average diameter/nm	Particle density /g cm ⁻³
0	247.64	0.194	3.0	-
500	209.52	0.171	3.2	3.432
800	169.33	0.148	3.2	3.752
1400	162.46	0.135	3.4	4.215
1700	147.77	0.130	3.4	4.510

Table 2: Effect of the pelletizing pressure on pore structural parameters of hopcalite catalyst derived from mercury intrusion experiments

Pelletizing pressure /kg cm ⁻²	V _p (mercury)/cm ³ g ⁻¹	Mesopore average diameter/nm	V _p total (porosity)/%
0	-	-	-
500	0.275	470.5	0.446 (37)
800	0.245	326.2	0.393 (35)
1400	0.165	236.5	0.300 (31)
1700	0.148	163.6	0.278 (30)

For the hopcalite catalyst prepared by using a pelletizing pressure of 500 kg cm⁻² and for the commercial sample of hopcalite (Hopcalite, Producer SIDACO Netherland B.V.) the protection time was determined in the assembled equipment described in the Fig. 2. The measured protection times were 610 min for the hopcalite sample prepared in this work and 300 min for the commercial sample of SIDACO.

DISCUSSION

A relatively wide peak at $2\theta = 13-16^\circ$ is present in all three diffractograms and it is known to belong to the ϵ -MnO₂ which is one of the more amorphous phases of the manganese oxide. The peak at $2\theta = 42.2^\circ$ comes from a crystalline glue used to stick the powder samples on the sample holder of the X-Ray diffraction apparatus. Another small peak at $2\theta = 21.5^\circ$ which is present at (a) and (b) but disappear after calcination at (c) comes probably from a hydrated form of MnO₂. The absence of other peaks in the diffractograms except of these originating from MnO₂ shows that the Cu atoms does not precipitate in a crystalline form and they do not create mixed crystals with MnO₂ either. The presence of MnO₂ in a highly amorphous form is a premise for a high surface contact with the copper atoms, which from the other hand is a prerequisite for the high activity of hopcalite catalyst (Kramer *et al.*, 2006). However this is still a point of discussion since an activity of the highly crystalline hopcalite is observed as well (Schwab and Canungo, 1977).

The increase of pelletizing pressure from 0-1700 kg cm⁻², brings a steady decrease to respective specific surface areas from 247.64-147.77 m² g⁻¹ and to

respective cumulative mesopore volumes from 0.194-0.130 cm³ g⁻¹, while the mesopore average diameter remains the same around 3.2 nm. The density of hopcalite increases steadily with the increasing pelletizing pressure from 3.432 g cm⁻³ for the pelletizing pressure 500 kg cm⁻² to 4.510 g cm⁻³ for the pelletizing pressure 1700 kg cm⁻².

The decrease in the macropore volume (from 0.275-0.148 cm³ g⁻¹) and in the average macropore diameter (from 470.5 nm to 163.6 nm), by increasing the pelletizing pressure from 500-1700 kg cm⁻² is quite significant.

All the hopcalite samples show nearly the same pore size distribution in the range of mesopores. The differences in the specific surface areas and cumulative mesopore volume, may originate from the different positioning of the amorphous basic copper carbonate in within and onto the samples surfaces, caused from the different pressures exerted on them. The mesoporous sample structure is partly created from the thermal decomposition of the basic copper carbonate, which releases CO₂ and H₂O gases. A superficial basic copper carbonate would less contribute to obtain a porous hopcalite sample with a high specific surface area. The influence of pelletizing pressure on the macropore structure of the hopcalite sample is clearly shown in their cumulative volume and average diameter. The hopcalite macropores are interparticle spaces which get smaller when an increasing pressure is exerted on the tiny, highly amorphous and humid particles.

The better efficiency of our sample shows the advantages of the two step precipitation method of preparation, but comes also from the small and carefully prepared amounts in laboratory conditions while the SIDACO catalyst is produced in industrial scale.

CONCLUSION

The efficiency of Mn-Cu hopcalite catalyst prepared by the two step precipitation method using a pelletizing pressure of 500 kg cm⁻² is proved to be better compared to one commercially available catalyst of producer SIDACO.

The hopcalite prepared by the two step precipitation method exhibit a low crystalline form manganese dioxide (ϵ -MnO₂). Copper containing crystals are not present.

The increasing pressure exerted in the pelletizing step of the hopcalite production is proved to decrease the specific surface area and the cumulative pore volume and to increase the density of the samples. The mesopore size distribution remains almost the same,

while the macropore volume and average diameter decreases significantly by increasing the pelletizing pressure. Because large specific surface areas of hopcalite samples leads to high activities of the hopcalite catalyst, it is not recommended to exert pelletizing pressures higher than 500 kg cm⁻² in the hopcalite catalyst preparation. The protection time of the hopcalite catalyst prepared by two step precipitation method is 610 min and its efficiency better, than the protection time of 300 min shown from a commercial hopcalite catalyst of producer SIDACO.

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