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SILICA – TITANIA SUPPORT FOR HVOC'S COMBUSTION CATALYSTS

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Abstract

Preparation of support series for catalysts of combustion of halogenated volatile organic compounds (H-VOC's) was carried out. It was stated that all they allow preparing active catalysts however their main drawback is the lack of hardness against products of H-VOC's combustion *e.g.* hydrogen chloride and chlorine. Laboratory tests showed that titania and silica – titania supports were characterized by the highest hardness against chlorine derivatives. In comparison to the titania supports, low content (*ca.* 10 wt.%) silica-containing supports have better mechanical properties, *i.e.* mechanical strength and attrition resistance. In this paper the method of preparation, composition and physicochemical properties of silica - titania support are presented.

Keywords: Silica, silica - titania support, H-VOC's combustion

INTRODUCTION

Different methods of destroying halogenated VOC's have been worked out in which two main types of catalyst formulations are commercially available: supported or not supported base metal oxides, such as chromium oxide and supported noble metal catalysts (Pt and/or Pd) [1]. Application of the highly active chromium oxide based catalysts is restricted to the low operation temperature range because of forming of toxic chromium oxychloride in an incineration process.

There are two important factors influencing activity and stability of the catalysts applied in the process of H-VOC's combustion: activity in combustion reaction and stability of the support resulting from chemical resistance against HCl and Cl₂ released in the process. The second problem can be solved by chemical stabilization of supports against HCl and Cl₂, *e.g.* by doping of pure supports by other metals or by special treatment of carbon based support. Hydrogen chloride can react with support material, with forming Me-Cl bonds and lowering mechanical strength of support. There are some indications that some regeneration of support is possible, *e.g.* in the case of alumina by hydrolyzing of Al-Cl bonds with water vapor [2]. Other support materials such as sodium doped alumina, titania, silica and sulfated zirconia were also used as supports for Cl-VOC's combustion catalysts [3,4]. The support prepared precursors can be mixed with the active phase precursor and formed in the form of catalyst grain or used as precursor of wash-coat and active phase for supporting on monolithic supports.

The main practical purpose of the research presented was to work out a preparation method of thermally and chemically stable support for oxidation catalysts for low concentration chlorinated VOC's. In this paper we present a method of preparation and basic physicochemical properties of the silica – titania support obtained, which can be applied for preparation of catalysts for incineration of Cl-VOC's containing gas streams.

EXPERIMENTAL

Preparation of support

Catalyst supports were prepared from technical grade raw materials. Titania precursor, a suspension of the product of titanium sulfates hydrolysis was obtained from Zakłady Chemiczne "Police" in Szczecin, Polish producer of titania pigments, while silica precursor, hydrated silica gels, were obtained from Inowrocławskie Zakłady Chemiczne in Inwrocław. Silica gel was used as titania binder and its content in the final support was changed from 10 to 25 wt.%. Before support preparation the titania precursor was dried at 110°C. A dry titania precursor was mixed and kneaded with wet silica gel, the product was formed using a screw extruder, dried and calcined in the temperature range of 550 – 750°C. Chemical composition of the final SM-1 support obtained in our laboratory is presented in Table 1.

C1 and C2 catalysts were prepared by impregnation of the SM-1 support with noble metal compound solutions (0.3 wt.% of Pt or Pd in the catalysts, respectively), while C3 catalyst was obtained by impregnation of SM-1 support

with CrO_3 solution (15 wt.% in the catalyst) and C4 catalyst with using of V_2O_5 in oxalic acid solution (8 wt.% in the catalyst). Supports in extrudate form were impregnated, dried and calcined in the temperature range of 500 – 850°C.

Catalyst activity was determined in a flow reactor, catalyst weight 0.3 g, grain size 0.25-0.30 mm, GHSV 30 000 h^{-1} , TCE concentration: 1 200 ppm, GC analysis, FID detector.

Determination of physicochemical properties of the support

The resistance tests against chloride ions were carried out in a flow reactor at 500°C for 4 h, 100 dm^3 wet air saturated with HCl flowing by the bed of support. Chloride ions content in support was applied as resistance indicator.

The pore size distribution in the pore radius range of 1.5 to 100 nm was determined on the basis of benzene adsorption - desorption isotherms (Mc Bain - Backr balance) and with using of mercury porosimeter Pascal 440.

Total pore volume was calculated from the volume of water adsorbed by a sample.

Surface acidity was measured by ammonia TPD in the temperature range 200 - 550°C.

Loss of attrition was measured by rotating of 10 g support (catalyst) in a drum at 60 rpm for 5 min. The ground dust with grain size less than 0.1 mm was sieved out and weighed.

The crushing strength was obtained by determination of the force necessary to crush extrudates along the radial direction.

RESULTS AND DISCUSSION

Chemical composition and the basic physicochemical properties of the typical silica – titania support SM-1 are presented in Table 1. The main components of the support are titania and silica, some impurities, K_2O and CaO as well as sulfate ions, were introduced with the titania precursor. Specific surface area of the SM-1 support was two times lower in comparison to silica gel based supports ($>300 \text{ m}^2/\text{g}$) but much higher than in titania support (40 – 50 m^2/g , (Table 2).

As a result of mixing of titania and silica precursors a larger pore support SM-1, with mean pore diameter of 3.8 nm was obtained (calcination at 550°C). Figures 1 and 2 present the results of determination of pore structure of SM-1 support using mercury porosimetry.

Table 1

Chemical composition and physicochemical properties of SM-1 support

Properties	Value	Properties	Value
Content of TiO ₂ (wt.%)	83.0	Surface area (BET) (m ² /g)	167.0
Content of SiO ₂ (wt.%)	10.5	Loss of attrition (wt.%)	1.3
Content of SO ₄ (wt.%)	7.4	Crushing strength (kg/extrudate)	0.6
Content of Al ₂ O ₃ (wt.%)	0.78	Total porosity (cm ³ /g)	0.32
Content of K ₂ O (wt.%)	0.03	Average pore radius (nm)	3.8
Content of CaO (wt.%)	0.25		

Table 2Comparison of specific surface area of SiO₂, TiO₂ and SM-1 supports

Support	Specific surface area (m ² /g)	Mean pore radius (nm)
Titania	45.6	2.5
Silica	323.0	3.3
Silica – titania, SM-1	167.2	3.7

The increase in calcination temperature from 550 to 850°C resulted first of all in the increase of pore volume and the decrease of specific surface area (calcination at *ca.* 700°C) but further increase in calcination temperature, up to 850°C, resulted in a decrease in both support parameters, while the mean pore radius increased from 6.2 to 10 nm at 700 and 850°C although pore volumes and specific surface areas of the supports after calcination at these temperatures were quite different (Figs 1 and 2).

As was stated earlier the resistance against chloride ions is the most important property of H-VOC's combustion catalyst. Data presented in Table 3 clearly indicate that TiO₂ support is quite unreactive to HCl (there is no increase in chloride ion content in support during the test) and it is resistant to destruction during combustion process. However, some changes in mechanical properties, *i.e.* attrition resistance and crushing strength were observed. On the other hand, alumina support is not resistant against chloride ions and one can observe appreciable increase in chloride content during the HCl resistance test although other mechanical properties did not change.

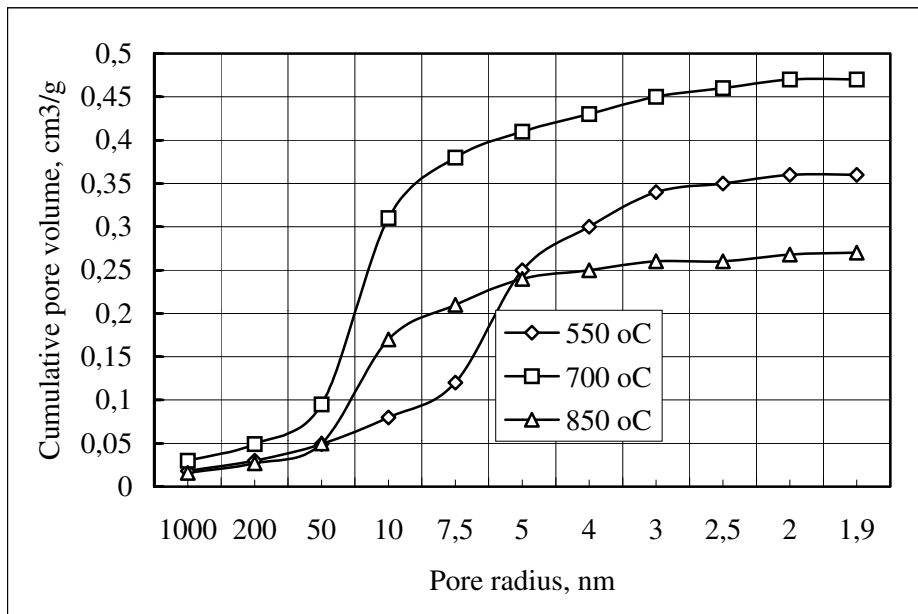


Fig. 1. Dependence of pore volume distribution of SM-1 support on calcination temperature

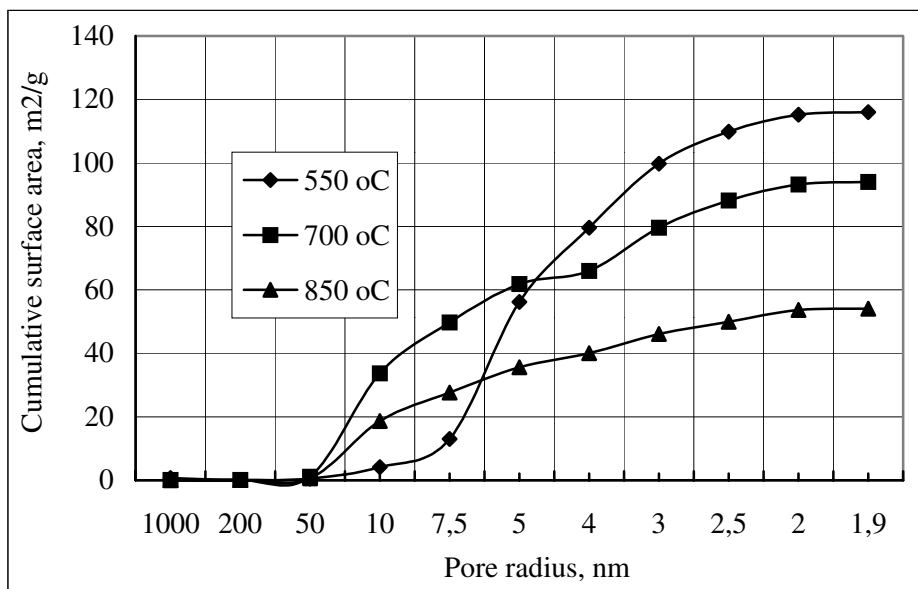


Fig. 2. Dependence of specific surface area distribution of SM-1 support on calcination temperature

SM-1 support occupies an intermediate position, its resistance is a little lower than that of titania and much higher than alumina while loss of attrition and crushing strength determined for alumina were almost the same as for titania.

The supports prepared are characterized by relatively high loss of attrition (*ca.* 1.5 wt.%) in relation to supports made of both alumina and natural clay, as well as by low crushing strength, especially in relation to supports made from natural clays (Table 4). However, it is necessary to notice that both, alumina and natural clay supports are characterized by excellent mechanical properties and that the properties of SM-1 are only insignificantly worse.

Table 3

Resistance of the selected supports against gaseous HCl

	TiO ₂		SM-1		Al ₂ O ₃	
	Before test	After test	Before test	After test	Before test	After test
Loss of attrition (wt.%)	0.7	1.1	1.3	1.0	0.19	0.25
Crushing strength, (kg/extrudate)	1.0	0.59	0.6	0.9	1.74	1.49
Cl content (ppm)	<0.1	<0.1	<0.1	63	44	532

Prolonged calcination time of the SM-1 support at moderate temperature, 550°C, results in a further small increase in loss of attrition and decrease in crushing strength (Table 4).

Table 4

Influence of thermal treatment (550°C) on the selected physicochemical properties of SM-1 and natural aluminosilicate supports

Support	Calcination time (h)	Loss of attrition, (wt.%)	Crushing strength, (kg/grain)	Pore volume (dm ³ /kg)
SM-1	8	1.6	1.10	0.43
	32	1.6	0.80	0.41
Alumina silicate	8	0.3	2.95	0.18
	32	0.7	2.76	0.18
Alumina	8	0.2	1.65	0.54
	32	0.2	1.59	0.58

All these supports calcined at 550°C almost did not change their pore volume. It was previously stated that appreciable changes in specific surface area are observed during calcination at higher temperatures, *ca.* 700°C and higher. It means, that SM-1 support is thermally stable in moderate combustion temperatures, *i.e.* *ca.* 550°C.

X-Ray studies of the SM-1 support revealed that the main crystalline phase is anatase (Table 5). This observation is verified both by the quite similar diffraction pattern obtained for our anatase sample and literature data as well as by the presence of the most typical bands for anatase in the diffraction pattern of SM-1 support. We did not find any other crystalline phase in the final support, such as rutile.

Table 5

XRD data for SM-1 (Diffractometer PW 3710, anode Cu) vs titania –anatase (International Center for Diffraction Data)

SM-1 support		Anatase		
Angle2 Θ (°)	Relative intensity	Angle2 Θ (°)	d-value	Relative intensity
25.281	100	25.425	3.500	100
37.800	20	38.135	2.358	14.6
48.049	35	48.13	1.889	23.1
53.890	20	54.290	1.6883	16.1

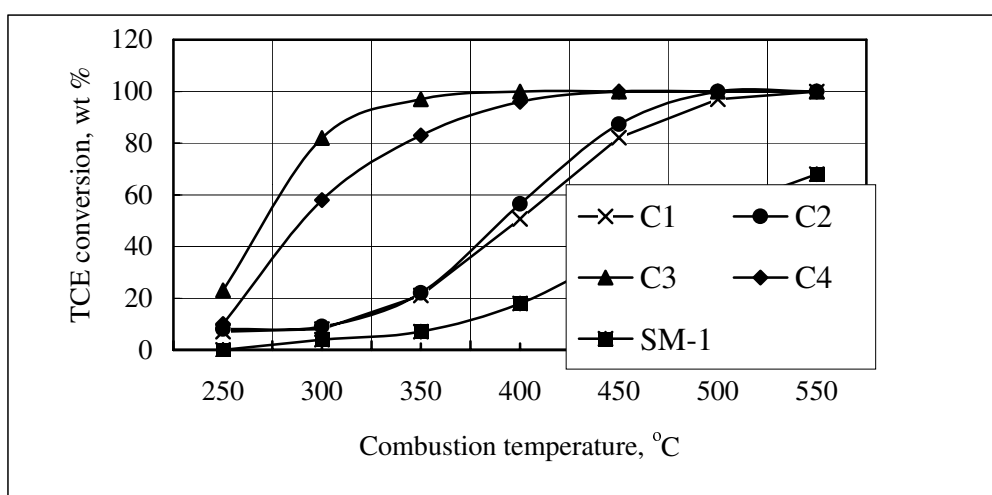


Fig. 3. Conversion of TCE over different catalysts supported on SM-1 support

Data presented in Fig. 3 indicate that the highest activity is attained by chromium and vanadium based catalysts on SM-1 support. Application of noble metals, Pt and Pd, as active phase gives worse results. The total combustion of TCE can be attained at *ca.* 350°C and 500°C in the case of chromium and palladium catalysts, respectively.

Application of chromium catalyst enables to attain appreciable conversion of TCE in the temperature range of 250 - 300°C, especially in the case of low concentration. This type of Cr₂O₃ can be applied as low temperature catalyst at small H-VOC's concentrations.

CONCLUSIONS

1. Silica – titania support can be produced by using commercially available semi-products, such as silica-gel and product of titania sulfate hydrolysis.
2. Physicochemical properties of the silica-titania support SM-1, pore volume, specific surface area and resistance against HCl enable its application for preparation of HVOC combustion catalysts.
3. Highly active Cr₂O₃ supported on silica – titania can be used as low temperature catalyst for combustion of low concentration H-VOC's in waste and/or flue gases, while Pt(Pd)/SM-1 catalyst for high temperature and/or high concentration H-VOC's combustion process .

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