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Supported metal oxides for catalytic combustion of CO and VOCs emissions: preparation of titania overlayers on a macroporous support

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Abstract

TiO_2 (anatase), SiO_2 and γ-Al_2O_3 were used as supports for Co-, Cu-, Fe- and Mn-oxide with a loading of active phase corresponding to one theoretical layer. The catalysts were tested for the combustion of CO and toluene, and the best combinations with active phase and support were submitted to a deactivation test in a waste gas incinerator for 50 days. The catalyst screening showed that CuO_x/TiO_2 was the most promising system. To design a catalyst with good activity and transport properties, a macroporous substrate was coated with TiO_2 for use as a support for Cu-oxide. Titania overlayers were prepared by precipitation from oxychloride, tetrachloride and alkoxide, and stabilisation with ZrO_2 and SiO_2 was tried. The results show that precipitation from oxychloride gives the best properties and that addition of ZrO_2 gives enhanced activity to the catalyst, while SiO_2 addition produces increased stability.

Keywords: Supported metal oxides; Catalytic combustion; Carbon monoxide; VOCs; Titania overlayers; Macroporous supports

1. Introduction

A common way of reducing the emissions of CO and volatile organic compounds (VOCs) is by catalytic combustion. Usually Pt and Pd metal catalysts are used. However, there is a potential for metal oxide catalysts, since these are cheaper and less sensitive to certain catalyst poisons, e.g., Cl. Precious metals are usually supported on a monolith or pellet structure, while commercial oxide catalysts are in the form of pellets. It is well known that mass transfer limitation is important in combustion [1]. The present work concerns the investigation and preparation of a macroporous substrate with a mesoporous overlayer (washcoat) as a support for metal oxides. The macropores give good transport properties, while the thin overlayer provides surface area to the active phase. To obtain a suitable combination of active phase and overlayer giving high dispersion to the former, Co-, Cu-, Fe- and Mn-oxide were deposited on silica, alumina and titania for tests in CO and toluene combustion.

A frequently used method to apply a washcoat on a monolith is by spraying or dipping the monolith in a colloidal sol [2,3]. However, this is more difficult with pellets, for which it is more suitable to use some kind of impregnation or precipitation. Mariscal et al. [4] have tried

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different techniques for the deposition of TiO_2 on a SiO_2 monolith, e.g., impregnation with $TiCl_3$ in HCl or water and precipitation with NH_4OH from dilute $TiCl_3$. Zhaobin et al. [5] have prepared an Al_2O_3 support with an overlayer of TiO_2 by precipitation from $TiCl_3$ with NH_4OH, impregnation with titanium *iso*-propoxide in 2-propanol and by grafting with $TiCl_4$. The grafting gave the best distribution of TiO_2 and also impregnation gave homogeneous dispersion, while precipitation gave a surface that was covered to less than 50%. The specific surface area decreased with increased loading of TiO_2, and Al_2O_3 stabilised the TiO_2 anatase phase. Although similar preparation methods can be adapted in the present application using a macroporous substrate with low surface area, it is here more important to increase the surface area, by precipitating the washcoat precursor in the pores of the substrate, than to obtain full coverage and even distribution. Since the results showed good performance for CuO on a titania overlayer and considering that it has been reported that CuO accelerates the sintering of TiO_2 [6], stabilisation was tried with SiO_2 and ZrO_2. SiO_2 is well known to stabilise and increase the specific surface area of TiO_2 by forming a mechanical and/or chemical mixture [7–9], while ZrO_2 and TiO_2 do not react and can be prepared with similar particle sizes.

2. Experimental

Co-, Cu-, Fe- and Mn-oxide were prepared on SiO_2, Al_2O_3 and TiO_2 by impregnation with nitrate solutions to a final loading of 12 μmol active cation/m^2 support, corresponding to a theoretical monolayer. The supports having similar mean pore size were from Norton. Drying was performed at 110°C for 16 h, followed by calcination for 4 h at 400 and 500°C for CO oxidation and toluene combustion, respectively. Deactivation of some of the catalysts was performed in the waste gas incinerator of a formaldehyde plant at Perstorp AB.

Overlayers of TiO_2 were prepared on a macroporous substrate from Perstorp AB with a surface area of about 1 m^2/g and μm-sized macropores. The preparation methods are summarised in Table 1. The experiments were usually designed to give a theoretical loading of about 10 wt%, but the theoretical loading obtainable in the experiments with the tetrachlorides was around 20 wt%. In the preparations with Ti and Zr or Si, the fraction of Zr and Si was 20 at%. The prepared supports were dried at 70°C for 16 h and then calcined at 550°C for 16 h. Parts of each support was thermally aged at 640°C for 24 or 168 h.

Six of the preparations with overlayers of TiO_2, TiO_2/ZrO_2 and TiO_2/SiO_2 were pre-

Table 1
Preparation methods and notations for oxide washcoats on a macroporous substrate

Notation [a]	Washcoat (wt%)	Preparation method [b]
PS/Ti(O)	13	Precipitation with $NH_3(aq)$ from $TiOCl_2(aq)$.
PS/Ti(T)	27	Impregnation with $TiCl_4$ in conc. HCl.
PS/Ti(A)	8	Precipitation with $H_2O(l)$ from $Ti(OC_4H_9)_4$ in C_2H_5OH.
PS/TiZr(O)	13	Precipitation with $NH_3(aq)$ from $TiOCl_2(aq)$ and $ZrOCl_2(aq)$.
PS/TiZr(T)	22	Precipitation with $NH_3(aq)$ from $ZrCl_4$ in $TiCl_4(l)$.
PS/TiZr(A)	10	Precipitation with $NH_3(aq)$ from $Ti(OC_4H_9)_4$ and $Zr(OC_2H_5)_2Cl_2$ in C_2H_5OH.
PS/TiSi(O)	12	Precipitation with $NH_3(aq)$ from $TiOCl_2(aq)$ and $Si(OH)_xCl_y$.
PS/TiSi(T)	16	Precipitation with $NH_3(aq)$ from $TiCl_4(l)$ and $SiCl_4(l)$.
PS/TiSi(A)	10	Precipitation with $NH_3(aq)$ from $Ti(OC_4H_9)_4$ and $Si(OC_2H_5)_4$ in C_2H_5OH.

[a] PS: Macroporous substrate from Perstorp AB. (O), (T), and (A) indicate oxide preparations from oxychloride, tetrachloride and alkoxide, respectively.

[b] All preparations, after drying at 70°C for 16 h, were eventually calcined in air at 550°C for 16 h.

pared with one theoretical layer of CuO by impregnation with an appropriate amount of nitrate solution. Drying was performed at 70°C for 16 h, followed by calcination at 500°C for 16 h. Catalytic tests were performed on both fresh and thermally treated (550°C) catalysts.

The catalytic tests were carried out in an adiabatic reactor. The inlet temperature was increased linearly by 2°C/min. Specific surface area, pore volume and pore size distribution were determined with a Micromeritics ASAP 2400 instrument.

3. Results and discussion

3.1. Supported metal oxides for CO and toluene combustion

Fig. 1 shows the activities for Co-, Cu-, Fe- and Mn-oxide supported on SiO_2, γ-Al_2O_3 and TiO_2 (anatase). There is generally no significant difference in the activity for MnO_x on the three supports, indicating the absence of support-active phase interaction and possibly formation of crystals of similar size on the various supports. For FeO_x, the data are somewhat scattered, but for use in toluene oxidation it seems that titania is a better support than silica and alumina. On the other hand, for both CoO_x and CuO_x there are clear dependencies on the type of support. In the case of CoO_x, the activities for toluene and CO oxidation both decrease with the type of support in the order $SiO_2 > Al_2O_3 > TiO_2$. For supported CuO_x the reverse order is observed, i.e., $TiO_2 > Al_2O_3 > SiO_2$. It has been reported that for the unsupported oxides the activities for CO and toluene oxidation decrease in the order $Co_3O_4 > CuO > Mn_2O_3 \geq Fe_2O_3$ [10,11]. The differences to the present results in Fig. 1 for the supported oxides, especially regarding CoO_x and CuO_x, can be due to differing degrees of dispersion and interaction between the support and the active phase.

Fig. 1 shows that titania and alumina greatly enhances the activity of CuO_x, making these active phase-support systems excellent catalysts for both toluene and CO combustion. However, CoO_x/SiO_2 and CoO_x/Al_2O_3 also have high activity. These four catalysts together with MnO_x/SiO_2, as a representative manganese oxide catalyst, were selected for the stability test

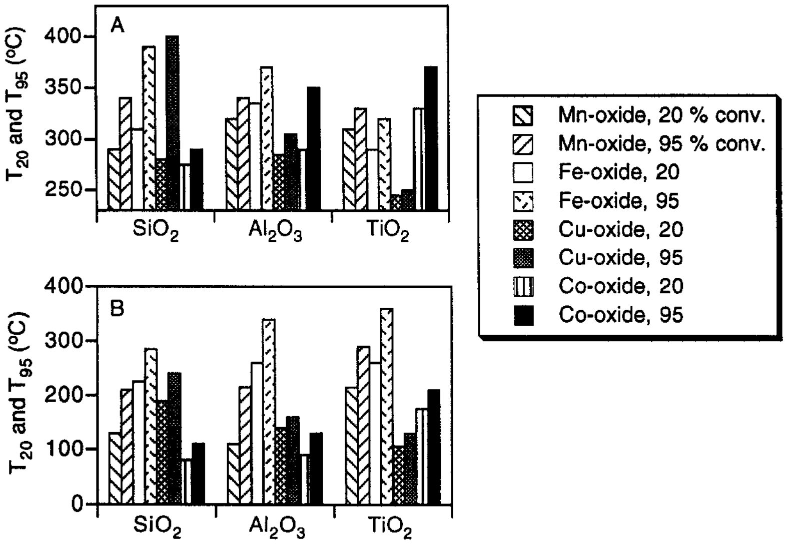

Fig. 1. Supported metal oxides for the combustion of (A) 1000 ppm toluene in air and (B) 1 vol% CO in air. Activities are expressed in terms of the reaction temperature that is required to give 20% and 95% conversion, respectively, over 1063 m^2 of catalyst surface area at a volumetric gas flow rate of 14.5 l/min. Particle size: 150–355 μm.

in the incinerator for the waste gas from a formaldehyde plant. The temperatures that are required for obtaining 20% conversion in a CO test before and after use for 50 days in the incinerator are compared in Fig. 2. It is apparent that both cobalt catalysts as well as the manganese oxide catalyst have been strongly deactivated, while the copper oxide catalysts show much less deactivation. Though CuO_x/Al_2O_3 shows less deactivation than CuO_x/TiO_2 does, the latter is more active per unit surface area both before and after the deactivation test. Recently, we have shown that the deactivation of CuO_x/TiO_2 is due to loss of surface area and sintering of the active phase, while XRD, XPS, EDX and TPR showed no difference between fresh and used CuO_x/Al_2O_3 [12]. Deactivation of CoO_x/Al_2O_3 was found to be caused by the formation of a Co–Al–O spinel. Reduction of the active phase was possibly the reason for deactivation of CoO_x/SiO_2 and MnO_x/SiO_2 [12].

Since the CuO_x/TiO_2 system is the most promising of the active phase-support combinations that were investigated, the CuO_x loading on a titania support was varied. Fig. 3 shows that the activity greatly increases when the loading is increased from a third of a monolayer up to one theoretical layer. With further increase in loading there is almost no increase in activity. These results together with detailed characterisation [13] indicate that copper oxide is spread over the titania surface, forming highly dispersed and active species of monolayer type.

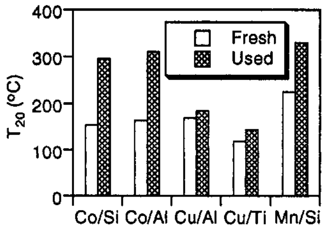

Fig. 2. Comparison of activities before and after use for 50 days in an incinerator for the waste gas from a formaldehyde plant. The activity is expressed as the temperature that gives 20% conversion of 1 vol% CO in air. Particle diameter: 3 mm; charged surface area: 1063 m^2; and volumetric gas flow rate: 10 l/min.

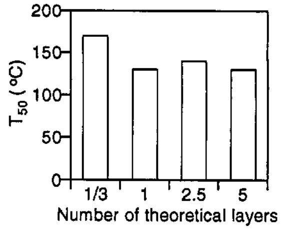

Fig. 3. Comparison of the activities of CuO_x/TiO_2 catalysts (34 m^2/g) with various loadings of CuO_x. The activity is expressed as the temperature that gives 50% conversion of 1 vol% CO in air. One theoretical layer corresponds to 12 μmol Cu/m^2 surface area of support. GHSV: 20000 h^{-1}; and particle size: 3 mm×6 mm.

When the loading is increased above the amount required for forming a theoretical layer, CuO crystallites are formed, contributing little to the total surface area. Similar dependence on loading with CuO_x for CO oxidation has been reported using CeO_2 as a support [14].

3.2. Titania overlayers on a macroporous substrate

For the development of a macroporous substrate with titania washcoat as a support for copper oxide, washcoats were prepared and characterised regarding surface area and pore size distribution before and after thermal treatment in air at 640°C. The results are collected in Table 2. Generally, there is in the range investigated no relationship between high specific surface area (Table 2) and high loading of washcoat (Table 1). Considering the data in Table 2 for the washcoats prepared from oxychlorides, apparently addition of zirconia and silica to the titania does not give higher specific surface, but a slight increase in the average pore diameter. Comparison of the washcoats prepared from the alkoxides shows that PS/Ti(A) and PS/TiZr(A) have similar pore sizes and specific surface area. However, silica additive gives higher specific surface area and considerably smaller pores, cf. PS/TiSi(A). The overlayers of titania and titania/zirconia that were prepared from alkoxides have smaller specific surface areas compared with those of the corresponding wash-

Table 2
Specific surface area and pore size distribution of supports before and after thermal treatment

Support [a]	Freshly prepared		After thermal treatment [b]	
	Surface area (m^2/g)	Pore size distribution [c] (Å)	Surface area [d] (m^2/g)	Pore size distribution [c,e] (Å)
PS/Ti(O)	24.1	30–200 (137)	(18.8) 16.6	50–300 (195)
PS/Ti(T)	14.3	40–2000 (298)	(11.4) 9.3	70–2000 (405)
PS/Ti(A)	12.4	50–200 (180)	(9.7) 8.9	50–600 (146)
PS/TiZr(O)	18.1	50–200 (165)	(13.9) 13.8	60–250 (207)
PS/TiZr(T)	23.6	30–150 (96)	(19.7) 17.8	30–200 (131)
PS/TiZr(A)	13.3	30–200 (157)	(11.4) 9.9	40–300 (244)
PS/TiSi(O)	18.0	40–300 (194)	(–) 15.2	50–300 (216)
PS/TiSi(T)	31.5	20–200 (101)	(25.7) 14.1	40–300 (171)
PS/TiSi(A)	27.6	20–70 (54)	(25.8) 21.4	20–70 (59)

[a] Support: Substrate with washcoat. Cf. Table 1 for notations.

[b] Thermal treatment was carried out in air at 640°C.

[c] The mean pore diameter in Å is given within brackets.

[d] Two values are given. The first value within brackets is the specific surface area measured after 24 h, while the second value is after thermal treatment for 168 h.

[e] After thermal treatment for 168 h.

coats obtained from oxychlorides. Preparation of a washcoat by impregnation with tetrachloride and subsequent drying and calcination, PS/Ti(T), gives smaller surface area and larger pore sizes than are obtained when the washcoat is precipitated from the tetrachloride with ammonia, PS/TiZr(T) and PS/TiSi(T). The specific surface areas expressed per unit mass of washcoat were calculated to be in the range 100–200 m^2/g, and were found to agree with values reported in the literature [7,9].

The data in Table 2 show that thermal treatment of the supports with washcoat at 640°C leads to reduction of the specific surface area, and for some preparations there are a concurrent increase of the pore sizes. Generally, the major reduction of the surface area occurs during the first 24 h, except for the preparations with silica additive, where sintering proceeds over a longer time. Zirconia and silica add improved stability to the titania washcoat except for PS/TiSi(T), which is the least stable of the preparations. Thus, it seems for the Si component that $SiCl_4$ is not preferred and that hydroxychloride and alkoxide are better. Upon thermal treatment for 168 h, the specific surface area for the titania overlayers decreases by about 30–35%. The corresponding decrease for the titania/zirconia and titania/silica overlayers is about 25% and 20%, respectively.

Regarding washcoating a macroporous substrate, it is more desirable to obtain an overlayer with relatively large specific surface area and pores of medium size compared with having an overlayer with either large or small pores. The reason for this preference is that the washcoat shall form a relatively thin layer with active phase, which is reached from the bulk of the gas phase through diffusion along the macropores of the substrate. Using this criterion and considering as well the thermal stability of the washcoat (Table 2), the supports that were selected for deposition with active copper oxide were PS/Ti(O), PS/Ti(A), PS/TiZr(O), PS/TiZr(T), PS/TiSi(O) and PS/TiSi(A).

3.3. Stability of overlayers after deposition of copper oxide

Upon deposition of CuO_x the specific surface area of the washcoat decreases (Table 3), and the decrease is more pronounced for the samples with the largest original surface areas. This effect can be seen as a consequence of pore blocking. After thermal ageing at 550°C, the surface areas have diminished further to values that are similar to those obtained for the pure washcoat after 168 h at 640°C without copper oxide. This observation shows that copper oxide promotes to some extent the sintering of the titania overlayer, in agreement with a previous report [6].

3.4. Combustion of CO and toluene

Activity data for CO oxidation are presented in Fig. 4 for the copper oxide preparations that are described in Table 3. Measurements with constant mass of catalyst were carried out before and after thermal ageing of the catalysts at 550°C. PS/Ti(O)/CuO_x is more active than PS/Ti(A)/CuO_x and shows less deactivation upon thermal treatment. The difference can be due to the larger specific surface area of the former sample and its higher stability to thermal treatment (Table 3), since the pore sizes of the two washcoats were of similar magnitude (cf. Table 2). Comparison of the curves for PS/TiSi(O)/CuO_x with those for PS/TiSi(A)/CuO_x reveals more severe deactivation of the latter, in spite of its surface area being larger both before and after thermal treatment (Table 3). Obviously, the deactivation of PS/TiSi(A)/CuO_x is due to the small pores of the washcoat, 20–70 Å (Table 2), and sintering of the copper oxide. PS/TiZr(O)/CuO_x is superior to PS/TiZr(T)/CuO_x even though the specific surface area of the latter preparation is higher (Table 3). According to the data in Table 2 the difference in performance can be due to the difference in average pore diameter of the fresh overlayers, which is 165 and 96 Å for PS/TiZr(O)/CuO_x and PS/TiZr(T)/CuO_x, respectively. Since the surface area of PS/TiZr(T)/CuO_x is unchanged after thermal ageing, the deactivation is mainly due to sintering of CuO_x. The results clearly demonstrate that the pore diameters of the washcoat preferably shall be larger than about 100 Å and that a suitable balance between surface area and pore diameter is required. Moreover, the comparisons in Fig. 4 reveal that for preparation of the washcoat it is advantageous to start from the oxychlorides.

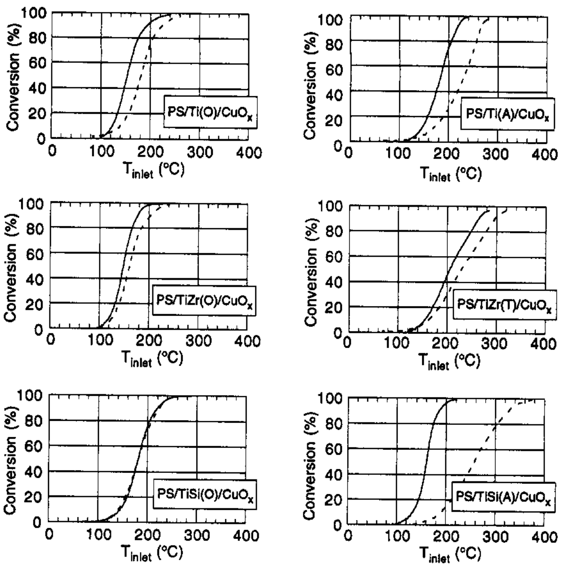

Fig. 4. Comparison of different washcoats with copper oxide for the combustion of 1 vol% CO in air as a function of the inlet temperature. Solid curve: fresh sample; and dashed curve: after thermal treatment at 550°C for 24 h. In the experiment the inlet temperature was increased from 65°C by 2°C/min. Amount of catalyst: 9.4 g; gas flow rate: 8.65 l/min; GHSV: ca. 21000 h^{-1}; and particle size: 3 mm×6 mm. Notations for washcoats: see Table 1.

Table 3

Specific surface area of supported copper oxide catalysts before and after thermal ageing

Catalyst [a]	Specific surface area (m^2/g)		
	Fresh support	Fresh catalyst [b]	Catalyst after thermal ageing [c]
PS/Ti(O)/CuO_x	24.1	18.5	17.0
PS/Ti(A)/CuO_x	12.4	12.2	9.4
PS/TiZr(O)/CuO_x	18.1	15.6	13.1
PS/TiZr(T)/CuO_x	23.6	20.1	20.2
PS/TiSi(O)/CuO_x	18.0	16.6	14.7
PS/TiSi(A)/CuO_x	27.6	22.9	19.8

[a] Copper oxide on the supports defined in Table 1. The copper oxide loading was 12 μmol/m^2 surface area of fresh support.

[b] Calcined in air at 500°C for 16 h.

[c] Thermally treated in air at 550°C for 24 h after the first calcination.

PS/TiZr(O)/CuO_x is more active than PS/Ti(O)/CuO_x, especially at high conver-

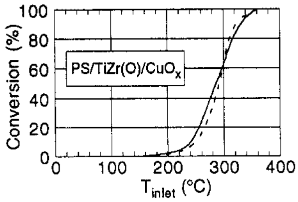

Fig. 5. Combustion of 450 ppm toluene in air as a function of the inlet temperature over copper oxide on a washcoat of titania/zirconia prepared by precipitation from the oxychlorides. Solid curve: fresh sample; and dashed curve: after thermal treatment at 550°C for 24 h. In the experiment the inlet temperature was increased from 65°C by 2°C/min. Amount of catalyst: 9.4 g; gas flow rate: 8.65 l/min; GHSV: 20760 h^{-1}; and particle size: 3 mm × 6 mm.

sions, in spite of its lower surface area. Since the pore sizes of both overlayers are in the same interval (Table 2), it can be concluded that addition of zirconia to the titania gives improved specific activity as well as some stabilisation. The conversion curves in Fig. 4 for PS/TiSi(O)/CuO_x, before and after thermal treatment, are almost identical. Thus, silica addition to the titania gives good resistance toward deactivation, possibly because the two constituents are efficiently mixed and the copper oxide is dispersed and evenly distributed. The prone deactivation of PS/TiSi(A)/CuO_x then can be caused by insufficient dispersion of the silica in the titania matrix, allowing for sintering of the copper oxide. PS/TiSi(O)/CuO_x is somewhat less active than PS/Ti(O)/CuO_x and, considering that the former sample has a lower specific surface area (Table 3), it can be concluded that addition of silica to the titania washcoat does not give improved activity per unit surface area of catalyst. This conclusion agrees with the comparisons presented in Fig. 1, showing that CuO_x/SiO_2 is less active than CuO_x/TiO_2.

In Fig. 5, curves are presented for toluene oxidation over PS/TiZr(O)/CuO_x. Almost no deactivation is observed after thermal treatment at 550°C, though the data for CO oxidation over the same samples show small deactivation. The difference can be due to sintering of some micropores during the thermal treatment, pores to which CO but not toluene has access.

4. Conclusions

Copper oxide supported on titania (anatase) shows good activity and longevity for the combustion of CO and VOCs.

A monolayer of dispersed CuO_x forms on TiO_2 an active surface and excess CuO gives no improved activity due to formation of crystallites, contributing little to the surface area.

A macroporous substrate with an overlayer of titania is a good support for copper oxide.

Washcoat preparations from oxychloride, tetrachloride and alkoxide show that precipitation from the oxychloride gives the best balance between surface area and pore size.

Addition of zirconia to the titania washcoat gives enhanced specific activity of the copper oxide catalyst, while silica addition gives improved longevity.

Acknowledgements

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