PREPARATION OF SUPPORTED VANADIUM AND MOLYBDENUM OXIDE CATALYSTS USING METAL ACETYLACETONATE COMPLEXES

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ABSTRACT

Supported vanadium and molybdenum oxide catalysts were prepared by reaction of the corresponding acetylacetonate complex in a non-aqueous solution with the surface hydroxyl groups of the carrier. Continuous or batch adsorption of the metal acetylacetonate from toluene, as well as wet impregnation from ethanol, resulted in a uniform coverage of the support. The applied metal oxide was probably present on the surface as a monomolecular dispersion. When readsorption or reimpregnation from toluene was carried out with TiO_2 as support, metal oxide crystallites were formed, which could readily be detected with laser Raman spectroscopy. Reimpregnation from ethanol led to a complete occupancy of the surface hydroxyl groups of the carrier without the formation of metal oxide multilayers or crystallites.

INTRODUCTION

The heterogeneously catalyzed gas phase oxidation of hydrocarbons is an interesting process, both from scientific and industrial points of view. The catalysts generally used for selective oxidation consist of one or more transition metal oxides [1]. In order to increase the activity and the lifetime, these catalysts can be doped with promoting agents and/or supported on a carrier. It is obvious that when the metal oxide is applied to the carrier surface as a monomolecular layer, it is not only most efficiently used but also maximally influenced by the carrier oxide. Such an influence can considerably affect the activity and selectivity of the active species in oxidation reactions, as was observed by several research groups [2,3].

Monolayer catalysts can be prepared in different ways. Complete and partial monolayer catalysts of vanadium and molybdenum oxide on a number of supports were prepared by Fransen et al. [4] and Roozeboom et al. [5] by adsorption of vanadate and molybdate ions from aqueous solutions. Recently, Bond et al. [6] described a technique for the preparation of V/TiO_2 monolayer catalysts by reaction of VOCl_3 from organic solutions with the hydroxylated surface of titania. The two methods described give good results for vanadium and molybdenum but cannot be used for a great number of other transition metal oxides. We therefore looked for metal complexes which are stable, soluble and can easily be applied to a carrier oxide.

Because nearly all transition metals form stable acetylacetonates [7], a start was made to investigate the preparation of supported catalysts by the adsorption of these complexes, in particular of iron, vanadium and molybdenum. The results of the preparation of the iron oxide catalysts, used for total oxidation processes, are reported elsewhere [8]. This paper deals with the preparation of supported vanadium and molybdenum oxide catalysts. The catalytic properties of these catalysts in the selective oxidation of aromatic hydrocarbons will be published in a subsequent paper.

EXPERIMENTAL

Materials

γ - Al_2O_3 ($90 \text{ m}^2 \text{ g}^{-1}$), SiO_2 ($350 \text{ m}^2 \text{ g}^{-1}$) and TiO_2 (68% anatase, 32% rutile; $50 \text{ m}^2 \text{ g}^{-1}$) were obtained from Degussa. ZrO_2 (monoclinic; $11 \text{ m}^2 \text{ g}^{-1}$) was obtained from Viking Chemicals and a second type of TiO_2 (anatase; $10 \text{ m}^2 \text{ g}^{-1}$) from Tioxide. CeO_2 ($70 \text{ m}^2 \text{ g}^{-1}$) and ZrO_2 ($156 \text{ m}^2 \text{ g}^{-1}$) were prepared as described by Fransen et al. [4]. V_2O_5 and $\text{MoO}_2(\text{CH}_3\text{COCHCOCH}_3)_2$ ($= \text{MoO}_2(\text{AcAc})_2$) were Baker products (analytical grade) and $\text{VO}(\text{CH}_3\text{COCHCOCH}_3)_2$ ($= \text{VO}(\text{AcAc})_2$) were obtained from Merck (analytical grade). The solvents used, toluene and ethanol, were from Merck (analytical grade).

Methods

Catalyst preparation. Three methods were used to prepare the supported vanadium and molybdenum oxide catalysts.

The first method consisted of slowly passing a solution of the metal acetylacetonate in toluene or ethanol through a bed of support particles. This is called the continuous adsorption method. The process of adsorption was checked by determining the metal content in the effluent.

In the second method, called the batch adsorption method, a solution of the metal acetylacetonate complex in toluene or ethanol was added to an amount of carrier particles. This suspension was then shaken for a long time (10-20 days) to reach complete adsorption equilibrium. These two adsorption processes were carried out in a nitrogen atmosphere to avoid slow degradation of the acetylacetonate complex by oxidation.

The third method, wet impregnation, was carried out by adding an excess of a solution of the metal acetylacetonate in ethanol or toluene to the support particles. While this suspension was carefully stirred, the solvent was slowly evaporated.

After preparation by either of these methods the catalysts were washed with pure solvent, dried (140°C ; 1 h) and calcined (450°C ; 2 h).

Analysis

X-ray fluorescence. The metal content of the catalysts was determined with a

Philips 1410 X-ray spectrometer [9].

BET surface area measurements. Surface areas of the catalysts were determined as described previously [10]. In most cases the surface area of the catalysts equalled that of the carriers. Only relatively high metal contents, achieved by wet reimpregnation or batch readsorption from toluene or by wet impregnation without washing resulted in a lower surface area, probably due to the presence of metal oxide crystallites in the pores of the carrier.

Laser Raman spectroscopy. The Laser Raman spectra of the samples were recorded with a spectrometer consisting of a Jobin-Ivon Ramanor HG2S monochromator and an EMI 9863 photomultiplier detector. The green (514.5 nm) emission line from a coherent-CR4 Ar⁺ laser was used for excitation. The output power of the laser was reduced to 1-10 mW, the spectral slit width was 11 cm⁻¹ and the scanning speed was usually 50 cm⁻¹ min⁻¹. The calcined samples were placed without further treatment under a microscope (Nikon Optiphot; 40x) making it possible to point the laser beam at any desired particle.

Crystalline V₂O₅ can readily be detected by laser Raman spectroscopy; sharp lines are seen at ~ 996, 700 and 485 cm⁻¹ [11]. The vanadium oxide catalysts (50 m² g⁻¹), prepared as mentioned above, did not exhibit these lines; only TiO₂ bands were present in the Raman spectra. Catalysts prepared by wet reimpregnation or batch readsorption from toluene or by wet impregnation without washing contained crystalline V₂O₅ above about 3 wt % V as shown in Figure 1. The shielding effect, reported by Roozeboom et al. [12], was also observed in our case.

Edax. The metal dispersion in the catalyst grains was studied by means of energy dispersive analysis of X-rays (EDAX), attached to a scanning electron microscope (JSM-U3) at an optical magnification of 100x. The vanadium was observed to be uniformly dispersed through the grains, even if the catalysts contained crystalline V₂O₅ (> 3 wt % V).

RESULTS AND DISCUSSION

In several batch adsorption experiments it was observed that the metal complex could not be removed from the carrier surface by washing with pure solvent at room temperature. In addition, thermogravimetric analysis (TGA) showed the experimental weight loss to be much less (15-30%) than that calculated from the degradation of VO(AcAc)₂ to V₂O₅. From these observations it was concluded that the metal acetylacetonate complex was not physically adsorbed on the carrier surface but was bonded more tightly, probably by reaction with the surface. During this reaction degradation products were formed (e.g. acetylacetone) which influenced the preparation process by competitive interaction with the reaction sites of the carrier surface, as shown by Van Ommen et al. [8].

Continuous adsorption

The continuous adsorption technique was studied with vanadium acetylacetonate

FIGURE 1 Laser Raman spectra of V_2O_5 , V_2O_5/TiO_2 catalysts and TiO_2 .

FIGURE 2 Concentration of vanadium in the effluent as a function of time for the adsorption of vanadium acetylacetonate on ZrO_2 ($11 \text{ m}^2 \text{ g}^{-1}$).

(= $\text{VO}(\text{AcAc})_2$) and TiO_2 and ZrO_2 as oxidic supports. The experimental results are presented in Table 1. A typical example of a "breakthrough" curve is given in Figure 2.

Although the reproducibility of the experiments was not very high, the results show that the vanadium content of none of the catalysts corresponded to that of a complete monolayer of vanadium oxide [5]. The TiO_2 catalysts took up roughly the same amount of vanadium as the corresponding ones prepared by Roozeboom et al. [5] by ion-exchange with NH_4VO_3 , while the vanadium content of the ZrO_2 catalysts was lower.

TABLE 1

Results for the preparation of catalysts by continuous adsorption of $\text{VO}(\text{AcAc})_2$ from toluene^a.

Carrier	Surface area of carrier/ $\text{m}^2 \text{ g}^{-1}$	V content/wt %	% of theoretical monolayer of V_2O_5 ^c	V content from ref. [5]/wt %
TiO_2	50	1.7 - 2.0 ^b	41 - 49	1.75
ZrO_2	11	0.1 - 0.2 ^b	11 - 22	-
ZrO_2	156	3.5	27	9.3

^a $\phi_V = 50 \text{ cm}^3 \text{ h}^{-1}$; $C_0 = 1\text{--}1.3 \text{ g VO}(\text{AcAc})_2 \text{ dm}^{-3}$; 1-2 g carrier; $T = 25^\circ\text{C}$; $t = 24 \text{ h}$.

^b results of several experiments.

^c $\phi_{\text{VO}_2,5} = 10.3 \times 10^4 \text{ pm}^2$ [5].

The influence of the pretreatment of the carrier, the adsorption temperature and the solvent used was investigated. The first variable considered was the pretreatment of the carrier. Before the adsorption experiment the TiO_2 carrier ($50 \text{ m}^2 \text{ g}^{-1}$) was saturated with water, dried at 150°C (2 h), 300°C (2 h) or at 450°C (2 h) in vacuum. None of these pretreatments had an influence on the metal content of the catalyst, which was equal to that of the catalyst with no pretreatment ($\sim 1.8 \text{ wt \% V}$). Boehm et al. [13] showed that evacuation at 450°C leads to dehydroxylation of the titania surface. When there is a reaction of the metal acetylacetonate complex with the surface hydroxyl groups, dehydroxylation of the carrier should have an effect on the metal content of the catalyst. However, according to Parkyns [14], a dehydroxylated titania surface takes up water very readily, unless special precautions are taken to avoid this. Because the continuous adsorption experiments were carried out without taking these extreme precautions, the carrier surface was (re)hydroxylated in all these cases and no influence of the pretreatment of the carrier was observed.

The influence of the adsorption temperature is presented in Figure 3, showing that the vanadium content increases slightly with temperature. This may be caused by more complete desorption of the degradation products at higher temperatures.

FIGURE 3 Influence of the temperature during the continuous adsorption of $\text{VO}(\text{AcAc})_2$ from toluene on the vanadium content of TiO_2 supported catalysts.

TABLE 2

Results for the preparation of catalysts by batch adsorption of $\text{VO}(\text{AcAc})_2$ and $\text{MoO}_2(\text{AcAc})_2^{\text{a}}$.

Carrier	Carrier surface area/ $\text{m}^2 \text{ g}^{-1}$	Metal	Solvent ^b	M content /wt %	% of theoretical ^c monolayer of MO_x
TiO_2	50	V	tol.	1.75	43
	50	V	eth.	0.4	10
	50	Mo	eth.	2.6	49
ZrO_2	11	V	tol.	0.2	22
	11	Mo	eth.	0.17	15
SiO_2	350	V	tol.	1.52	5
	350	Mo	eth.	0.1	0.3
Al_2O_3	90	V	tol.	1.32	18
	90	Mo	eth.	2.22	23
CeO_2	70	V	tol.	2.21	39
	70	Mo	eth.	3.32	45

^a $t = 10\text{--}20$ days; $1\text{--}1.5$ g carrier; $C_0 = 1\text{--}2$ g $\text{MO}_x(\text{AcAc})_2 \text{ dm}^{-3}$; $V = 160 \text{ cm}^3$; $T = 25^\circ\text{C}$.

^b the solubility of $\text{MoO}_2(\text{AcAc})_2$ in toluene (tol.) was too small and ethanol (eth.) was therefore used as a solvent.

^c $\phi_{\text{VO}_{2.5}} = 10.3 \times 10^4 \text{ pm}^2$ [5]; $\phi_{\text{MoO}_3} = 15 \times 10^4 \text{ pm}^2$ [4].

The use of ethanol as a solvent resulted in a lower vanadium content of the catalyst (~ 0.2 wt % V), caused either by a better solvation of the vanadium acetylacetonate complex in ethanol and/or by strong adsorption of ethanol on the carrier surface.

Batch adsorption

The batch adsorption technique also resulted in homogeneous catalysts, as shown by the EDAX results, with a vanadium content comparable with that of the catalysts prepared by the continuous adsorption technique. The experimental results are given in Table 2.

Because the solubility of $\text{MoO}_2(\text{AcAc})_2$ in toluene was too small, ethanol was used as a solvent. The solubility of the molybdenum complex in ethanol was of the same order of magnitude as that of the vanadium complex in toluene. From the results presented in Table 3, it is clear that the coverage of the carrier surface by molybdenum oxide is almost the same as that by vanadium oxide, indicating a comparable reaction path. The better solvation of vanadium acetylacetonate in ethanol resulted in a lower vanadium content, as was also observed during the continuous adsorption experiments.

The metal contents again do not correspond to that of a theoretical monolayer. The vanadium and molybdenum oxide are probably present on the surface as monomolecular dispersions covering 40-50% of the TiO_2 and CeO_2 surfaces and ~20% of the Al_2O_3 and ZrO_2 surfaces. The metal content of the silica supported catalyst was relatively low because of a weak interaction of the vanadium and molybdenum ions with the carrier, as was also observed by Roozeboom et al. [5] and Fransen et al. [4].

In order to try to reach a more complete coverage of the carrier surface, batch adsorption experiments with $\text{VO}(\text{AcAc})_2$ were repeated several times for TiO_2 and ZrO_2 .

FIGURE 4 Results of the preparation of catalysts by readsorption of $\text{VO}(\text{AcAc})_2$ from toluene; $\circ$, ZrO_2 ($11 \text{ m}^2 \text{ g}^{-1}$); $\blacktriangle$, TiO_2 ($50 \text{ m}^2 \text{ g}^{-1}$); ---, theoretical monolayer V_2O_5 .

After every experiment, the catalyst was calcined (450°C; 2 h) to remove all organic material. The experimental results are presented in Figure 4.

It can be seen that almost equal amounts of vanadium oxide can be added in each successive treatment. After the first treatment, the vanadium complex is well spread over the support surface. By calcining at 450°C, all organic material is removed and vanadium oxide is formed. On this vanadium oxide, new hydroxyl groups can be formed when small amounts of water are present. In the following treatment, the acetylacetonate complex can react with these groups, forming multilayers of vanadium oxide upon calcination.

Wet impregnation

The third preparation technique, wet impregnation, was studied using $\text{VO}(\text{AcAc})_2$ and $\text{MoO}_2(\text{AcAc})_2$ dissolved in ethanol with TiO_2 as support. When the catalyst was washed thoroughly with pure solvent at room temperature after slow evaporation of the solvent, the metal content was comparable with that of the catalysts prepared by the other two methods. The experimental results are listed in Table 3.

TABLE 3

Results of the preparation of catalysts by wet impregnation using $\text{VO}(\text{AcAc})_2$ and $\text{MoO}_2(\text{AcAc})_2^a$.

Carrier	Surface area of carrier/ $\text{m}^2 \text{ g}^{-1}$	Metal	Metal content/wt %	% of theoretical monolayer of MO_x
TiO_2	50	V	1.7	41
	50	Mo	2.6	49
TiO_2	10	V	0.36	44
	10	Mo	0.60	57

^a 1-2 g carrier; $C_0 = 1.5 \text{ g MO}_x(\text{AcAc})_2 \text{ dm}^{-3}$; $V = 160 \text{ cm}^3$ ethanol; $T = 50^\circ\text{C}$.

When, after evaporation of the solvent, the catalyst was dried and calcined without washing, the vanadium content was directly proportional to the amount of $\text{VO}(\text{AcAc})_2$ present. In this case the catalyst contained a well dispersed layer of vanadium oxide together with crystalline V_2O_5 , detectable by laser Raman spectroscopy.

The effect of successive treatments was also studied for this preparation technique. After every impregnation experiment, the catalyst was washed with pure solvent, dried (140°C; 1 h) and calcined (450°C; 2 h). The experimental results are presented in Figure 5.

From these results, it is clear that reimpregnation of $\text{VO}(\text{AcAc})_2$ and $\text{MoO}_2(\text{AcAc})_2$ from ethanol leads to a constant metal content. After 2-3 impregnations, the acetylacetonate complex evidently does not react with the surface any more and

FIGURE 5 Results of the preparation of catalysts by wet reimpregnation; ●, V/TiO_2 ($10 \text{ m}^2 \text{ g}^{-1}$)/ethanol; +, V/TiO_2 ($50 \text{ m}^2 \text{ g}^{-1}$)/ethanol; ○, Mo/TiO_2 ($50 \text{ m}^2 \text{ g}^{-1}$)/ ethanol; ▲, V/TiO_2 ($50 \text{ m}^2 \text{ g}^{-1}$)/ toluene.

can easily be removed by washing with pure solvent. From the data in Figure 5 it can be calculated that for molybdenum about 65% of the surface is covered and for vanadium about 55%. Thus the maximum coverage of the carrier surface is comparable for both oxides.

When toluene instead of ethanol was used as a solvent, equal amounts of vanadium oxide could be added to the catalyst in every treatment. The same effect was observed during the batch readsorption experiments from toluene (Figure 4). From these results, it is obvious that the solvent has a great influence on the reaction of the metal acetylacetonate and the surface of the catalyst. This effect is caused by a different interaction of the two solvents with the surfaces of TiO_2 and V_2O_5 or MoO_3 . An apolar solvent gives only a small interaction with the surface hydroxyl groups of both metal oxides. Because of this, the acetylacetonate complex can react not only with the hydroxyl groups of TiO_2 but also with those formed on the vanadium oxide after calcination. Successive treatments thus lead to the formation of multilayers of vanadium oxide.

The interaction of aliphatic alcohols with TiO_2 has been studied by Carrizosa et al. [15]. They found that approximately two molecules of ethanol could be adsorbed irreversibly per nm^2 , corresponding to a surface coverage of ~40%. Little is known about the interaction of ethanol with V_2O_5 or MoO_3 , but from the greater acid strength of these oxides compared with TiO_2 [16], a much stronger interaction can be assumed. This is supported by the work of Kurina et al. [17] who studied

the adsorption of methanol on V_2O_5 and found surface coverages approximately equivalent to one monolayer. The experimental results, shown in Figure 5, strongly suggest that, because of this difference in interaction, the acetylacetonate complex reacts exclusively with the titania surface and not at all with the surfaces of the vanadium or molybdenum oxides when ethanol is used as a solvent. Reimpregnation from ethanol thus leads to complete coverage of the hydroxyl groups of the TiO_2 with the vanadium or molybdenum oxides without the formation of multilayers. This is also supported by the fact that the total number of hydroxyl groups reacted, calculated from the constant level of the metal content (3.6 wt % Mo or ~ 4.5 OH groups per nm^2 ; 2.1 wt % V or ~ 5.0 OH groups per nm^2), corresponds very well with the maximum number of hydroxyl groups as found by Boehm et al. [13] to be present on the surface of the same type of TiO_2 (4.9 OH groups per nm^2).

CONCLUSIONS

Supported vanadium and molybdenum oxide catalysts can be prepared by reaction of the corresponding acetylacetonate complexes with the surface hydroxyl groups of the carrier. All three preparation techniques studied (i.e. continuous and batch adsorption from toluene and wet impregnation from ethanol) give catalysts uniformly covered with approximately equal amounts of metal oxide, probably present on the surface of the support as a monomolecular dispersion. Readsorption or reimpregnation of the TiO_2 results in the formation of metal oxide crystallites when toluene is used as a solvent but reimpregnation of TiO_2 from ethanol leads to complete occupancy of the surface hydroxyl groups of the carrier without the formation of multilayers or crystallites of metal oxide.

The catalytic properties of the prepared catalysts for the selective oxidation of aromatic hydrocarbons is currently being studied in our laboratory and the results will be published in the near future.

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