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MOLECULAR ENGINEERING OF SUPPORTED METAL OXIDE CATALYSTS

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ABSTRACT

This study demonstrates that molecular engineering of supported metal oxide catalysts is currently possible from molecular level information about the number of active surface sites and reactivity per site. Such fundamental information is currently obtainable from molecular spectroscopies such as Raman spectroscopy. The critical parameters that determine the number of active surface sites and reactivity per site are the specific oxide support, catalyst composition, and calcination temperature. The oxide support determines the maximum number of active surface sites and reactivity per site, and the catalyst composition and calcination temperature primarily determine the number of active surface sites. The synthesis method of supported metal oxide catalysts is not critical since it does not influence the number of active surface sites and the reactivity per site. The approach outlined in this study can be used to assist in the molecular engineering of numerous supported metal oxide catalytic systems.

KEYWORDS

Catalyst; metal oxide; molecular engineering; synthesis; oxide support; composition; calcination temperature; oxidation.

INTRODUCTION

Many recent studies have demonstrated that two-dimensional transition metal oxide overlayers are formed when one metal oxide component (i.e., Re_2O_7, CrO_3, MoO_3, WO_3, V_2O_5, Nb_2O_5, etc.) is deposited on a second metal oxide substrate i.e., Al_2O_3, TiO_2, SiO_2, etc. (Bartlett and Cooney, 1983; Dixit et al., 1986; Haber, 1983; Hardcastle and Wachs, 1988; Wachs et al., 1986). The molecular structures and reactivity of these surface metal oxide species have been intensively investigated over the past decade because of the importance of these supported metal oxide materials in numerous catalytic applications (Thomas, 1970). The major structural information about these surface metal oxide species has been derived from Raman spectroscopy studies because of the molecular nature of this characterization method and its ability to discriminate between different metal oxide species that may simultaneously be present in the catalyst (Bartlett and Cooney, 1987; Dixit et al., 1986; Hardcastle and Wachs, 1988; Wachs et al., 1986). Corresponding reactivity studies have demonstrated that these surface metal oxide species possess the active sites for many catalytic reactions (Kim et al., 1989; McDaniels, 1985; Moulijn and Mol, 1988; Wachs et al., 1985). The fundamental information currently available about these oxide catalysts is beginning to allow us to molecular engineer supported metal oxide catalysts . The molecular engineering of supported metal oxide catalysts requires that we specify the synthesis method, oxide support, catalyst composition, calcination temperature, location and structure of the surface metal oxide species, as well as its reactivity. Consequently, the influence of each of the above parameters upon the catalytic properties of supported metal oxide catalysts needs to be examined.

The present paper focuses on the molecular engineering aspects of supported vanadium oxide catalysts. Supported vanadium oxide catalysts have been found to be very versatile oxidation catalysts and, as a result, are employed in industry for numerous oxidation reactions (Gellings, 1985). For example, supported V_2O_5/TiO_2 catalysts are the catalyst of choice for selective catalytic reduction of NO_x from stationary sources to reduce acid rain formation and partial oxidation of hydrocarbons for the production of several important chemical intermediates. Supported V_2O_5/SiO_2 catalysts are also used for the oxidation of SO_2 to SO_3 for the manufacture of sulfuric acid and for the partial oxidation of naphthalene to phthalic anhydride. Technology for the ammoxidation of aromatic hydrocarbons over supported V_2O_5/Al_2O_3 and V_2O_5/TiO_2 catalysts was also developed in the past few decades. Thus, supported vanadium oxide catalysts constitute a very important class of heterogeneous oxide catalysts.

RESULTS AND DISCUSSION

Synthesis Method

Many different synthesis methods have been used to prepare supported vanadium oxide catalysts. In the case of supported V_2O_5/TiO_2 catalysts, the catalysts were prepared by vapor phase grafting with $VOCl_3$ (Bond and Bruckman, 1981), nonaqueous impregnation (vanadium alkoxides (Wachs et al., 1988) and vanadium acetate (Van Hengstum et al., 1983)), aqueous impregnation (vanadium oxalate (Wachs et al., 1985)), as well as dry impregnation with crystalline V_2O_5 (spontaneous dispersion) (Haber et al., 1985). Commercial preparations employ aqueous impregnation with vanadium oxalate because of its simplicity, but some authors have argued that V_2O_5/TiO_2 catalysts synthesized by vapor phase grafting of $VOCl_3$ result in superior catalytic properties (Bond and Bruckman, 1981).

To investigate the influence of the synthesis method upon the state of V_2O_5/TiO_2 catalysts, a series of V_2O_5/TiO_2 (anatase) catalysts were prepared by $VOCl_3$ grafting, nonaqueous impregnation with vanadium ethoxide, aqueous impregnation with vanadium oxalate, and dry impregnation with V_2O_5. The V_2O_5/TiO_2 catalysts were characterized by Raman spectroscopy, after calcination, to determine the molecular structures of the supported vanadium oxide component (Machej et al., 1990). The V_2O_5/TiO_2 catalysts prepared by grafting of $VOCl_3$, nonaqueous impregnation with vanadium ethoxide, and aqueous impregnation with vanadium oxalate exhibited the same Raman band at ~990 cm^{-1} due to the surface vanadium oxide species on the TiO_2 support (Van Hengstum et al., 1983; Deo et al., 1989). The V_2O_5/TiO_2 catalyst prepared by dry impregnation of crystalline V_2O_5 powder, however, exhibited a sharp Raman band at 994 cm^{-1} due to the presence of crystalline V_2O_5 as well as the broad Raman band at ~990 due to the surface vanadium oxide species. *In situ* Raman measurements further confirmed the formation of surface vanadium oxide species by dry impregnation of crystalline V_2O_5 powder. The presence of crystalline V_2O_5 in the dry impregnated catalyst suggests that additional heating is required to completely convert the crystalline V_2O_5 phase to the surface vanadium oxide phase. Thus, with the exception of the dry impregnation method which requires more extensive calcination times, the synthesis method of supported vanadium oxide catalysts is not critical since all the preparations yield the same surface vanadium oxide overlayer on the titania support.

Location of Supported Metal Oxide

The location of the supported vanadium oxide component in the catalysts can be determined by complementary Raman and infrared characterization studies. Infrared characterization studies of V_2O_5/Al_2O_3 catalysts reveal that the surface hydroxyls of the alumina support are consumed upon the addition of vanadium oxide to the alumina support (De Canio and Wachs, 1990). *In situ* Raman studies demonstrate that the supported vanadium oxide component directly coordinates to adsorbed molecules since the Raman band shifts about 40-100 cm^{-1} during adsorption/desorption experiments (Chan et al., 1984). The consumption of the support hydroxyls and coordination to adsorbed molecules confirm the conclusion that the supported vanadium oxide component is present as a two-dimensional metal oxide overlayer on the high surface area oxide supports. The reaction between the vanadium oxide component and the oxide support surface hydroxyls is thermodynamically driven and, consequently, leads to the same surface vanadium oxide overlayer independent of the catalyst preparation method.

Oxide Support

The maximum amount of vanadium oxide that can be formed in the two-dimensional vanadium oxide overlayer, monolayer coverage, depends on the oxide support surface area and concentration of reactive surface hydroxyls. Above monolayer coverage, the crystalline V_2O_5 phase forms a sharp Raman band at 994 cm^{-1} because all the reactive surface hydroxyls have been consumed. Monolayer coverages for supported vanadium oxide on Al_2O_3, TiO_2, and SiO_2 have been determined by Raman spectroscopy and are presented in Table 1. The alumina support has a high surface area and a high surface concentration of reactive surface hydroxyls (Anderson, 1975). The titania support has an intermediate surface area and a high surface concentration of reactive surface hydroxyls (Anderson, 1975). The silica support, however, has a high surface area and a low surface concentration of reactive surface hydroxyls (Anderson, 1975). Consequently, the surface density of the supported vanadium oxide overlayer is very similar on Al_2O_3 and TiO_2, but significantly lower on SiO_2.

Table 1. Monolayer Coverages for Supported Vanadium Oxide Catalysts

Oxide Support	BET Surface Area	Vanadium Oxide Monolayer Coverage	Vanadium Oxide Surface Density
Al_2O_3	180 m^2/g	20 wt%	0.11% V_2O_5/m^2
TiO_2	50 m^2/g	6 wt%	0.12% V_2O_5/m^2
SiO_2	300 m^2/g	1.5 wt%	0.005% V_2O_5/m^2

Catalyst Composition

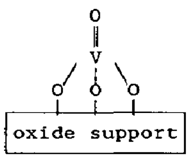
The catalyst composition determines the type of vanadium oxide species present in supported vanadium oxide catalysts. Below monolayer coverage (see Table 1), the entire vanadium oxide component in the catalyst is present as a two-dimensional surface vanadium oxide overlayer on the oxide support. Above monolayer coverage (see Table 1), microcrystalline V_2O_5 particles are also present in the catalyst in addition to the surface vanadium oxide monolayer. The catalytic properties of the surface vanadium oxide species and microcrystalline V_2O_5 particles have been shown to be dramatically different for supported V_2O_5/TiO_2 catalysts. For example, the surface vanadium oxide species possess a higher activity and selectivity than microcrystalline V_2O_5 for the oxidation of o-xylene to phthalic anhydride (Wachs et al., 1985). Moderate amounts of microcrystalline V_2O_5 do not significantly affect the catalytic performance of supported V_2O_5/TiO_2, because of the low effective surface area and poor catalytic activity of this phase, but large amounts of microcrystalline V_2O_5 significantly decrease the catalyst activity and selectivity. Furthermore, it was found for this particular reaction that the titania support must be covered by a complete monolayer of the surface vanadia species since exposed titania sites lead to complete combustion of the partial oxidation products. Thus, the catalyst composition has a critical effect on the catalytic properties of supported vanadium oxide catalysts.

Calcination Temperature

The state of vanadium oxide in supported vanadium oxide catalysts is strongly dependent on calcination temperature. For example, the properties of supported V_2O_5/TiO_2 catalysts prepared from vanadyl oxalate change with calcination temperature (Saleh et al., 1986). At low calcination temperatures, 100-200°C, the vanadium oxide component exists as inactive vanadyl oxalate and the catalyst needs to be activated by decomposing the oxalate ligands. At intermediate calcination temperatures, 350-575°C, the vanadium oxide component is present as a surface vanadium oxide overlayer on the titania support and optimum catalytic performance is obtained. At calcination temperatures of 575°C and above, the TiO_2 support undergoes a loss in surface area which transforms the surface vanadium oxide overlayer to microcrystalline V_2O_5 particles as well as a $V_xTi_{1-x}O_2$ (rutile) solid solution. The destruction of the surface vanadium oxide overlayer at elevated temperature dramatically decreases the catalyst activity and selectivity, and is responsible for catalyst deactivation. Thus, the calcination temperature is a critical parameter that controls the activation and deactivation of supported vanadium oxide catalysts.

Molecular Structure of Surface Metal Oxide Species

The molecular structures of the surface vanadium oxide species in supported vanadium oxide catalysts depend on surface coverage and extent of surface hydration (Deo et al., 1989; Eckert and Wachs, 1988). Under typical reaction conditions, usually 200-500°C, the surface concentration of adsorbed moisture is practically zero and the supported vanadium oxide catalyst surface is essentially dehydrated. Solid state ^{51}V NMR studies have revealed that for dehydrated surfaces and low surface vanadium oxide coverages, predominantly tetrahedrally coordinated vanadium oxide surface species, VO_4 units, exist in the oxide overlayer (Eckert and Wachs, 1988). These tetrahedral surface VO_4 units give rise to a strong Raman band in the 1020-1040 cm^{-1} region which is characteristic of a very short V=O bond (Chan et al., 1984; Cristiani et al., 1989; Oyama et al., 1989). The combined Raman and NMR studies suggest the following structure for the surface VO_4 unit:



This distorted surface VO_4 species appears to be present on different oxide supports (Al_2O_3, TiO_2, and SiO_2) and suggests that the molecular structure of surface vanadium oxide species is independent of these specific oxide supports for low surface vanadium oxide coverages and dehydrated surfaces.

Catalytic Reactivity

The reactivity of supported 1% V_2O_5 on Al_2O_3, TiO_2, and SiO_2 catalysts was probed with the methanol oxidation reaction (Deo and Wachs, 1990). The TiO_2 and SiO_2 supports were essentially inactive for methanol oxidation, but the Al_2O_3 support was very active for the conversion of methanol to dimethyl ether, and the supported V_2O_5/Al_2O_3 catalyst had to be corrected for the alumina support reactivity. The reaction rates were normalized per surface vanadium oxide species since the Raman measurements showed that, at these low surface vanadium oxide coverages, the vanadium oxide was 100% dispersed on the support surface. The turnover rate for methanol oxidation over the different supported vanadium oxide catalysts were found to vary by three orders of magnitude as shown in Table 2.

Table 2. Reactivity of Supported Vanadium Oxide Catalysts.

Catalyst	Turnover Rate (sec^{-1})
1% V_2O_5/TiO_2	3.8×10^0
1% V_2O_5/Al_2O_3	3.0×10^{-3}
1% V_2O_5/SiO_2	2.0×10^{-3}
V_2O_5	2.0×10^{-2}

These reactivity studies demonstrate that the same surface vanadium oxide species exhibits vastly different reactivities which markedly depend on the specific oxide support. The dramatic promotional effect of the oxide supports suggests that the active site in the supported vanadium oxide catalysts during partial oxidation reactions is the bridging oxygen that anchors the surface vanadium oxide species to the oxide support. Thus, the relatively inert Al_2O_3 and SiO_2 supports sluggishly release this bridging oxygen whereas the somewhat reducible TiO_2 supports more readily release this bridging oxygen. The influence of surface vanadium oxide coverage upon the turnover rates of V_2O_5/TiO_2 catalysts was also investigated and the turnover rate was found to be essentially independent, $4.6 \pm 0.8 \times 10^0$ sec^{-1}, of surface vanadium oxide concentration below monolayer coverage. The oxide supports also affected the reaction selectivity since on the inactive TiO_2 and SiO_2 supports H_2CO was the primary reaction product, and on the active Al_2O_3 support, which contains a high concentration of Lewis acid sites, CH_3OCH_3 was the primary reaction product. Thus, the specific oxide support employed for the preparation of supported vanadium oxide catalysts is critical since it controls the catalyst reactivity and selectivity.

CONCLUSIONS

This study demonstrates that molecular engineering of supported metal oxide catalysts is currently possible from molecular level information about the number of active surface sites and reactivity per site. Such fundamental information is currently available from molecular spectroscopies such as Raman spectroscopy. The critical parameters that determine the number of active surface sites and reactivity per site are the specific oxide support, catalyst composition, and calcination temperature. The oxide support surface area and concentration of reactive surface hydroxyls determine the total number of potential active surface sites, surface metal oxide species, in supported metal oxide overlayers. The oxide support also acts as a ligand and determines the reactivity per active surface site (surface metal oxide species). The TiO_2 support increases the reactivity per active surface vanadium site by three orders of magnitude relative to Al_2O_3 and SiO_2 supports for methanol oxidation over supported vanadium oxide catalysts. The catalyst composition determines the number of active surface sites that are actually formed by reaction with the oxide support surface hydroxyls. The calcination temperature controls the total number of active surface sites via catalyst activation and deactivation. A critical activation temperature is required to transform the metal oxide precursors to surface metal oxide species, the active surface sites. Calcination at elevated temperatures may result in catalyst deactivation by conversion of the surface metal-oxide species, the active sites, to crystalline metal oxide phases. The synthesis method of supported metal oxide catalysts is not critical since it does not influence the number of active surface sites and the reactivity per site. The location and molecular structures of the surface metal oxide species are also not determined by the synthesis and are controlled by the surface properties of the oxide supports. The approach outlined in this study can be used to assist in the molecular engineering of supported vanadium oxide catalysts for different applications as well as the molecular engineering of other supported metal oxide catalytic systems.

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