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Palladium–vanadium interaction in binary supported catalysts

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Abstract

We have studied the activity and selectivity of Pd/γ-Al_2O_3, VO_x/γ-Al_2O_3 and Pd–VO_x/γ-Al_2O_3 catalysts for the decomposition of NO and the reduction of NO with CO. Pd–VO_x/γ-Al_2O_3 catalysts were prepared by anchoring $Pd(AcAc)_2$ on VO_x/γ-Al_2O_3. Characterization of the binary samples by hydrogen chemisorption and TPR measurements indicated that the reduction of VO_x is enhanced by a close contact with palladium and that partially reduced vanadia decorate noble metal particles. This palladium–vanadium interaction alters the catalytic properties of palladium: the activity for NO decomposition is higher for the binary sample and, for the NO–CO reaction, both the activity and the selectivity to N_2 increase when vanadium is in contact with palladium. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Pd–VO_x/γ-Al_2O_3 catalysts; NO decomposition; NO reduction

1. Introduction

The addition of MoO_3, WO_3 and V_2O_5 to Pd or Pt supported catalysts has been reported to improve the catalytic properties for NO reduction [1–3]. Based on these results, we have studied the decomposition of NO and its reduction with CO catalyzed by a binary palladium–vanadium supported catalyst: Pd–VO_x/γ-Al_2O_3. These simple reactions are analyzed as a first approximation to the complex network of reactions that take place during the elimination of NO, CO and HCs in automotive exhaust emissions.

The main objective of our work was to investigate how the interaction between palladium and vanadium influences the catalytic properties of Pd–VO_x/γ-Al_2O_3. In order to create the desired interaction, binary catalysts were prepared by anchoring $Pd(AcAc)_2$ on a monolayer of vanadium oxide supported on γ-Al_2O_3.

Taking into account that NO decomposition as well as NO reduction with CO are redox type reactions, the reducibility of the samples is a relevant aspect to be investigated. Characterization of samples was performed by hydrogen chemisorption, temperature programmed reduction (TPR) and oxygen uptake measurements (OUM).

2. Experimental

2.1. Catalyst preparation

Two samples of vanadia supported on γ-Al_2O_3 (BET area 77 m^2/g), designated as V1 and V2, were prepared by impregnating the support with aqueous solutions of NH_4VO_3 of appropriate concentration at constant pH.

In order to obtain the binary catalysts, palladium was anchored to samples V1 and V2 using a solution of $Pd(AcAc)_2$ in toluene, containing 4.4×10^{-3} g $Pd(AcAc)_2$/ml. In this way samples PV1

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and PV2 were obtained. A Pd/γ-Al_2O_3 catalyst, sample P, was also prepared by adding the $Pd(AcAc)_2$ solution to γ-Al_2O_3.

All samples were calcined at 400°C for 2 h after washing with fresh solvent.

2.2. Catalyst characterization

The vanadium and palladium loading was determinated by A.A. analysis. Hydrogen chemisorption measurements were performed in a volumetric apparatus in the 50–500 torr pressure range. Samples P, PV1 and PV2 were previously reduced at 300°C in flowing H_2. The double isotherm method was used to determine the amount of irreversibly chemisorbed hydrogen, $(H/Pd)_{irr}$, at room temperature. The palladium dispersion was calculated assuming a 1:1 chemisorption stoichiometry.

Using the same technique, hydrogen chemisorption measurements were performed at 68°C in order to study the α–β hydride transition region.

TPR experiments were conducted in a conventional apparatus. The samples were heated linearly (10°C/min) from 0 to 500°C in a H_2(5%)/Ar mixture. Oxidation was carried out at 350°C in air during 1 h prior to switching the gas flow to H_2/Ar.

The OUM for all samples were investigated at 300°C in the volumetric apparatus. The samples were prereduced in H_2 flow at 300°C for 1 h and evacuated at 300°C overnight. The O/Me ratio (Me: Pd, V or Pd+V) was then measured in the 50–500 torr pressure range.

2.3. Catalytic tests

Two experiments were carried out: the decomposition of NO and the reduction of NO with CO. For both, approximately 200 mg of VO_x/γ-Al_2O_3, Pd/γ-Al_2O_3 or Pd–VO_x/γ-Al_2O_3 samples were placed in a U shaped Pyrex glass flow reactor. Before introducing the reactants, catalysts were calcined at 300°C for 1 h and then reduced at the same temperature for half an hour in H_2. After this pretreatment, the NO conversion (X_{NO}) dependence with time was measured at 300°C, using a flow of 50 cm^3/min of a NO–He mixture (420 ppm of NO). For the NO–CO reaction, a stoichiometric feed was used (210 ppm of NO, 210 ppm of CO in He). Reaction products were analyzed by gas chromatography, employing a TCD detector, He as carrier gas and two Porapack Q columns. One of them held at −10°C was used to separate N_2, O_2, CO and NO. The other column operated at 40°C and allowed the separation of N_2O and CO_2. Catalyst PV2 was not tested for the NO–CO reaction.

3. Results

3.1. Catalyst characterization

The main characterization results are reported in Table 1. Considering the low vanadium loading, and that vanadia highly interacts with alumina, it is reasonable to assume that vanadium is molecularly dispersed on the support. The fraction of a monolayer achieved may be estimated taking into account that each VO_x unit occupies 0.2 nm^2 [4]. As can be observed in Table 1, the alumina surface in sample V1 is fully covered by vanadia, while in sample V2 half a VO_x monolayer has been obtained.

The metal loading and noble metal dispersion for Pd/γ-Al_2O_3 and Pd–VO_x/γ-Al_2O_3 catalysts are also reported in Table 1. Palladium concentrations are slightly higher for binary samples. This result suggests that VO_x species are anchoring sites for the $Pd(AcAc)_2$ precursor due to the low concentration of OH groups expected on the alumina support after vanadium addition. In other words, a palladium–vanadium interaction occurs in the preparation step. However, the $(H/Pd)_{irr}$ ratios indicate that the fraction of exposed palladium atoms is lower for the PV than for P samples. The study of the α–β

Table 1
Metal loading, hydrogen chemisorption and oxygen uptakes

Sample	V (wt.%)	θ (%)[a]	Pd (wt.%)	$(H/Pd)_{irr}$	O/Me
P	–	–	0.68	0.47	1
PV1	3.1	96.7	0.87	0.28	0.60
PV2	1.4	43.7	0.75	0.24	0.50
V1	3.1	96.7	–	–	0.63
V2	1.4	43.7	–	–	0.46

[a] Fraction of vanadium monolayer, assuming a surface coverage of 0.2 nm^2 per VO_x species [4].

hydride transition region shows that it is similar for both P and PV samples indicating that palladium crystals have approximately the same size. Thus, the decrease of palladium dispersion in samples PV1 and PV2 is not related to a higher size of noble metal particles but to a decoration of the metal surface by partially reduced vanadia. At this point it is interesting to note that the presence of bulk vanadia has been reported for $VO_x/\gamma\text{-}Al_2O_3$ samples prepared in the same way as V1 and V2 catalysts [5]. Consequently, we can argue that the major part of vanadia is molecularly dispersed but a low concentration of crystalline V_2O_5 may be present. If this oxide is reduced during the hydrogen pretreatment and spread on the palladium surface, the decrease in the fraction of exposed palladium atoms is explained.

TPR profiles for samples V1 and V2 are shown in Fig. 1. As it is clearly seen, the reduction of VO_x in these samples begins at approximately 300°C. The hydrogen consumption peak is more noticeable for sample V1 due to the higher vanadium loading.

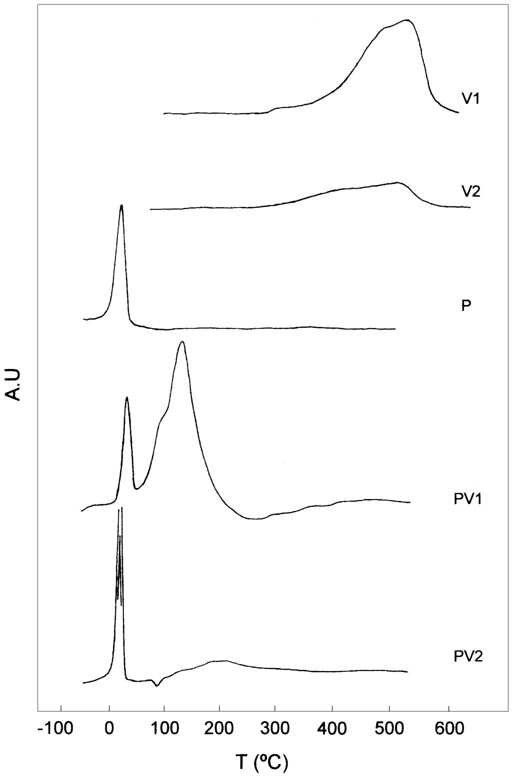


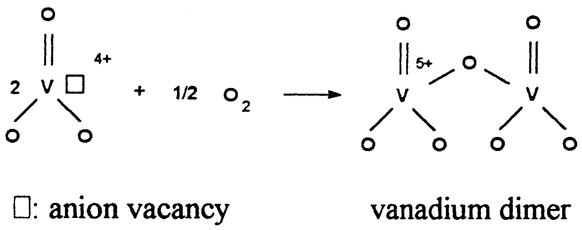
Fig. 1. TPR profiles for samples P, PV1, PV2, V1 and V2 treated in oxygen at 350°C.

On the other hand, the TPR profiles for samples P, PV1 and PV2, also shown in Fig. 1, present other features. A low temperature peak, at approximately 20°C, is assigned to the reduction of PdO. For the monometallic sample the hydrogen consumption indicates that the whole amount of palladium is reduced. On the other hand for the binary samples the amount of hydrogen consumed at low temperature represents a reduction of 50 and 90% of palladium on samples PV1 and PV2, respectively. These results suggest that the reducibility of the noble metal is diminished by interaction with vanadium. This effect is less pronounced on sample PV2 probably due to the lower vanadium and palladium content. In addition a palladium hydride decomposition peak at about 95°C is also observed. This palladium hydride peak was not observed in sample P due to the higher metal dispersion (Table 1).

The reduction profiles for the binary samples present an additional hydrogen consumption peak at about 180°C, which is assigned to a partial reduction of VO_x species due to close contact with the noble metal. Here again the peak is well defined on sample PV1, an indication that the palladium–vanadium interaction is higher. Comparing the high temperature peaks of samples V1 and V2 with those of samples PV1 and PV2 it is clear that the interaction lowers the vanadia reduction temperature by 300°C approximately.

According to these assignments, a fraction of palladium in the binary samples, 50 and 10% in samples PV1 and PV2, respectively, is not reduced. In other words, the reduction of VO_x takes place at the expense of a fraction of Pd that remains in an oxidized state. A similar interpretation was given for the oxidation state of Ce supported palladium [6]. Another possibility is that the fractions of palladium not reduced at a low temperature, become reduced along with the VO_x species, that is at a higher temperature. Unfortunately we cannot distinguish between these two alternatives.

Regarding the OUM, a Pd/O atomic ratio of unity for sample P (Table 1) was obtained. This result indicates that complete oxidation of palladium takes place at 300°C. On the other hand, for vanadium containing samples, the O/Me ratio is in the 0.5–0.6 range. These values are related to a reoxidation of vanadium dimers, according to the following reaction



(1)

The high loading of vanadium compared with palladium renders the contribution of the noble metal to the O/Me ratio negligible. Consequently, the oxygen uptake due to palladium oxidation cannot be determined.

Summing up, we could describe the binary samples as palladium particles (not fully reduced) decorated by partially reduced vanadium oxide and supported on a VO_x monolayer (sample PV1) or a VO_x submonolayer (sample PV2).

4. Catalytic test

4.1. NO decomposition

VO_x/γ-Al_2O_3 catalyst: The conversion of NO versus time at 300°C is shown in Fig. 2 for sample V1. This catalyst shows a much higher initial conversion, 70%, than that corresponding to catalyst V2 (8%) (not shown in Fig. 2). N_2 was the main product observed. It is evident from Fig. 2 that the vanadium sample deactivates with reaction time; after 20 min the catalyst is totally inactive.

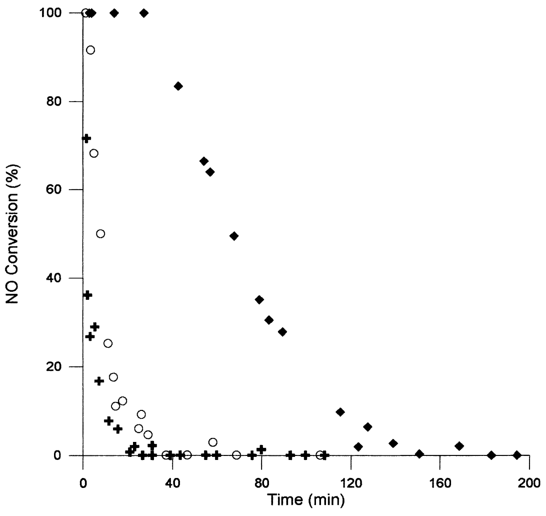
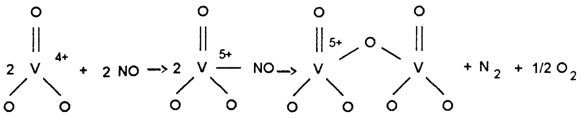


Fig. 2. NO decomposition as a function of time for samples V1 (+), P (○) and PV1 (◆). Feed conditions: [NO]=420 ppm; GHSV=13 000 h^{-1}; T=300°C.

In spite of extensive research related to NO decomposition, to our knowledge, the reaction on vanadium supported catalysts has not been reported. Only unsupported V_2O_5 has been investigated and it was found to be inactive at temperatures lower than 640°C [7].

Before discussing the catalytic results of NO decomposition over the vanadium samples it is important to recall that our catalysts were prereduced at 300°C in pure hydrogen for half an hour. According to the TPR experiments, this temperature level may be too low to accomplish the partial reduction of VO_x. However the TPR experiments were conducted with a H_2(5%)/Ar mixture; the reduction of VO_x/γ-Al_2O_3 starts at 300°C and the peak maximum is located at 500°C. Using pure hydrogen and a longer treatment time the partial reduction of vanadium could be accomplished. A change in the color of sample V1 and V2, from yellow (after oxidation) to gray (after reduction), demonstrated that the reduction takes place at 300°C.

We can assume that a mechanism similar to that proposed by Winter [7] take places over a V^{4+} center: NO from the gas phase is adsorbed by a V^{4+}, then two adjacent adsorbed NO molecules would react to form N_2. The following reaction describes this mechanism:



(2)

This reaction also explains the deactivation of V samples, since the fixation of oxygen is an irreversible reaction and V^{5+} is not active for further NO decomposition.

Using the data in Fig. 2, we have estimated that the amount of NO reacted was one order of magnitude lower than the total amount of vanadium atoms in the sample, indicating that for the present experimental conditions not every vanadium atom is an active site for NO decomposition.

Pd/γ-Al_2O_3: Fig. 2 shows the decomposition of NO versus time for this sample. A high initial activity

(100%) is obtained but here again a deactivation process is observed. After 40 min the sample is no longer active. In this case, the adsorption of NO takes place on metallic palladium sites, followed by the dissociation into nitrogen and oxygen atoms. N_2 is desorbed and the metal surface is covered by oxygen atoms making the palladium inactive for further NO adsorption [8]. It is speculated that each palladium atom is an active site for the NO decomposition. From our catalytic data, quantification of the amount of NO converted indicates that all palladium atoms are oxidized to PdO.

Pd–VO_x/γ-Al_2O_3: The catalytic results for sample PV1 are also shown in Fig. 2 (PV2 follows the same trend and is not shown). When compared with results of V and P samples, important differences arise. The high initial conversion (100%) is maintained for 30 min and then it decays slowly to become inactive in about 120 min. Therefore, the binary sample is active for a longer period of time than monometallic samples. The modifications in the catalytic performance could not be ascribed to the simple fact that more active sites are available on the binary sample than in samples P or V. A synergetic effect between palladium and vanadium should be invoked; we could argue that oxygen that poisons the palladium surface is taken away by partially reduced vanadium. As shown by TPR measurements, reducibility of VO_x is enhanced in binary samples and more V^{4+} centers are available in Pd–VO_x/γ-Al_2O_3 than in V1 or V2.

It is interesting to recall that, according to the characterization results, palladium particles in binary samples were partially covered by reduced vanadia. Even so, palladium seems to be as active in this case (samples PV) as it is on monometallic P where the dispersion is higher.

4.2. Reduction of NO with CO

Fig. 3 shows the variation of NO conversion with time for samples PV1 and P. The results for V catalysts are not shown, since the observed trend for the conversion of NO is similar to that corresponding to NO decomposition (Fig. 2). Furthermore, the conversion of CO for V samples was always null. Thus, VO_x seems inactive towards CO.

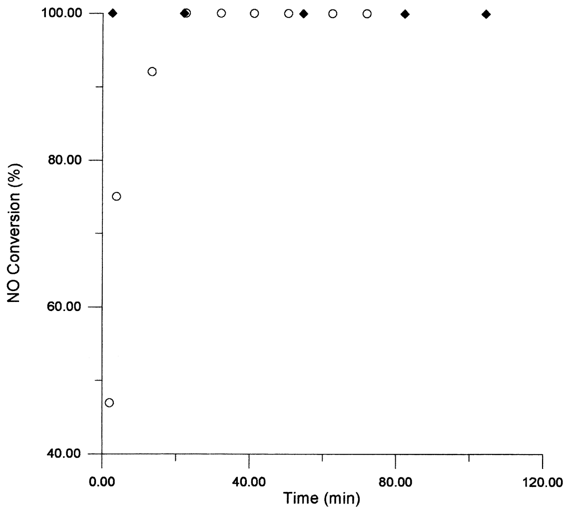


Fig. 3. NO conversion versus time for the NO+CO reaction over samples P (○) and PV1 (◆). Feed conditions: [NO]=210 ppm; [CO]=210 ppm; GHSV=16 000 h^{-1}; T=300°C.

Regarding NO reduction by CO, both samples P and PV1, remain active after 2 h of reaction time. The maximum value for NO conversion, 100%, is reached immediately by sample PV1. On the other hand, an activation of sample P takes place; the values of X_{NO} increase from 40 to 100% in the first 20 min (Fig. 3). Regarding X_{CO} for samples P and PV1, it is worth noting that for both catalysts a 100% value is immediately reached. Thus, for the case of sample P, it seems rather difficult to explain why the conversion of NO is not also 100% from the beginning. This behavior seems to be related to the presence of oxygen impurities introduced in the system while switching from helium to feed mixture flow. Due to the low concentration of CO (210 ppm) the elimination of adsorbed oxygen is delayed, which in turn affects the adsorption and decomposition of NO. The larger concentration of active sites in sample PV1 (surface palladium atoms plus VO_x species) than in sample P would explain the absence of this transient conversion of NO.

The main reaction products for the NO+CO reaction were N_2 , N_2O and CO_2. The selectivity will be discussed in terms of N_2, that is the major nitrogen containing product. For the sake of simplicity we discuss the results obtained at 100% conversion of CO; significant differences arise when comparing samples P and PV1.

The selectivity to N_2 versus reaction time is shown in Fig. 4. The palladium–vanadium sample is always

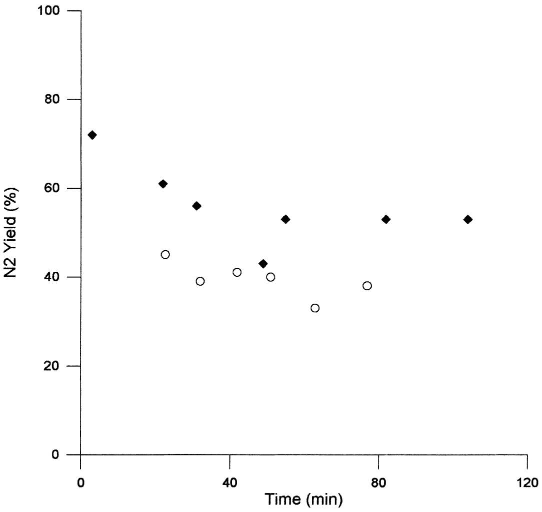


Fig. 4. Yield of N_2 versus time for the NO+CO reaction over samples P (○) and PV1 (◆) at X_{NO}=100%. Feed conditions: [NO]=210 ppm; [CO]=210 ppm; GHSV=16 000 h^{-1}; T=300°C.

more selective than sample P. After about 80 min constant N_2 yield values seem to be reached for both PV1 and P catalysts; 55 and 37%, respectively. To explain the enhanced selectivity to N_2 in the presence of vanadium we consider that palladium atoms and VO_x species are both active sites for the production of N_2. Supported vanadia does not deactivate during the NO conversion, as in the case of samples V1 and V2, due to the interaction with palladium. The oxygen taken up by the VO_x species seems to be removed by CO as CO_2. In other words, palladium would be able to catalyze the reduction of V^{5+} to V^{4+} by CO, and the production of N_2 by reaction (2) is maintained. The availability of VO_x active sites even after 80 min of reaction time seems to be the only explanation for the higher selectivity of sample PV1.

Once again, as was the case for NO decomposition, the presence of partially reduced VO_x on the surface of palladium seems to be responsible for the higher catalytic activity and selectivity exhibited by Pd–VO_x/γ-Al_2O_3 catalysts. One question that is difficult to answer is the oxidation state of palladium under reaction conditions. Because we speculated that palladium facilitates the reduction of V^{5+} to V^{4+}, at least a fraction of palladium is in an oxidized state. Since oxidized palladium is easily reduced by CO, new Pd^0 sites may be formed to promote the reaction. Therefore, it seems reasonable to state that both Pd^0 and Pd^+ are present under reaction conditions.

5. Conclusions

The characterization of Pd–VO_x/γ-Al_2O_3 catalysts indicated that they should be envisaged as palladium crystals supported on alumina and partially covered by vanadia. Consequently, a strong interaction between palladium and vanadium exists in these binary catalysts. The reducibility of VO_x is enhanced and more V^{4+} sites are formed. These species seem to render palladium more active in the decomposition of NO and are both more active and more selective to N_2 in the reduction of NO with CO.

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