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The morphology component in DeNO$_x$ catalyst activity

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Abstract

An experimental design was done to study the effects of initial support morphology (porosity and BET surface area) and catalyst synthesis conditions (vanadia loading and calcination temperature) on performance of DeNO$_x$ catalysts. The results show that final catalyst surface area is independent of initial support morphology, but NO conversion is sensitive to the initial state of the support as well as to synthesis conditions. Conclusions challenge the convention that catalyst performance benefits from high support surface area. The findings also teach that increased porosity improves catalyst stability against sintering.

Keywords: DeNO$_x$ catalyst; Selective catalytic reduction; Titania

1. Introduction

The most widely used catalyst for the selective catalytic reduction (SCR) of nitrogen oxides in power plant emissions is a form of vanadium pentoxide supported on tungsten doped titania. It is generally accepted that a high surface area titania substrate is beneficial to SCR catalyst performance. The structure of titania, in terms of pore volume and pore size distribution, is also important but often overlooked.

The purpose of this study is to determine if, and to what extent the initial morphology state of the tungsten on titania support, its surface area and porosity, influence the final properties of a SCR catalyst. If important, then the system will retain some "memory" of the initial state at the completion of catalyst synthesis. If they are not, then all memory will be erased by procedures used to make the catalyst.

Statistical design of experiments (DOE) is an effective means by which to determine the relationship between catalyst performance and initial support properties. Since it is a statistical measurement, the differences in initial states do not have to be extreme in order to determine an effect. Additionally, experimental design probes interactions between factors as well as the influence of the factors themselves.

2. Experimental

The surface area of the tungsten on titania support powder as well as the finished catalyst was determined using a Micromeretics TriStar automated physisorption unit. The pore volume distributions were determined by fitting the isotherms with a linear combination of pre-determined isotherms from a density functional theory model using Micromeretics' DFTPlus software. NO conversion was determined using catalyst powders in a fixed bed reactor. The composition of the reactor feed was 300 ppm NO, 360 ppm NH_3, 3% O_2, 10% H_2O, and balance N_2. Space velocity was 83,000/h, and conversion was measured at 270 °C.

Four 12 wt.% tungsten on titania powders with high or low surface area and high or low porosity were synthesized in pilot plant quantities using Millennium Chemical's proprietary technology. The porosity and BET surface area were changed in every combination of high and low as a means to vary initial powder properties. The rigors of experimental design demand very little error in the actual values of initial factors, otherwise the propagation of errors to the results creates problems when fitting the model [1]. For this reason, rather than use the actual values of BET surface area and porosity, the synthetic conditions that govern these properties, which are more amendable to controlled discrete values, were used in model determination. Their values as coded variables are included in Table 1.

The judgment as to whether a particular set of factors is significant in influencing a response will be made using analysis

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Table 1
Experimental design catalyst preparation conditions, measured NO conversion and catalyst surface area

Catalyst	Measured porosity (<30 nm) (ml/g)	Measured support BET (m^2/g)	V_2O_5 loading (wt.%)	Calcination temperature (°C)	NO conversion at 270 °C (%)	Catalyst surface area (m^2/g)
16	0.085	73.5	0.9	600	74.5	60.9
9	0.085	73.5	0.9	700	76.8	41.6
6	0.085	73.5	1.8	600	85.5	61.6
4	0.085	73.5	1.8	700	60.4	19.9
3	0.098	100	0.9	600	61.6	66.4
14	0.098	100	0.9	700	57.3	41.2
10	0.098	100	1.8	600	87.7	55.6
1	0.098	100	1.8	700	55.4	17.2
7	0.106	79.7	0.9	600	68.4	68.5
15	0.106	79.7	0.9	700	76.7	48.7
13	0.106	79.7	1.8	600	73.2	51.1
8	0.106	79.7	1.8	700	64.9	21.3
5	0.107	95.5	0.9	600	65.5	71.1
2	0.107	95.5	0.9	700	66.7	48.9
12	0.107	95.5	1.8	600	81.6	61.2
11	0.107	95.5	1.8	700	71.6	28.1

of variance (ANOVA). The specific criteria used are adjusted R^2 and the probability that the null hypothesis (or random error) explains data variability as well as the model (P-value). The convention of a P-value <5% as the standard for significance will be used in this study [2].

Catalysts were prepared from these powders by depositing aqueous vanadia solutions at two different loadings and activating at two different calcination temperatures. The four parameters, porosity, initial support surface area, vanadium oxide loading, and calcination temperature are combined into a two level, full factorial design study of 16 catalysts. The parameter levels and responses are listed in Table 1. Catalyst numbers in the table do not increment numerically due to the randomization of the measurements.

3. Results and discussion

Table 1 shows that both increased vanadia loading and high temperature calcination induce sintering. The catalyst surface area ANOVA shows that only these two variables significantly influence sintering. The adjusted R^2 for the model is 95.4% with the P-value of 0.

The dependence of surface area on the four factors as well as the fit to the model are represented in Fig. 1 where surface area is plotted as a function of calcination temperature and vanadia loading. As a point of convention and clarity, the independent variables are represented by their coded values with +1 representative of the high value and −1 representing the low. The close fit to data confirms the ANOVA results that vanadia loading and calcination temperature are determinant. The close spacing of the data at each of the corners verifies that the two variables not considered in the figure (support BET and porosity) have little influence.

By comparison, NO conversion exhibits a more complex dependence on the design factors. The ANOVA shows that three main factors of support BET, vanadia loading, and calcination temperature are significant with P-values of 0.052, 0.053 and 0.003, respectively. Porosity is insignificant as a main factor at 0.502. In addition, there are three important interactions. They are the interactions of support BET with vanadia loading (P-value = 0.007), porosity with support BET (P-value = 0.035), and porosity with calcination (P-value = 0.012). The adjusted R^2 shows that the total fit can account for over 86% of the data variability with a P-value of 0.007.

The dependencies of conversion on the design factors are shown in Figs. 2 and 3, the following two figures. Since there are so many influencing factors, the need for accuracy dictates that conversion at each point be represented as the average of values measured at the specific set of conditions. For example, the value for conversion in Fig. 2 below for the set of experiments at low support BET and low vanadia loading, i.e. (−1, −1), respectively, is the performance average of catalysts

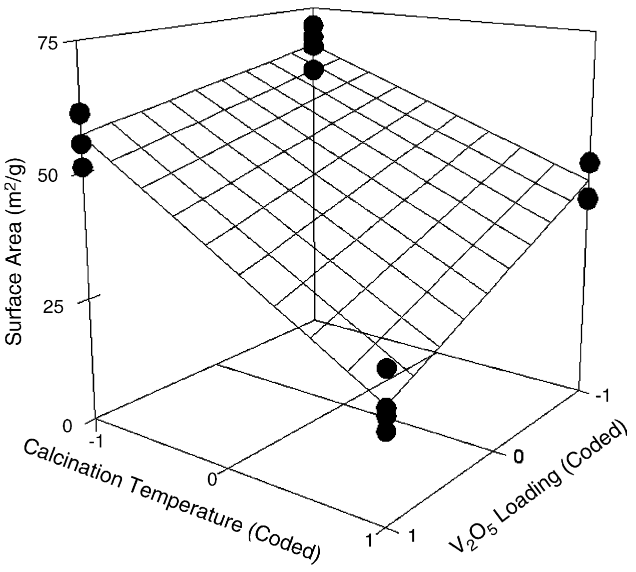
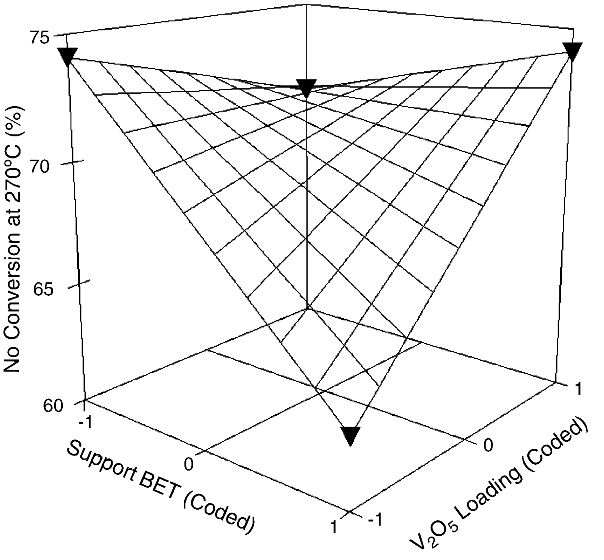
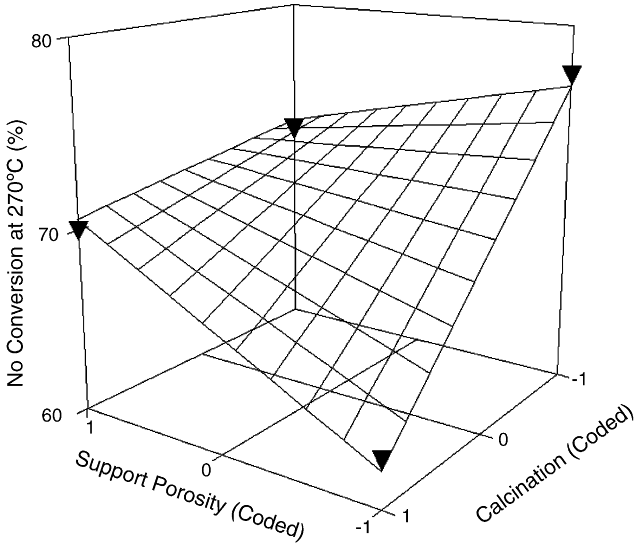


Fig. 1. Catalyst surface area versus calcination temperature and vanadia loading.



Design Parameter Levels		
Support BET	V2O5 Loading	Averaged Conversion
		(%)
-1	-1	74.1
-1	1	71.0
1	-1	62.8
1	1	74.1

Fig. 2. Averaged NO conversion versus support BET and V_2O_5 loading. The data table is added for clarity.



Design Parameter Levels		
Support Porosity	Calcination	Averaged Conversion
		(%)
-1	-1	77.3
-1	1	62.5
1	-1	72.2
1	1	70.0

Fig. 3. Averaged NO conversion versus support porosity and calcination temperature. The data table is added for clarity.

7, 9, 15 and 16 from Table 1. The results of the averaging are included in tables below the figures for clarity.

Fig. 2 shows that NO conversion is sensitive to vanadia loading at high support surface area, and to support surface area at low vanadia loading. There is little difference in average conversion at the support BET, vanadia loading combinations of $(-1, 1)$, $(-1, -1)$ and $(1, 1)$. It is generally agreed that the DeNO$_x$ active site is composed of at least two adjacent vanadium ions anchored to the oxide support and joined by at least one oxygen bridge [3]. Simple proximity arguments can be used to contend that this configuration is less probable at high surface areas and low loadings resulting in the average conversion at this point being lower compared to the other three combinations.

The unexpected result is that conversion stays constant with lower vanadia loadings at low support BET compared with the combinations at high vanadia loadings. These findings in conjunction with the surface area measurements suggest that the most stable catalyst would be prepared at low support BET and low vanadia loading. The lower surface area support allows a lower vanadia loading to yield comparable activity given the proportionate increase the number of vanadia active sites as the data suggests. The lower vanadia loading is less deleterious to surface area (Fig. 1), thus improving stability. Also, the lower initial support BET will have little affect upon final catalyst surface area within the limits tested in this study.

Another surprising result is represented in Fig. 3 where the interaction between calcination temperature and initial support porosity becomes apparent. Within the scope of this study, the role of calcination may be considered as either a means to activate vanadia or as a test to estimate catalyst performance under process conditions that promote thermal sintering. The figure suggests that a more porous support will be more robust to calcining variations during catalyst synthesis, as well as being more resistant to long term deactivation under process conditions.

The explanation of this behavior is related to how porosity changes with sintering. We have learned (data not presented) that in both cases of sintering due to increased vanadia loading and increased temperature, smaller pores are destroyed first. Larger pores, those in excess of 30 nm in diameter, are not affected by the variations employed in this study. For this reason, supports with a larger number of narrow pores and smaller total pore volume will be less stable against sintering. Since smaller pores induce higher capillary pressure, any solvent impregnation, as that used in these catalyst preparations, will certainly deposit a significant, if not a disproportionate amount of active component in the more narrow pores [4]. Collapse of these pores will limit exposure of the active component to the process and reduce activity. Therefore, a support with small pores will be inherently less stable to thermally induced deactivation.

4. Conclusions

The lack of dependence of catalyst surface area on initial support morphology shows that this response shows no memory of the initial state of the support within the ranges tested in this study. However, the dependence of NO conversion on initial powder morphology suggests that there is a relationship between the initial support structure and the ultimate performance of the catalyst. The most striking of these is the finding that catalyst supports with lower surface area improve catalyst activity at low vanadia loadings. The lower vanadia loadings, in turn, help stabilize the catalyst against thermal sintering. This study also shows that higher support pore volume and larger average pore diameter stabilize the catalyst against thermal sintering. Therefore, deliberate catalyst design should begin with careful support selection even to the detail of specifying porosity.

The different responses of the two measurements, i.e. catalyst surface area and NO conversion, to the initial powder structure suggest that it is possible to decouple catalyst activity from a strong correlation to surface area. In this way, the harmful effects to activity caused by thermal sintering under process conditions may be mitigated.

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