

Chapter 14

Interactions in Alumina-Based Iron–Vanadium Catalysts under High-Temperature Oxidation Conditions

M. C. Springman¹, F. T. Clark¹, D. Willcox², and I. E. Wachs³

¹Amoco Research Center, Naperville, IL 60566

²Department of Chemical Engineering, University of Illinois at Chicago, Chicago, IL 60607

³Zettlemoyer Center for Surface Studies, Department of Chemical Engineering, Lehigh University, Bethlehem, PA 18015

Alumina supported iron and vanadium oxides have been studied under a variety of conditions in an effort to understand the metal oxide-support interactions which occur during oxidative regeneration of spent hydrotreating catalysts. Iron and vanadium - two common contaminant metals found in petroleum feedstocks - were deposited on gamma alumina at levels of 5 to 10wt%, as oxides. The catalysts were subjected to calcination temperatures between 500°C and 900°C, and to atmospheres of dry air, wet air, NH₃, and SO₂/O₂. Characterization by XRD, N₂ desorption porosimetry, XPS, ICP, and Raman Spectroscopy was performed before and after treatment.

Under conditions of dry air calcination, vanadium oxides form hydrated surface metavanadates at low temperature, but at higher temperatures, vanadium migrates to the particle surface where crystalline vanadium pentoxide forms. Vanadium oxides catalyze the loss of surface area and a transition of the alumina phase from gamma to theta at elevated temperature. Iron oxides alone do not affect the surface area or pore structure of alumina under the conditions studied. In the presence of iron oxides, however, vanadium oxides form hydrated surface pyrovanadates at low calcination temperature, and at higher temperatures, vanadium migration and alumina pore sintering are enhanced. A transition from gamma to kappa alumina occurs when the catalyst containing both iron and vanadium oxides is calcined at elevated temperature.

Treatment at 900°C in atmospheres of wet air, NH₃, and SO₂/O₂ did not induce significant changes in the blank alumina or in catalysts containing only iron oxides. These catalysts retained the high surface area, gamma alumina phase. For catalysts containing only vanadium oxides, vanadium migrated to the surface of the catalyst particle at about the same rate regardless of atmosphere

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after 900°C treatment. However, for catalysts containing both iron and vanadium oxides, the rate of vanadium migration to the particle surface after 900°C treatment increased in the order: dry air < wet air < NH₃. Surface area and pore volume are retained to a greater degree for the catalyst containing only vanadium oxides after NH₃ treatment compared with dry and wet air treatment. Analysis of the catalyst residues after high temperature treatment in the SO₂/O₂ environment indicates that exposure to SO₂ retards the destructive interactions which occur between vanadium and alumina in the absence of SO₂. These results are discussed in terms of existing models for alumina desurfacing and implications for laboratory aging of commercial catalysts.

Petroleum refining operations represent one of the most important industrial applications of catalysis. Of the three major U.S. catalyst markets in 1990, petroleum refining was the largest, representing 37% of the 1.8 billion dollar industry (1). Hydrotreating catalysts are used at several stages of the refining process. The primary cause of deactivation in hydrotreating catalysts is coke deposition; accumulation of V, Fe, and Ni contribute as well. Once a catalyst has become deactivated, it must be replaced or regenerated in order to maintain activity. Regeneration is more desirable economically since it represents savings not only in catalyst replacement costs, but also in the disposal of spent catalyst, which often contains hazardous materials.

Regeneration of spent hydrotreating catalysts has been approached in a number of ways. Coke deposits can be removed by a controlled burn off, but metals such as nickel, iron, and vanadium often remain in substantial concentrations. These metals not only interfere with catalyst performance, but can be destructive to the catalyst itself, especially during the high temperature removal of coke. In regeneration studies which have focused on the effects of temperature, oxygen, and steam on the removal of coke and sulfur from spent hydrotreating catalysts (2-7), it is generally concluded that full activity can be restored if coke deposits are removed under carefully controlled oxidation conditions, including moderate temperatures and the absence of steam. Vanadium, nickel and iron are deposited along with coke and sulfur and contribute to deactivation in hydrotreating catalysts by reducing hydrogenation and heteroatom removal activity, however, little is known about how these metals interact with the support and with each other under regeneration conditions.

Recent work performed at Amoco suggests that iron and vanadium are particularly harmful to hydrotreating catalysts during high temperature regeneration (8). In this work, the activity of a spent resid hydrotreating catalyst for Ramsarbon removal, desulfurization, devanadation, and denitrogenation returned to near fresh catalyst levels after decoking, but the mechanical strength or attrition resistance of the catalyst deteriorated considerably. Samples of the regenerated (decoked) catalyst were subjected to an attrition test, after which the fines generated during the test and the extrudates remaining afterwards were

analyzed by a number of techniques. The fines were found to be enriched in iron and vanadium compared to the extrudates, and mesopore sintering was observed in the fines while the pore size distribution of the extrudates remained similar to that of fresh catalyst.

While the removal of coke deposits has been shown effective in reactivating spent hydrotreating catalysts, the physical integrity of the catalyst must be maintained in order for the regeneration to be of practical use. In this work, we consider the interactions which occur between iron and/or vanadium and alumina under regeneration conditions as an extension of previous work which suggests that iron and vanadium play an important role in altering the physical characteristics of decoked catalysts. The metals are studied as dispersed metal oxides since this is the form they take during regeneration, and they are considered both alone (VO_x on alumina and FeO_x on alumina) and together (VO_x and FeO_x on alumina) in order to determine what effect, if any, they have on each other.

Experimental

A highly purified alumina, PHF gamma alumina (American Cyanamid, $196.4\text{m}^2/\text{g}$), was used as the starting material for all catalysts. Extrudates were crushed to a fine powder and dried at 538°C for 90 minutes prior to impregnation and calcination. Catalysts containing iron and/or vanadium oxides were prepared by incipient wetness impregnation. Metal loadings of 5-10 wt% as oxides were chosen because these are typical concentrations seen in spent resid hydrotreating catalysts. Spent resid hydrotreating catalysts were used in previous studies focusing on the feasibility of regeneration (8) which formed the basis for the work currently being reviewed. Multiple 15 gram batches of each of the starting materials were prepared as follows:

5wt% and 10wt% Fe_2O_3 : impregnation with a solution containing $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ (EM Science) in methanol, and aging for one hour in room air, followed by drying at 121°C for 16 hours under nitrogen.

5wt% and 10wt% V_2O_5 : impregnation with a solution containing vanadium triisopropoxide oxide (Alpha, 95-99%) in isopropanol and aging for one hour within a nitrogen purged glovebox, because of the moisture sensitive nature of the vanadium salt, followed by drying at 121°C for 16 hours under nitrogen.

5wt% Fe_2O_3 + 5wt% V_2O_5 : impregnation with vanadium triisopropoxide oxide in isopropanol as described above. After drying, the sample was ground to its original consistency, and impregnated with $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, also described above. The iron impregnation took place in a nitrogen purged glovebox as well. Separate impregnations were required because the iron and vanadium salts were not soluble in the same alcohol. The vanadium impregnation was done first in order to insure dispersion of the vanadium.

Table I summarizes the preparation and nomenclature of these starting materials.

TABLE I
CATALYST PREPARATIONS AND NOMENCLATURE

CATALYST	DESCRIPTION
Blank	PHF gamma alumina
5% V ₂ O ₅	5wt% V ₂ O ₅ on PHF gamma alumina
5% Fe ₂ O ₃	5wt% Fe ₂ O ₃ on PHF gamma alumina
5% V ₂ O ₅ + 5% Fe ₂ O ₃	5wt% V ₂ O ₅ + 5wt% Fe ₂ O ₃ co-impregnated on PHF gamma alumina
10% V ₂ O ₅	10wt% V ₂ O ₅ on PHF gamma alumina
10% Fe ₂ O ₃	10wt% Fe ₂ O ₃ on PHF gamma alumina

Sample Preparation

Three gram portions of each of the starting materials, as well as blank alumina powder, were calcined at 500°C, 700°C, 800°C, and 900°C in a 60cm x 1.75cm inner diameter quartz reactor with upward air flow at 100cc/minute. The temperature was ramped to its final setting at 300°C/hour, and held there for 2 hours after which the reactor was cooled under nitrogen. This procedure was repeated for some catalysts in wet air and NH₃ environments as well. The wet air environment was created by bubbling dry air through distilled water at 100cc/minute, 25°C. The NH₃ environment was established by bubbling dry air through a 1wt% solution of NH₄OH at 100cc/minute, 25°C. Selected samples were treated at 900°C in an SO₂/O₂ environment in the course of determining SO₂ oxidation activity. Activity test results are reported elsewhere (9). These catalysts were exposed to a 5% SO₂/5% O₂ (balance argon) gas mixture while the temperature was ramped to 900°C at 10°C/minute. Table II describes specifically all of the catalysts prepared.

Standards

V₂O₅ (Fisher Scientific) and Fe₂O₃ (Matheson Coleman and Bell) were used as reference materials.

Characterization

X-ray Photoelectron Spectroscopy: XPS spectra were recorded on a Surface Science SSX-100 XPS spectrometer using monochromatic Al K- α radiation.

Typical operating parameters were 600 μ spot size at an analyzer pass energy of 100eV. A flood gun operating at about 2eV was used for charge

TABLE II
EXPERIMENTAL CONDITIONS

CATALYST	500 °C			700 °C			800 °C			900 °C			SO ₂ /O ₂
	dry	wet	NH ₃	dry	wet	NH ₃	dry	wet	NH ₃	dry	wet	NH ₃	
Blank	x			x	x		x			x	x		x
5% Fe ₂ O ₃	x			x	x		x			x	x		
5% V ₂ O ₅	x			x			x			x			x
5% V ₂ O ₅ + 5% Fe ₂ O ₃	x			x			x			x	x		x
10% V ₂ O ₅	x												x
10% Fe ₂ O ₃	x												x

'x' indicates conditions at which each catalyst was treated.

neutralization during analysis. Iron and vanadium binding energies were referenced to Al 2p at 74.5eV since changes in the oxidation state of the aluminum would be negligible as a result of the oxidation experiments conducted in this study.

Inductively Coupled Plasma/X-ray Fluorescence: ICP analysis were performed on an Applied Research Laboratory Model 3560 ICP Atomic Emission Analyzer. Samples were prepared by acid digestion and microwave irradiation. Catalysts treated at 900°C were analyzed by X-ray fluorescence rather than ICP because of difficulty in dissolving them by the acid digestion technique. XRF analysis were performed on a Phillips model 1404 XRF Analyzer. Sample preparation involved fusing the catalysts with lithium borate mixtures and casting them into sample discs.

Raman Spectroscopy: Raman spectra were obtained with a Spex model 1877 spectrometer coupled to a Princeton Applied Research, model 1463 multichannel analyzer equipped with an intensified photodiode array detector (1024 pixels, cooled to -35°C). The 514.5 nm line of an argon laser (Spectra Physics) was used as the excitation source and the laser power at the sample was 10-50 mW. Samples were pressed onto KBr and spun at 2000 rpm during analysis.

X-ray Diffraction: A Scintag PAD V Powder Diffractometer equipped with an Ortec intrinsic germanium detector and 4 position sample chamber was used to obtain the XRD patterns. The instrument was configured with 2mm and 4mm incident beam slits, and 0.5mm and 0.3mm diffracted beam slits. Incident radiation was unfiltered Cu K- α radiation. Monochromatization was done in the detector. The Powder Diffraction File was used for phase identification.

Porosity: Nitrogen desorption porosimetry was performed with a Micrometrics Corporation model ASAP 2400 instrument, using the ASTM D32 procedure. Sample pre-treatment consisted of drying at 250°C in situ under vacuum for 16 hours.

Results and Discussion

Raman Spectra. Figure 1 shows the Raman spectra of the 5% V₂O₅ and 5% V₂O₅ + 5% Fe₂O₃ catalysts after calcination at 500°C. The major band at ~937cm⁻¹ and weak bands at ~885cm⁻¹, ~550cm⁻¹, ~350cm⁻¹, and ~220cm⁻¹ seen in the 5% V₂O₅ spectrum are assigned to a hydrated surface metavanadate, (VO₃)_n species (10). This agrees with solid state ⁵¹V-NMR studies with similar catalysts (11). Broad bands at ~885cm⁻¹ and ~800cm⁻¹ are observed in the spectrum of the 5% V₂O₅ + 5% Fe₂O₃ catalyst after 500°C calcination. This shift in band intensity from 937cm⁻¹ to 885cm⁻¹ indicates a conversion of hydrated metavanadates to hydrated pyrovanadates (V₂O₇) (10) in the presence of iron oxides. Under the ambient conditions in which these spectra were obtained, the surface of the oxide support is hydrated and the surface metal oxide overlayer can be thought of as existing in an aqueous medium. As a result, the structure of the supported metal oxides follow the metal oxide aqueous chemistry. The appearance of the hydrated pyrovanadate may result from a change in the aqueous environment in the presence of iron oxides - aqueous iron oxides are

basic in nature and cause an increase in the pH at which the surface possesses zero surface charge (pzc). The pyrovanadate appears to be more stable in the basic environment of the iron oxides.

Figure 2a-d shows Raman spectra of the 5% V₂O₅ catalyst after calcination at 500°C, 700°C, 800°C, and 900°C, respectively. The 500°C, 700°C, and 800°C spectra (Figures 2a,b,c) have broad bands at ~937cm⁻¹, ~825cm⁻¹, ~550cm⁻¹, and ~350cm⁻¹ which are assigned to the tetrahedrally coordinated surface species (hydrated metavanadate). The 900°C spectrum (Figure 2d) has sharp bands at 994cm⁻¹, 700cm⁻¹, 525cm⁻¹, 480cm⁻¹, 400cm⁻¹, 310cm⁻¹, 290cm⁻¹, and 200cm⁻¹, which are attributed to crystalline vanadium pentoxide. A band at 250cm⁻¹ also appears in the 900°C spectrum, and is assigned to a theta-alumina phase. The appearance of crystalline V₂O₅ after 900°C calcination can be attributed to two events. Migration of vanadium to the particle surface and a loss of surface area, which are discussed next, both serve to increase the surface vanadium concentration. Crystalline V₂O₅ forms when the surface vanadium concentration exceeds a monolayer (20wt% on gamma alumina) as a result of one or both of these events (12,13,14).

XPS and ICP. XPS and ICP results for all of the vanadium containing catalysts are given in Table III. Table IV lists similar results for the iron containing catalysts. The V 2p_{3/2} XPS binding energies average 517.4 eV and are constant within the precision of the method. This binding energy indicates a +5 oxidation state, which is expected. The Fe 2p_{3/2} XPS binding energies for the dry air treated catalysts average 711.2 eV and are constant within the precision of the method, indicating a +3 oxidation state. The Fe 2p_{3/2} binding energies for the wet air and NH₃ treated 5% Fe₂O₃ catalysts are slightly higher at 712.4 +/- 0.1eV, which also indicate a +3 oxidation state, but suggests a possible change in speciation due to the wet air and NH₃ environments. The wet air and NH₃ treated 5% V₂O₅ + 5% Fe₂O₃ catalysts have Fe 2p_{3/2} binding energies of 711.7 +/- 0.1eV which lie between the values of the dry air catalysts and the wet air/NH₃ 5% Fe₂O₃ catalysts. This can be interpreted as another species or a combination of the 711.2 and 712.4 eV species. Mossbauer data, which are reported elsewhere (9), confirm that all iron is in the +3 oxidation state, but confirmation of any change in speciation would require further characterization.

Bulk vanadium, iron, and aluminum concentrations as measured by ICP (and XRF in the case of the 900°C catalysts) remain constant within the error of the method under all conditions tested.

Figure 3 describes the V/Al and Fe/Al atomic ratios at the particle surface, as measured by XPS, relative to that at 500°C for the dry air treated catalysts.

The data in Figure 3 are based on the data in Tables III and IV. Surface iron concentration remains relatively constant at the temperatures considered, but surface vanadium concentration increases with increasing calcination temperature indicating migration of vanadium to the particle surface. The increase in surface vanadium concentration is more pronounced in the presence of iron oxides and the migration of vanadium begins at a lower temperature in

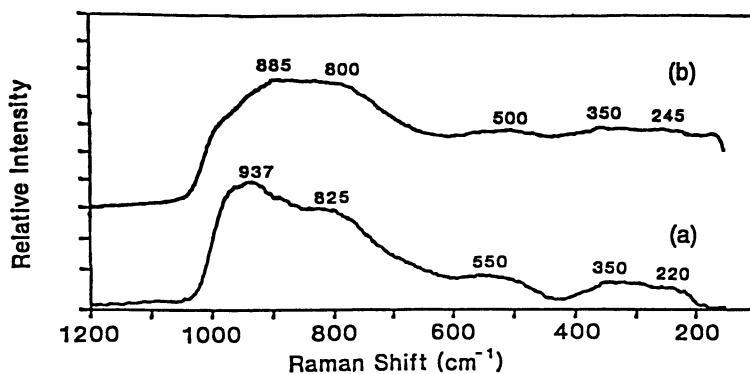


Figure 1: Raman spectra of catalysts treated at 500°C.
a) 5% V_2O_5 b) 5% V_2O_5 + 5% Fe_2O_3

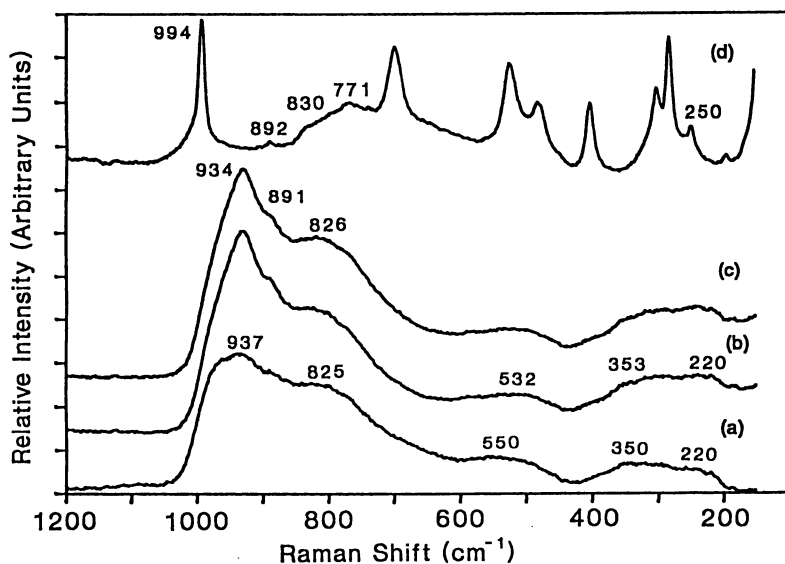


Figure 2: Raman spectra of the 5% V_2O_5 catalyst as a function of temperature.

a) 500°C b) 700°C c) 800°C d) 900°C

TABLE III
XPS AND ICP RESULTS: VANADIUM

CATALYST	XPS BINDING ENERGY (V 2p _{3/2} , eV)	V/A1	ICP V/A1
5% V₂O₅			
500°C, dry	517.1	.03	.051
700°C, dry	517.1	.03	
800°C, dry	517.3	.03	
900°C, dry	517.3	.11	.053
900°C, wet	517.5	.13	.049
900°C, NH ₃	517.7	.11	.056
5% V₂O₅ + 5% Fe₂O₃			
500°C, dry	517.1	.02	.052
700°C, dry	517.2	.03	
800°C, dry	517.7	.04	
900°C, dry	517.2	.12	.054
900°C, wet	517.5	.15	.049
900°C, NH ₃	517.5	.17	.056

dry= ambient air flowing at 100cc/minute

wet= ambient air bubbled through distilled water at 100cc/minute, 25°C.

NH₃= ambient air bubbled through a 1 wt% solution of NH₄OH at 100cc/minute, 25°C.

TABLE IV

XPS AND ICP RESULTS: IRON

CATALYST	XPS BINDING ENERGY (Fe 2p _{3/2} , eV)	Fe/Al	ICP Fe/Al
5% Fe₂O₃			
500°C, dry	711.2	.01	.069
700°C, dry	711.4	.01	
800°C, dry	711.3	.02	
900°C, dry	711.5	.02	.070
900°C, wet	711.5	.02	.071
900°C, NH ₃	712.4	.02	.071
5% V₂O₅ + 5% Fe₂O₃			
500°C, dry	710.8	.01	.066
700°C, dry	711.5	.01	
800°C, dry	711.1	.01	
900°C, dry	711.1	.02	.067
900°C, wet	711.8	.02	.065
900°C, NH ₃	711.6	.02	.060

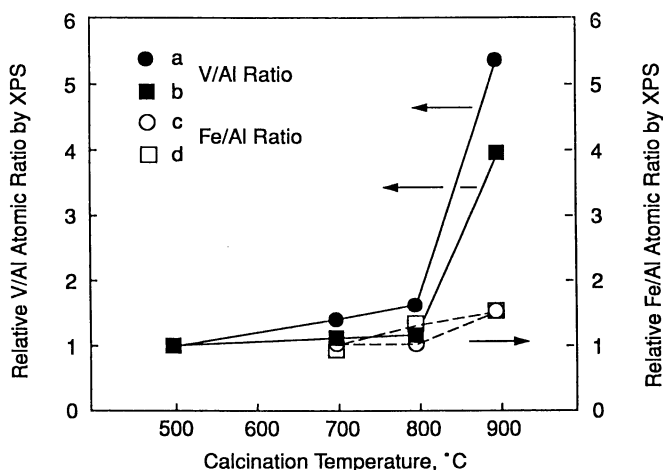
dry= ambient air flowing at 100cc/minute**wet**= ambient air bubbled through distilled water at 100cc/minute, 25°C.**NH₃**= ambient air bubbled through a 1 wt% solution of NH₄OH at 100cc/minute, 25°C.

Figure 3: Particle surface concentrations as a function of temperature.
 a) 5% Fe₂O₃ b) 5% V₂O₅ + 5% Fe₂O₃ c) 5% V₂O₅

the presence of iron oxides as well. The mobility of vanadium on catalyst surfaces due to the low melting temperature of vanadium oxides is well documented (15,16,17). The reason for the enhanced migration of vanadium in the presence of iron is not completely clear, however, Raman data have shown that the surface vanadates formed in the presence and absence of iron oxides differ, and it is possible that these different vanadium oxide species vary in volatility. This would explain the onset of vanadium migration at different temperatures in the presence and absence of iron oxides.

Figure 4 shows surface V/Al ratios at 900°C in various atmospheres relative to that at 500°C in dry air. The dry air case has been discussed. The V/Al ratio at the surface of the 5% V₂O₅ catalyst particle remains relatively constant in dry air, wet air, and NH₃ environments as indicated by the relative V/Al ratios of 3.96, 4.33, and 3.67 respectively. Although some previous work suggests that vanadium migration will not occur in the absence of steam (18,19), our results for this catalyst agree with studies indicating that vanadium will migrate during dry calcination at sufficiently high temperatures (17). In the case of the 5% V₂O₅ + 5% Fe₂O₃ catalyst, the surface V/Al ratio increases to 6.0 times that observed at 500°C in dry air after treatment at 900°C in dry air, to 7.5 times after wet air treatment at 900°C, and to 8.5 times after NH₃ treatment at 900°C. These results again suggest that the surface vanadate formed in the presence of iron (pyrovanadate, V₂O₇) might behave differently than that formed in its absence (metavanadate, (VO₃)_n), since vanadium migration occurs at a lower temperature in the 5% V₂O₅ + 5% Fe₂O₃ catalyst, (Figure 3) and the migration appears more sensitive to steam and NH₃ atmospheres as well (Figure 4). Fe/Al ratios after treatment at 900°C in wet air and NH₃ were similar to those seen after 900°C treatment in dry air.

Porosity. Porosimetry results are listed in Table V. The blank alumina and 5% Fe₂O₃ catalysts are quite similar; both retain at least 80% surface area and at least 90% pore volume after 900°C calcination. The 5% V₂O₅ catalyst, however, retains only 38% of its pore volume and only 23% of its surface area after 900°C treatment, and the most dramatic changes occur in the 5% V₂O₅ + 5% Fe₂O₃ catalyst where, after 900°C calcination, only 3% and 5% of surface area and pore volume, respectively, are retained.

A similar trend was seen in the pore size distributions, which are reported in detail elsewhere (20). The pore size distribution of the 5% Fe₂O₃ catalyst and blank alumina remain fairly constant over the entire temperature range, so the addition of iron oxides alone to the alumina support does not appear to have an effect on the alumina pore structure after calcination at temperatures as high as 900°C. The presence of vanadium does appear to affect the pore structure of alumina after high temperature calcination. Mesopore sintering is observed after 900°C calcination of the 5% V₂O₅ catalyst, and as early as 700°C calcination in the 5% V₂O₅ + 5% Fe₂O₃ catalyst.

TABLE V
POROSIMETRY RESULTS

CATALYST	SURFACE AREA (m ² /g)	PORE VOLUME (cc/g)	4V/A (Å)
Blank			
500°C, dry	191	0.51	107
700°C, dry	183	0.50	109
900°C, dry	161	0.49	121
900°C, wet	152	0.50	132
900°C, NH ₃	152	0.50	132
5% Fe₂O₃			
500°C, dry	191	0.49	103
700°C, dry	175	0.46	105
900°C, dry	157	0.44	112
900°C, wet	141	0.46	130
900°C, NH ₃	139	0.46	132
5% V₂O₅			
500°C, dry	191	0.47	98
700°C, dry	189	0.47	99
900°C, dry	44	0.18	164
900°C, wet	40	0.22	220
900°C, NH ₃	50	0.38	304
5% V₂O₅ + 5% Fe₂O₃			
500°C, dry	190	0.44	93
700°C, dry	173	0.45	104
900°C, dry	6	0.02	*
900°C, wet	6	0.02	*
900°C, NH ₃	4	0.08	*

* high analytical uncertainty using N₂ desorption with low surface area samples.

note: $4V/A = (4 \times \text{pore volume})/(\text{surface area})$

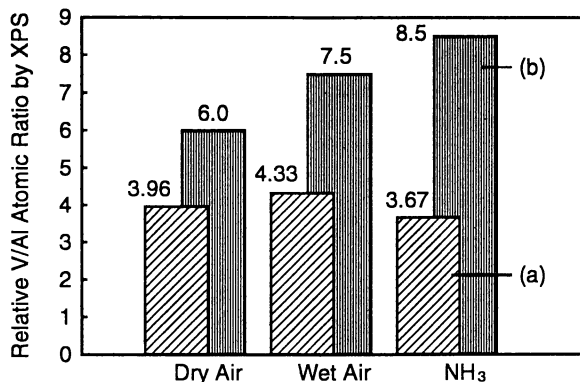


Figure 4: Surface vanadium concentrations in various atmospheres at 900°C (relative to analogous catalysts treated at 500°C in dry air).

a) 5% V₂O₅ b) 5% V₂O₅ + 5% Fe₂O₃

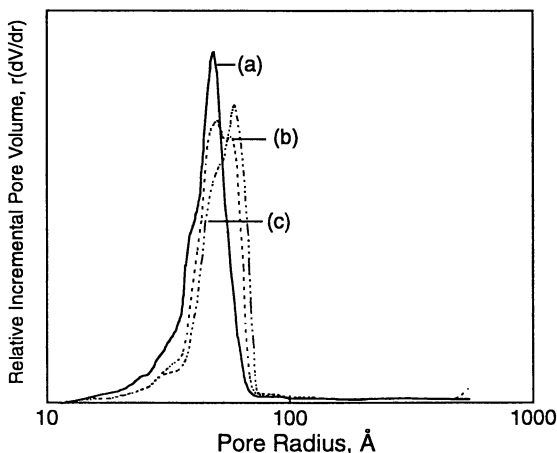


Figure 5: Effect of atmosphere on pore size distribution of the 5% Fe₂O₃ catalyst at 900°C.

a) dry air b) wet air c) NH₃

Note the correlation between the onset of vanadium migration and pore sintering. Migration of vanadium was not observed in the 5% V_2O_5 catalyst until 900°C calcination. This is the temperature at which pore sintering is first observed in the 5% V_2O_5 catalyst. In the case of the 5% V_2O_5 + 5% Fe_2O_3 catalyst, vanadium migration occurs at 700°C, the temperature at which pore sintering is first observed in this catalyst. The change in pore structure may be a consequence of either the vanadium migration itself, or the increase in local vanadium concentration which results from the migration, since the earlier the migration occurs, the earlier pore sintering occurs, and the more pronounced the migration, the more extensive the pore sintering. A recently proposed model for the mechanism of alumina pore sintering suggests that the loss of surface area occurs by successive elimination of water from hydroxyl groups residing on adjacent particles resulting in Al-O-Al linkages (21). Vanadium is known to interact with alumina by reaction with surface hydroxyl groups (22,23,24). In the context of the pore sintering model, the migration of vanadium might be visualized as a means of displacing hydroxyl groups and therefore accelerating the sintering process.

The pore size distributions of the 5% Fe_2O_3 catalyst at 900°C in dry air, wet air, and NH_3 atmospheres are shown in Figure 5. They are very similar to those of the blank alumina catalysts treated under the same conditions. A slight shift toward larger pores is seen in the wet air and NH_3 catalysts. This is also indicated by the 4V/A pore diameters (4 times pore volume per gram of catalyst/surface area per gram of catalyst) of 121A for the dry air catalyst and 130A and 132A for the wet air and NH_3 catalysts, respectively, as listed in Table V. Enhanced pore sintering in the presence of steam has been documented previously (25). The small magnitude of the increase in pore diameters may be due to the low H_2O partial pressure used in these experiments (P_{H_2O} at 25°C = 25mmHg or 0.03 atm.). The NH_3 atmosphere appears to have very little, if any, effect on the pore structure of the blank alumina and 5% Fe_2O_3 catalyst. Figure 6 shows the pore size distributions of the 5% V_2O_5 catalyst treated at 900°C in various atmospheres. Again, a shift toward larger pores is seen in the wet air and NH_3 catalysts. In this case, the average pore diameter in the NH_3 treated catalyst (304A from Table V) is significantly larger than that of the dry air treated catalyst (164A). This could be interpreted to indicate a greater degree of pore sintering in the NH_3 treated catalyst. For the 5% Fe_2O_3 , 5% V_2O_5 , and 5% V_2O_5 + 5% Fe_2O_3 catalysts treated in dry air, increases in the average pore diameter were accompanied by decreasing pore volumes (Table V). However, the NH_3 treated 5% V_2O_5 catalyst retains about twice the pore volume of the dry air treated 5% V_2O_5 catalyst (0.38cc/g vs. 0.18cc/g, respectively), despite the increase in average pore diameter. Comparison of these results suggests that the type of changes in pore structure which occur with high temperature treatment vary in nature depending on the atmosphere in which the catalysts are treated. This result is consistent with a proposed mechanism for the destruction of cracking catalysts in the presence of vanadium and steam in which it is

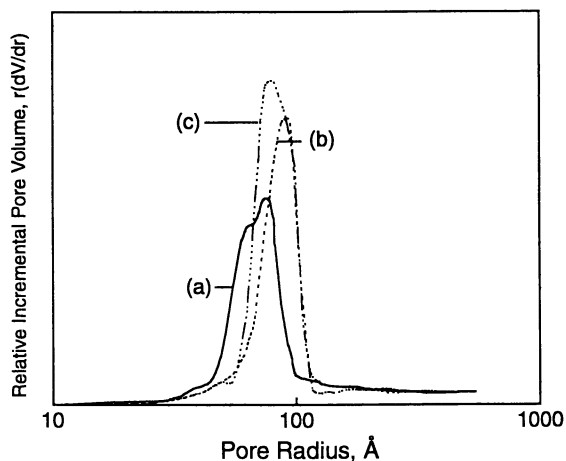


Figure 6: Effect of atmosphere on pore size distribution of the 5% V_2O_5 catalyst at 900°C.

a) dry air b) wet air c) NH_3

TABLE VI
ALUMINA PHASES AT 900°C

CATALYST	DRY AIR	WET AIR	NH_3	SO_2/O_3
Blank	gamma	gamma	gamma	gamma
5% Fe_2O_3	gamma	gamma	gamma	gamma
10% Fe_2O_3				gamma
5% V_2O_5	theta	theta	theta	gamma
10% V_2O_5				theta
5% V_2O_5 + 5% Fe_2O_3	kappa, delta	kappa, delta	kappa, delta	delta

suggested that the destruction of zeolite crystallinity results from the formation of vanadic acid and subsequent hydrolysis of the zeolite (17). If this mechanism applies to the case of pure alumina, it is possible that the basic NH_3 may in some way neutralize the deleterious effect of the vanadic acid, resulting in a greater retention of pore volume.

XRD

The pore sintering and loss of surface area and pore volume shown in the previous section were accompanied by changes of alumina phase. At temperatures as high as 800°C , all catalysts retained the gamma alumina phase. Table VI describes the alumina phases, as determined by XRD, after 900°C treatment in various atmospheres.

Comparison of the dry air phases suggests that vanadium catalyzes the conversion from gamma to higher temperature alumina phases. This accelerated conversion of alumina phases in the presence of vanadium has been demonstrated by previous workers (13). A similar effect has been observed in the conversion of titania (anatase) to titania (rutile), as well (26-29). Again, these results are consistent with the Johnson model for alumina desurfacing (21). If we consider vanadium migration to be a mechanism by which surface hydroxyls are displaced, then the dehydration of the alumina and resulting phase transformation might be considered, in part, to be a function of vanadium migration.

Wet air and NH_3 environments do not affect the alumina phase transitions, however, the phase changes are less dramatic in the SO_2/O_2 environment than in the other atmospheres. For example, the 5% V_2O_5 catalyst subjected to calcination at 900°C underwent a conversion from gamma to theta alumina, but the gamma phase was retained when this same catalyst was treated at 900°C in an SO_2 environment. Conversion from gamma to theta alumina was observed in the SO_2 atmosphere only in the catalyst containing 10 wt% V_2O_5 . For the 5% $\text{V}_2\text{O}_5 + 5\% \text{Fe}_2\text{O}_3$ catalyst, calcination at 900°C resulted in conversion to a minor phase of delta alumina and a major phase of kappa alumina, but when this same catalyst was heated to 900°C in SO_2 , the alumina phase changed only to delta, a less severe transition.

Mesopore sintering and the consequent change of alumina phase have been discussed in terms of vanadium migration and the Johnson model (21) for alumina pore sintering. The Johnson model proposes that pore sintering occurs by successive elimination of water from hydroxyl groups residing on adjacent particles. Vanadium migration may serve to displace hydroxyls and therefore accelerate the process. It is unlikely that the SO_2 environment prevented migration since crystalline V_2O_5 , which forms as a result of vanadium migration, was detected in the SO_2 treated catalysts. A possible explanation for the apparent "buffering" effect of the SO_2 lies in the formation of aluminum sulfate, which forms under these conditions at the catalyst surface (9). This aluminum

sulfate surface layer may serve to reduce the number of interactions between vanadium and surface hydroxyls during vanadium migration, i.e. vanadium migration still takes place, but the interaction with surface hydroxyl groups is reduced, so that the elimination of water and resulting condensation of alumina are diminished on the presence of SO_2 . This observation may find application in commercial catalyst testing. Under typical laboratory aging of FCC catalysts, the catalysts are steamed at high temperature in order to simulate regeneration conditions (17,18,30). Heat treatment in an atmosphere of steam and SO_2 would be more realistic since SO_2 forms when sulfur which has deposited onto cracking catalysts is burned off in the regenerator. The results of our SO_2 oxidation experiments suggest that the SO_2 environment has a significant effect on the catalyst, and so should be included in the laboratory aging process.

Conclusions

The interactions between iron and vanadium oxides and alumina support vary with temperature and atmosphere, and in the presence or absence of additional metal oxides. A hydrated surface metavanadate forms when vanadium oxides alone are deposited on gamma alumina, and a hydrated surface pyrovanadate forms in the presence of iron oxides. At elevated temperatures, vanadium migrates to the particle surface and catalyzes pore sintering and alumina phase changes. Vanadium migration, pore sintering, and changes of alumina phase are enhanced in the presence of iron oxides, possibly due to the differing nature of the surface vanadates formed when iron oxides are present, and the deleterious effects of vanadium are diminished in the presence of SO_2 . These results are consistent with an existing model for alumina desurfacing.

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