

Supported Transition Metal Oxides as Acid Cracking Catalysts: Periodic Trends and Their Relationship to Activity and Selectivity

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Received September 10, 1986; revised May 8, 1987

Surface phase oxides bonded to a support such as alumina have not been recognized previously to have acid cracking activities in the league of amorphous silica-alumina to the best of our knowledge. In this paper the relative gas-oil cracking activities of all Group IV, V, and VIB oxides supported on alumina (including alumina and rhenia on alumina) are reported. All of the supported oxides are at a surface coverage about one-third that of a monolayer. Tungsten oxide and niobium oxide on alumina have been identified as solid acids with high activity; while molybdenum oxide and rhenium oxide on alumina lead to high coke and gas make even with steam present as a cofeed in the cracking test. The periodic trends of cracking activity are those expected from the charge-to-radius ratio of the metal cation. This class of surface phase oxide solid acids has a wide range of activities (two orders of magnitude) and may prove useful for matching acid strength to specific reactions. In addition, this class of solid acids maintains surface area and cracking activity following high temperature steam treatment, in contrast to many conventional solid acid catalysts. © 1987 Academic Press, Inc.

INTRODUCTION

Bulk tungsten oxide has been known to be an acid catalyst for hydrocracking of *n*-heptane for over 10 years (1). In addition, tungsten oxide and reduced tungsten oxides have recently been studied as acid catalysts for olefin isomerization (2) and for alcohol dehydration (3). A recent paper also reported the strong chemisorption of *n*-butylamine on reduced tungsten oxide (4). The acidic properties of WO₃-based mixed oxide catalysts have also been reported (5, 6). Tungsten oxide, reduced tungsten oxide, and mixed oxides containing-WO₃ have been recognized as possessing acidic character.

In contrast to these studies with bulk tungsten oxide catalysts much less work has been done employing supported tungsten oxide as an acid catalyst (7). However, a great many papers deal with the characterization (6, 8-14), metathesis activity (15-18), and hydrodesulfurization activity

(11, 19) of sulfided tungsten oxide catalysts.

In this paper a systematic study of the Group IV, V, and VIB oxides and rhenium oxide supported on alumina for gas-oil cracking is reported (20). It will be apparent that the systematic trends in cracking activity and selectivity to coke and gas make are associated with the position of the supported oxides in the periodic table. Niobium and tungsten oxide on alumina have been identified as acid catalysts with acid strength comparable to that of amorphous silica-alumina cracking catalysts, whereas molybdenum and rhenium oxide on alumina lead to high coke and gas formation in the cracking of gas oil. The catalytically active transition metal oxides on alumina are unique solid acids in that they have exceptional steam stability in high temperature environments (1173°K), in contrast to most conventional amorphous silica-alumina and zeolite composite catalysts (20).

TABLE 1
ETLGO Feed Inspection

Feed symbol	
Gravity, API	33.3
Aniline point	192
Reference Index, N_D , at 67°C	1.4777
Sulfur, wt%	0.20
ASTM D-1160 distillation	
5%	546°F
10%	552°F
50%	592°F
90%	653°F
95%	664°F
FBP	678°F

TABLE 2
GC Distillation of
ETLGO Feed

% off	°F	°C
0	421	216
1	442	228
5	491	255
10	520	271
25	559	293
50	605	318
75	656	347
90	695	368
95	713	378
99	761	405
100	850	454

EXPERIMENTAL

Catalyst testing. The reactor employed in this work is a typical downflow gas phase reactor of 40-cm³ capacity which can operate at temperatures up to 828°K. Liquid hydrocarbon is introduced by a dual-barrel Ruska pump, and water is introduced by a Lapp pump. Gas feeds are controlled by Research Control valves coupled to a Foxboro flow controller. The reactor is heated by a fluidized sandbath. Typical operating conditions are 783°K (950°F) and 30 psig and the liquid weight hourly space velocity was 1.4 hr⁻¹ for both oil and water. The hydrocarbon feed used in this work was East Texas Light gas-oil (ETLGO) the properties of which are given in Tables 1–3.

Catalyst steam treatment. The catalyst samples in this study were steamed at either 1143°K (1600°F) or 1173°K. The steam treatments were carried out either in an upflow three-zone furnace operated at ambient pressure with a gas feed consisting of 90% steam and 10% nitrogen or in a horizontal tube furnace with a gas feed consisting of 10% H₂O in air, respectively.

The amorphous silica–alumina catalyst employed in this study was Davison Chemical Company Lo-Al, DA-1 catalyst with 13 wt% Al₂O₃ content. The standard catalytic cracking catalyst containing 10 wt% zeolite was Davison FLX-5.

Titration procedure. The solid acids used in this work were characterized by the standard Benesi method (21) employing a dry box procedure (22) which was also employed by Reitsma and Boelhouwer (23).

Catalyst preparations. All catalysts were prepared by the incipient wetness impregnation method. Either an aqueous or a nonaqueous solution of the metal salt was impregnated onto alumina extrudates (reforming grade, Engelhard Industries, Inc., 180 m²/g surface area). In the case of the aqueous preparations, the catalysts were dried overnight at 110°C, and then calcined overnight in a muffle furnace at 500°C to decompose the metal salt. In the case of the

TABLE 3
Mass Spectrometric Analysis of
ETLGO Feed

Component type	wt%
Paraffins	42.37
Cycloparaffins	35.53
Alkylbenzenes	4.30
Indanes and tetralins	3.13
Indenes	1.01
Naphthalene	0.11
C ₁₁ + naphthalenes	3.41
Acenaphthenes	3.82
Acenaphthalenes	3.44
Tricycloaromatics	2.83
Total	99.99

nonaqueous preparations, catalyst impregnations were carried out in a dry box. Following impregnation of the metal chloride or metal alkoxide precursor in methanol (or heptane in the case of the alkoxides) solution the methanol was removed by vacuum drying at ambient temperature. The catalyst was then transferred to a tube furnace and treated in helium at 250°C for 3 hr. At this point the temperature was increased to 500°C with a 20% O₂ in a He flow rate of 500 cm³ per minute.

The metal salts employed in the nonaqueous preparations are TiCl₄ (99.9), Alfa; ZrCl₄ (99.6), Alfa; HfCl₄, Ventron; VOCl₃ (polymer grade), ROC/RIC; Nb₂(OC₂H₅)₁₀, Alfa; Ta₂(OC₂H₅)₁₀, Alfa; CrO₂Cl₂; ROC/RIC; WCl₆, Alfa; and HReO₄, Ventron.

Metal salts employed in the aqueous preparations are ammonium paramolybdate (NH₄)₆Mo₇O₂₄·xH₂O, Matheson, Coleman and Bell; ammonium metatungstate, Sylvania; chromium trioxide, Matheson, Coleman and Bell; ammonium metavanadate, NH₄VO₃; Alfa.

RESULTS AND DISCUSSION

Because of the limited amount of work employing supported transition metal oxides as solid acid catalysts (7) we decided to investigate all of the Group IV, V, and VIB oxides supported on γ -Al₂O₃. Rhenium oxide was also included as representing a quite reducible supported oxide (24, 25). All of the samples were prepared at a metal cation content of 430 μ mol/g of catalyst. This represents about 40% coverage of the alumina surface, assuming that the surface phase oxide is forming isolated units on the support surface with the metal oxide essentially 100% dispersed (8-10).

In an effort to measure the intrinsic activities of these alumina-supported transition metal oxides (hereafter referred to as TMOs) in their highest oxidation state during catalytic cracking water was cofed along with the hydrocarbon feed. This step is expected to retard, or possibly completely suppress, the reduction of certain of

TABLE 4
Relative Activities^a of TMO Solid Acids on Al₂O₃

Fourth period ^b	3.6% TiO ₂	4% V ₂ O ₅	4.5% Cr ₂ O ₃
½ hr	6	28	7
1 hr	4	16	4
Fifth period ^b	5.6% ZrO ₂	6% Nb ₂ O ₅	6.4% MoO ₃
½ hr	4	76	33
1 hr	4	58	5
Sixth period ^b	9.5% HfO ₂	10% Ta ₂ O ₅	10% WO ₃
½ hr	2	12	100
1 hr	3	8	87
Miscellaneous	Al ₂ O ₃	10.9% Re ₂ O ₇	
½ hr	1	7	
1 hr	1	5	

^a Relative to activity of WO₃/Al₂O₃ (100). Activity is defined as the grams of 430° liquid produced per hour per gram of catalyst. The specific activity of WO₃ is 1.09 g 430°/hr/g cat.

^b Periods of the transition metal elements.

the supported metal oxides under the highly reducing conditions experienced in catalytic cracking. In spite of steam being present, alumina-supported Mo and Re oxides showed extremely high coke formation indicative of a metal-like component being present during the catalytic reaction (26, 27). Table 4 contains the relative cracking activities of the alumina-supported Group IV-VIB TMOs, as well as of supported rhenium oxide and the alumina support base as a reference.

Catalytic activity in Table 4 is defined as the amount of gas-oil converted to gasoline range products boiling below 430°F (430°). Catalyst activities were measured after 0.5 and 1 hr on feed. Although these are relatively long reaction time periods compared with the 2- to 5-min time cycle usually employed (28) to study catalytic cracking, the results obtained for our longer reaction period closely parallel studies in a short-cycle test reactor, referred to as a micro activity test (MAT), (28) which was modified to cofeed water. The MAT reactor studies of TMO catalysts will be the subject of a subsequent report.

To more easily compare the activities of the catalyst in Table 4, the activity of the most active catalyst, WO₃ on Al₂O₃ after 0.5 hr on feed, was set equal to 100. All of the other activities in Table 4 were then

TABLE 5
Coke on Catalyst and Gas Make for Catalysts
Listed in Table 4

Fourth period ^a	3.6% TiO ₂	4% V ₂ O ₅	4.5% Cr ₂ O ₃
wt% coke on catalyst for 1-hr run	1.2	1.9	2.7
Total gas make, liters, for 1-hr run	0.6	0.7	0.7
Fifth period ^a	5.6 ZrO ₂	6% Nb ₂ O ₅	6.4% MoO ₃
wt% coke on catalyst for 1-hr run	0.6	1.5	14.2
Total gas make, liters, for 1-hr run	0.5	0.8	4.2
Sixth period ^a	9.5% HfO ₂	10% Ta ₂ O ₅	10% WO ₃
wt% coke on catalyst for 1-hr run	0.7	1.1	5.2
Total gas make, liters, for 1-hr run	0.2	0.4	2.2
Miscellaneous	Al ₂ O ₃	10.9% Re ₂ O ₇	
wt% coke on catalyst for 1-hr run	1.2	22.7	
Total gas make, liters, for 1-hr run	0.4	6.8	

^a Periods of the transitional metal elements.

referenced to this activity. The results in Table 4 indicate about two orders of magnitude difference in the activities of the catalysts. The coke formed on all of the catalysts (in wt%) and the amount of gas formed after 1 hr are given in Table 5. Coke formation on these catalysts is a function of cracking activity and reducibility of the transition metal oxide component (see below).

The γ -Al₂O₃ support in these studies was a reforming-grade material of 180 m²/g surface area. The alumina support had very low cracking activity in our studies as would be anticipated from previous work (28). Because the alumina support exhibited the lowest activity of any of the ten catalysts in Table 4 the cracking test proved to be a remarkably sensitive probe of the different TMO catalysts studied. All of the Group IVB TMOs (Ti, Zr, Hf) exhibited very low activity. Only Nb of the Group VB TMOs (V, Nb, Ta) had high activity, with V of intermediate activity. Interestingly, only W of the Group VIB TMOs (Cr, Mo, W) had high activity. Supported rhenium oxide showed very little cracking activity.

Before the basis of these activity trends is discussed, it is important to note that only one of the ten TMO catalysts exhibited a drastic decrease in activity in comparing a $\frac{1}{2}$ -hr to a 1-hr run period. This catalyst was MoO₃ on Al₂O₃. The reasons for this activity decline in the case of MoO₃ on Al₂O₃ is most probably due to coking of the catalyst surface (see Table 5). The coke on the Mo TMO catalyst after 1 hr on feed amounted to 14.2 wt%. Only in the case of the reducible rhenium oxide was more coke observed, 22.7 wt%. Comparatively high gas formation during the cracking test reaction was observed for both the Mo and Re TMO catalysts, also. Both high coke and gas formation for MoO₃ on Al₂O₃ indicate that in the presence of steam under cracking conditions, lower oxidation states of Mo are formed. The high coke level poisons the acidic sites and the catalyst deactivates. Recent temperature-programmed reduction studies have shown that MoO₃ on Al₂O₃ is significantly more reducible than WO₃ on Al₂O₃ (29). The greater ease of reduction of the Mo TMO compared with the W TMO catalyst is supported by the cracking activity differences in Table 4, as well as the coke and gas production differences in Table 5.

An experiment was designed to test the hypothesis of a metal-like component being present under cracking conditions in the case of the Mo TMO catalyst. A 1 wt% Rh on Al₂O₃ catalyst was placed in the reactor, first upstream and then downstream of the steam/hydrocarbon feed, with a tungsten oxide TMO catalyst. Only in the case of the rhodium catalyst downstream of the tungsten oxide catalyst were coke levels on the rhodium catalyst comparable to those found on the Mo TMO catalyst. It appears clear that olefins formed in the cracking reaction readily coke up the Mo and Re TMO catalysts by interaction with a reduced oxide phase. In the case of the rhodium catalyst upstream of the W TMO acid catalyst very little coke was formed on the Rh catalyst.

Returning now to the question of the activity trends in Table 4, it is quite important that only two of the ten TMOs in this study show appreciable catalytic cracking activity—Nb and W. An overview of the activities in Table 4 suggests that metal oxides with highest cation charge are the most active catalysts. This is entirely consistent with expectations from chemical periodicity (30). In the case of the third-period TMOs (Hf, Ta, W) these supported oxides should show the greatest resistance of all the TMOs studied to reduction under reaction conditions. This is an important consideration as we have seen in the case of the Mo TMO catalyst that coke formation can lead to significant modification of the cracking activity. Deactivation could serve to blur intrinsic activity differences between different TMO catalysts. The activity trends of the third-period TMOs are $W \gg Ta > Hf$. Although the W TMO catalyst showed appreciable coke formation, 5.2 wt%, good activity maintenance was observed. Apparently, the W TMO catalyst is not only the most active of the ten TMOs investigated, but also maintains high cracking activity in the presence of considerable coke on the catalyst surface.

Metal cation acidities are found to correlate with the charge-to-radius ratio of the metal cation (30). This is related to the fact that as a metal cation charge increases, the electron distribution is decreased by the increased charge at the metal center. The correlation of the metal charge-to-radius ratio with cracking activity will be considered in detail in subsequent discussion. The cracking activity trends of the second-period metals also reflect the expected metal cation acidities: $Nb^{5+} \gg Zr^{4+}$. Mo^{6+} does not correlate in this series due to coking of the catalyst as previously discussed. In the first period the activity trend is also consistent with the expected cation acidities: $V^{5+} > Cr^{3+} = Ti^{4+}$.

A very significant point with respect to the cracking activities for the TMO catalysts in Table 4 is that this class of catalysts

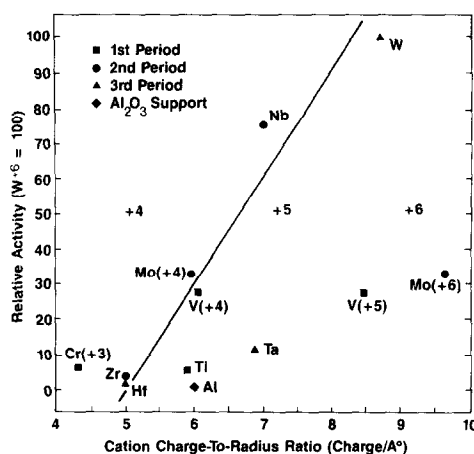


FIG. 1. The relative activity of various supported transition metal oxides on an alumina support as a function of the cation charge-to-radius ratio.

shows a wide range of activities. Alumina-supported W and Nb oxides are apparently strong acids, Mo (before deactivating) and V oxides are intermediate-strength acids, and Ta, Cr, Ti, Zr, Hf, and Re are weakly acidic. By control of the transition metal cation concentration and choice of TMO one can modify the acidity over a wide range. If one plots the cracking activities in Table 4 versus the cation charge-to-radius ratio for the ten metal cations one can see that a quite good correlation is obtained (Fig. 1) with three notable exceptions—Mo, V, and Ta.

Molybdenum oxide may not fit the correlation due to deactivation or due to partial reduction under reaction conditions. Reduction of MoO_3 on Al_2O_3 to a 4+ oxidation state has been reported in recent work (29). Partial reduction of V^{5+} to V^{4+} is also possible. Regardless of the oxidation state (5) of Mo and V TMOs under the oxidizing-reducing conditions of a cracking reactor with steam present there is no question that both V_2O_5 and MoO_3 on Al_2O_3 , of all the Group IV–VIB oxides, are the most easily reduced to lower valence states. It is well known that vanadium oxide on catalytic cracking catalysts leads to loss of liquid yield by coke formation (25, 26).

The low cracking activity of Ta compared with Nb TMO is the most surprising result of the correlation in Fig. 1. Both Ta and Nb in a 5+ oxidation state have essentially identical atomic radii (30). The low activity of Ta₂O₅ on Al₂O₃ may reflect such factors as the structure of the Ta surface phase and the extent of covalent bonding between the alumina surface oxide/hydroxides and the Ta cation. An investigation of Nb and Ta TMO catalysts for gas-oil cracking in a short-reaction-cycle MAT unit showed the same activity trends reported in Table 4.

The discovery of the relatively high catalytic cracking activity of WO₃ and Nb₂O₅ on Al₂O₃ is of considerable importance when coupled with the remarkable stability of such systems to high temperature steam or air regeneration conditions (19). In an effort to quantify the steam stability of the TMO catalysts in Table 4 four catalysts were steamed at 1173°K (900°C) in 10% steam in 90% air atmosphere for 16 hr. The four catalysts chosen for study were WO₃, Nb₂O₅, Ta₂O₅, and TiO₂ on Al₂O₃ (Table 5). These four samples cover a wide range of cracking activities as shown in Table 4. All four of these catalysts showed good surface area stability following this steam treatment; the surface areas of the four catalysts were 70, 110, 130, and 117 m²/g for W, Nb, Ta, and Ti TMO catalysts, respectively. The surface areas of Al₂O₃ before and after an analogous steam treatment were 180 and 70 m²/g, respectively. Therefore, the Group IV and Group V cations (excluding vanadium) retard surface area collapse to varying degrees, with the W TMO showing no stabilizing effect.

The cracking activities of these four steamed catalysts were again referenced to the WO₃ on Al₂O₃ catalyst of Table 4 set equal to 100. The WO₃ and Nb₂O₅ catalysts steamed at 900°C retained 87 and 80% of the activity of the unsteamed catalysts, respectively. In fact, in short-cycle MAT tests the activity of the steamed catalysts was considerably higher than that of the

TABLE 6

Relative Activities,^a Coke on Catalyst, and Gas Make for 900°C Steamed Catalysts

Catalyst	Relative activity		Coke on catalyst (%) for 1-hr run	Total gas make (liters)
	½ hr	1 hr		
3.6% TiO ₂	4	1	7.1	2.4
6% Nb ₂ O ₅	61	30	2.4	1.0
10% Ta ₂ O ₅	6	0	7.3	1.7
10% WO ₃	87	73	5.1	2.3

^a Relative to activity of fresh WO₃/Al₂O₃ (100). Activity is defined as the grams of 430⁻ liquid produced per hour per gram of catalyst. The specific activity of WO₃ is 1.09 g 430⁻/hr/g cat.

unsteamed catalysts. These results will be published elsewhere. The TiO₂ on Al₂O₃ and Ta₂O₅ on Al₂O₃ catalysts steamed at 900°C showed a pronounced decline in activity and high coke formation compared with the unsteamed catalysts. This may be due to restructuring of the supported oxide structure during surface area reduction and/or due to interactions between adjacent transition metal oxide centers as the surface group separation distance is decreased by steam treatment. In summary, TMO solid acid catalysts with high cracking activity retained their activity after a high temperature steam treatment whereas those catalysts of lower activity without steam treatment also showed lower activity after steam treatment coupled with greatly enhanced coke production.

In an effort to understand the periodic trends in Tables 4 and 6, the four unsteamed and steam catalysts were characterized by *n*-butylamine titration using a modified Benesi method reported elsewhere (21, 22) (see Table 7). In all four catalysts the number of strongest acid centers, corresponding to $H_0 \leq -8.2$ (21), remained quite high after high temperature steam treatment. The retention of a significant number of strong acid centers for all of these catalysts is consistent with the surface area stabilities of the samples after high temperature steam treatment. All of the catalysts characterized in Table 7 have

acid sites that correspond to acid strengths $H_0 \leq -8.2$ despite the significant change in the metal cation charge-to-radius ratio for this series of samples. Apparently, a charge-to-radius ratio of 6 is sufficient to trigger the indicator change of the $H_0 = 8.2$ Hammett indicator, which is not surprising since alumina itself has been known to have this strength of acid centers. Sites stronger than $H_0 = -8.2$ are apparently present on the W and Nb TMO catalysts which are responsible for the gas-oil cracking activity. Similar arguments have been made for amorphous silica-alumina cracking catalysts (32).

To compare the activity of a steam-treated 10% WO_3 on Al_2O_3 to an amorphous silica-alumina and a zeolite-composite catalyst, all three catalysts were steam treated at 1143°K (870°C) in 90% H_2O /10% N_2 for a 16-hr period. Figure 2 shows the unsteamed and steamed catalyst activities. Both the amorphous silica-alumina and the zeolite-composite catalyst show lower cracking activity after the steam treatment compared with the WO_3 catalyst. Not surprisingly, the amorphous silica-alumina catalyst had no strong acid centers ($H_0 \leq -8.2$) after this steam treatment (32). The surface area of the silica-alumina catalyst was decreased from 500 to 40 m^2/g by the 870°C steam treatment. The most active of the TMO catalysts, WO_3 on Al_2O_3 , unsteamed or steamed, has a level of catalytic cracking

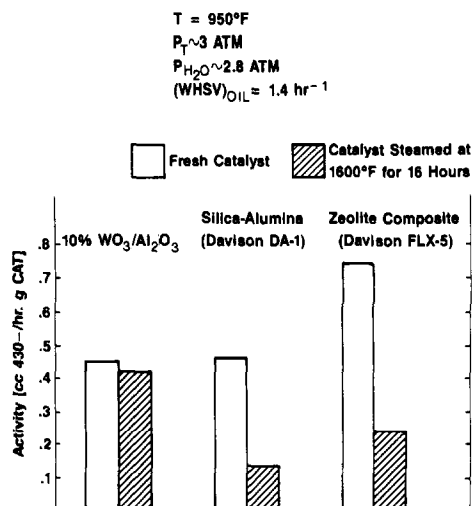


FIG. 2. Effect of steaming on activity for cracking gas-oil at 1 hr on oil.

activity similar to that found for a 1400°F (760°C) steamed amorphous silica-alumina cracking catalyst (32).

CONCLUSIONS

The potential impact of TMO-based acid catalysts stems from (1) the wide range of acidities of this class of catalysts, (2) high steam stability compared with conventional solid acids, (3) activity maintenance at high coke levels on the catalyst, and (4) retention of both surface area and pore volume following high temperature air or steam treatment.

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TABLE 7

Acid Site Distributions of Unsteamed and 900°C Steamed TMO Catalysts

Site strength H_0	3.6% TiO_2			6.0% Nb_2O_5		
	-8.2	-5.6	-3.0	-8.2	-5.6	-3.0
Fresh	325	375	425	125	225	275
Steamed	225	225	275	125	175	175
Site strength, H_0	10% Ta_2O_5			10% WO_3		
	-8.2	-5.6	-3.0	-8.2	-5.6	-3.0
Fresh	225	375	375	275	275	325
Steamed	175	225	275	125	225	225
Site strength, H_0	γ - Al_2O_3					
	-8.2	-5.6	-3.0			
Fresh	275	425	425			
Steamed	138	175	175			

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