Catalytic Hydrodesulfurization and Hydrodenitrogenation over Co–Mo on TiO$_2$–ZrO$_2$–V$_2$O$_5$

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Hydrodesulfurization (HDS) of dibenzothiophene and hydrodenitrogenation (HDN) of aniline over Co–Mo on TiO$_2$–ZrO$_2$–V$_2$O$_5$ catalysts and over Co–Mo on γ-Al$_2$O$_3$ catalysts were investigated and compared in a continuous-flow microreactor at 240–350°C and 3.55 MPa. HDS and HDN activities on Ti/Zr/V-supported catalysts depended on the amounts and the order of impregnation of molybdenum and cobalt. It was found that Ti/Zr/V-supported catalysts had higher HDS and HDN activities than alumina-supported catalysts. The optimal amounts of CoO and MoO$_3$ on TiO$_2$–ZrO$_2$–V$_2$O$_5$ were much less than on alumina. Moreover, the mutual inhibition of HDS and HDN over Ti/Zr/V-supported catalysts was less pronounced than that over alumina-supported catalysts. The Ti/Zr/V-supported catalyst was also more active than the commercial catalyst, HR-306, in hydrodesulfurization of petroleum feedstocks. © 1989 Academic Press, Inc.

INTRODUCTION

Catalytic hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) are important processes in petroleum and petrochemical industries. The catalysts used in industry are normally derived from oxides of an element of Group VIB (Mo or W) and an element of Group VIII (Co or Ni) supported on γ-alumina and are *in situ* presulfided with H$_2$S. In general, those catalysts possess hydrogenolysis, hydrogenation, and hydrocracking functions (*1, 2*). However, a more sophisticated hydrotreatment catalyst should have all these functions appropriately balanced.

It is well established that hydrotreatment of aromatic nitrogen-containing molecules generally occurs through saturation of aromatic rings prior to any C–N bond cleavage (*3*). In the case of simultaneous hydrodesulfurization and hydrodenitrogenation, Satterfield *et al.* (*4*) pointed out that pyridine hydrodenitrogenation would be retarded by thiophene. Nagai *et al.* (*5, 6*) indicated that nitrogen compounds were effective poisons for both dibenzothiophene hydrogenation and desulfurization.

These findings supported the proposals

(*7–9*) that (a) there were separate sites on the catalyst surface for hydrogenation and hydrodesulfurization and (b) the poisoning of hydrogenation sites was the major factor in reducing HDS and HDN activities. Thus, a better hydrotreatment catalyst could be designed by selecting an appropriate carrier that was able to provide additional hydrogenation sites or that was able to resist the poisoning of hydrogenation sites. Ng and Gulari (*10*) reported that low-loading titania-supported catalysts were more effective in the HDS reaction than alumina-supported catalysts. The inherent HDS and HDN capabilities of the titania–zirconia-supported catalysts were observed by Mikovsky and Silvestri (*11*) and Wang *et al.* (*12*). However, recently we found that ternary oxides, TiO$_2$–ZrO$_2$–V$_2$O$_5$, were more active than binary oxides, TiO$_2$–ZrO$_2$, in cyclohexane dehydrogenation (*13*). Thus, it is worthwhile to investigate HDS and HDN over Co–Mo on TiO$_2$–ZrO$_2$–V$_2$O$_5$.

EXPERIMENTAL

Catalysts. Both a γ-Al$_2$O$_3$ and a TiO$_2$–ZrO$_2$–V$_2$O$_5$ (1/1/0.05 mole ratio) were used as carriers. The preparation of TiO$_2$–ZrO$_2$–V$_2$O$_5$ was described in our previous paper

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TABLE 1

Physical Properties of Catalysts

Catalyst	wt%		Carrier[a]	Surface area $(m^2\ g^{-1})$	Pore volume $(cm^3\ g^{-1})$	Median pore diameter (Å)
	MoO_3	CoO				
TZV-1	0.0	0	A	138	0.30	82
TZV-4	4.0	0	A	129	0.30	87
TZV-7	8.0	0	A	117	0.31	94
TZV-4C	4.0	2.0	A	118	0.31	92
TZV-11	0	2.0	A	132	0.30	84
TZV-4F[b]	4.0	2.0	A	115	0.32	90
A-2	4.0	2.0	D	186	0.67	135
A-3	8.0	4.0	D	178	0.68	144
HR-306[c]	8.0	3.5	γ-Al_2O_3	188	0.47	100

[a] (A) TiO_2–ZrO_2–V_2O_5 (1/1/0.05), 550°C precalcined; (D) pural SB (Condea pseudoboehmite), 600°C precalcined.

[b] Impregnation with Co first.

[c] Manufactured by IFP (Institut Français du Petrole).

(13). Co/Mo/γ-Al_2O_3 and Co/Mo/TiO_2–ZrO_2–V_2O_5 catalysts were prepared by the incipient wetness method. First, an ammonium heptamolybdate solution, pH $\sim$ 8, was added to the carriers. This was followed by oven drying at 100°C and calcining at 500°C for 6 h. A cobalt nitrate solution, pH $\sim$ 3.5, was then added to molybdenum-containing catalysts and the resulting catalysts were oven dried and calcined at 500°C. A commercial catalyst, HR-306 with 8% MoO_3 and 3.5% CoO on γ-alumina, was used as a reference. The composition and the physical properties of the catalysts are summarized in Table 1.

Activity measurement. The kinetics of the HDS of dibenzothiophene (DBT) and the HDN of aniline (ANI) were measured via a stainless-steel microreactor under continuous flow conditions at elevated temperatures and pressures. A schematic diagram of the reaction system is shown elsewhere (15). After being loaded in the reactor, 6 g of catalyst was reduced and sulfided by the procedure described by Chu and Wang (15). A synthetic feed (15) containing 1% dibenzothiophene and 1% aniline in a mixed solvent of toluene and me-

sitylene was charged into the reactor. Reactions were then studied under the following conditions: temperature, 240–350°C; total pressure, 3.55 MPa; WHSV, 0.5–8 w/w/h; H_2/liquid mole ratio, 6. During each run, products were periodically sampled and analyzed (15) for conversions of dibenzothiophene and aniline until the steady state was reached.

When the concentrations of reactants and products were low, the hydrogen was present in excess, and the reactants and the products had similar adsorptivities, a pseudo-first-order rate expression could be selected for both HDS and HDN (14–16). In the case of an integral reactor, it gives the working equation

$$-\ln(1 - X_i) = k_i/WHSV \qquad (1)$$

where X_i is the conversion of dibenzothiophene or aniline, k_i is the apparent rate constant (h^{-1}), and WHSV $= F_t/w$ [g/h − g; w is the weight of the catalyst in reactor (g) and F_t is the total liquid feed rate (g/h)].

A heavy diesel and a vacuum gas oil were also used as feedstocks. The physical properties of the above petroleum fractions are given in Table 2. Both heavy diesel and

TABLE 2

Physical Properties of Petroleum Feedstocks

	Heavy diesel	Vacuum gas oil
Specific gravity	0.846	0.982
Sulfur (wt%)	1.14	2.15
Nitrogen (ppm)	—	520
Boiling point, 5/95 (°C)	160/370	320/510

vacuum gas oil contained various sulfur compounds with different reactivities. Although each compound reacted at a rate proportional to its concentration, a second-order dependency of the reaction rate of the total sulfur removal was observed. For a pseudo-second-order reaction, the working equation is

$$X_s/1 - X_s = k_{2nd}/WHSV \qquad (2)$$

where X_s is the total conversion of sulfur compounds in feed.

RESULTS AND DISCUSSION

Kinetic Analysis of Hydrotreatment of Synthetic Feed

The typical results of kinetic treatment of HDS of DBT and HDN of ANI are given in Figs. 1 and 2, respectively. As shown in these figures, the Ti/Zr/V-supported catalyst showed higher activities than the alumina-supported catalyst at high temperatures although both catalysts contained the same amounts of Co and Mo. The rate constants for hydrotreatment of the synthetic feed over various catalysts are summarized in Table 3.

Dehydrogenation and Isomerization of Cyclohexane over the Carriers

The catalytic properties of the carriers were compared with those of the dehydrogenation and isomerization reactions of cyclohexane. The results are listed in Table 4. The reactions were carried out in a continuous dilute flow system. Experimental details are given elsewhere (13). Benzene was considered as the dehydrogenation product and both methylcyclopentane and the open-
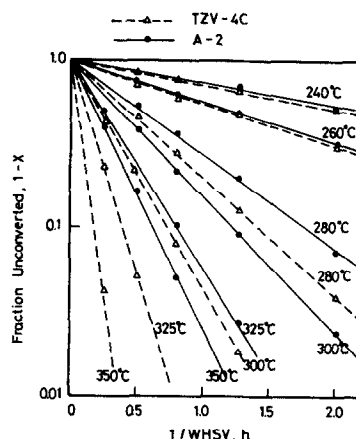

FIG. 1. Comparison of the pseudo-first-order kinetics of dibenzothiophene HDS of Ti/Zr/V- and alumina-supported catalysts.

chain products were considered isomerization products. To avoid competition from secondary reactions, the benzene yield was limited to the range 3–15%. The low conversion of cyclohexane ensures that the reaction network may be treated as a parallel first-order reaction for both dehydrogenation and isomerization. As shown in Table 4, TiO_2–ZrO_2–V_2O_5 not only showed higher dehydrogenation and isomerization activi-
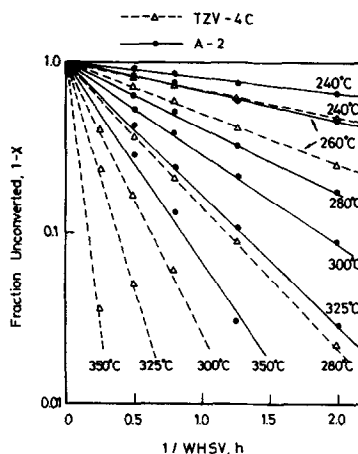

FIG. 2. Comparison of the pseudo-first-order kinetics of aniline HDN of Ti/Zr/V- and alumina-supported catalysts.

TABLE 3

Rate Constants of HDS and HDN over Various Catalysts

Reaction temperature (°C)	Catalyst: MoO$_3$ (%): CoO (%): Carrier[a]:	TZV-4 4 0 A	TZV-4C 4 2 A	TZV-11[b] 0 2 A	TZV-4F[c] 4 2 A	A-2 4 2 D	A-3 8 4 D	HR-306 8 3.5 γ-Al$_2$O$_3$
				HDS of DBT				
240		0.12	0.32	0	0	0.34	0.41	0.38
260		0.26	0.59	0	0.07	0.58	0.64	0.60
280		0.53	1.62	0.09	0.21	1.30	1.50	1.31
300		1.40	3.07	0.21	0.68	1.87	2.59	2.59
325		2.53	4.94	0.54	1.06	2.85	4.07	4.61
350		5.55	11.82	0.92	1.88	4.20	7.68	8.56
				HDN of ANI				
240		0.08	0.37	0	0	0.19	0.52	0.22
260		0.18	0.66	0.07	0.06	0.38	0.51	0.32
280		0.42	1.90	0.19	0.17	0.85	1.05	0.59
300		0.74	3.58	0.41	0.42	1.20	1.42	0.95
325		1.96	5.71	0.69	0.92	1.80	2.04	1.75
350		4.18	12.84	1.08	1.75	2.61	3.77	3.05

[a] (A) TiO$_2$–ZrO$_2$–V$_2$O$_5$ (1/1/0.05), 550°C; (D) pural SB, 600°C.
[b] Impregnation with cobalt only.
[c] Impregnation with cobalt first.

ties than γ-Al$_2$O$_3$, but also showed a higher selectivity to benzene than γ-Al$_2$O$_3$.

Mo Loading on TiO$_2$–ZrO$_2$–V$_2$O$_5$

The effects of Mo loading alone on the simultaneous HDS of DBT and HDN of ANI are given in Fig. 3. Both the HDS and the HDN rate constants showed maxima at a Mo loading of 4%. This optimal amount of Mo loading on Ti/Zr/V support is signifi-

cantly lower than alumina-supported samples (13%) (*18*) and titania-supported samples (7.5%) (*10*). The results in Fig. 3 also indicate that the intrinsic activities, which

TABLE 4

Comparison of the Catalytic Activities of Dehydrogenation and Isomerization of Cyclohexane of TiO$_2$–ZrO$_2$–V$_2$O$_5$ and γ-Al$_2$O$_3$ (at 540°C)[a]

Carrier	K_B/K_B, γ-Al$_2$O$_3$	K_{iso}/K_{iso}, γ-Al$_2$O$_3$	K_B/K_{iso}
γ-Al$_2$O$_3$	1	1	1.2
TiO$_2$–ZrO$_2$–V$_2$O$_5$	70	3.5	24

[a] K_B = rate constant of dehydrogenation, min^{-1} g^{-1}. K_{iso} = rate constant of isomerization, min^{-1} g^{-1}.
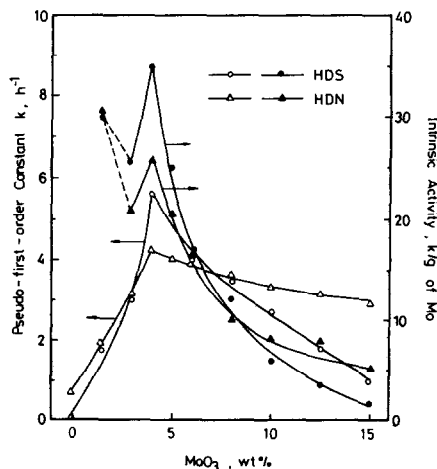

FIG. 3. Pseudo-first-order rate constant and intrinsic activity of HDS and HDN over MoO$_3$ on TiO$_2$–ZrO$_2$–V$_2$O$_5$ (1/1/0.05) at 350°C.
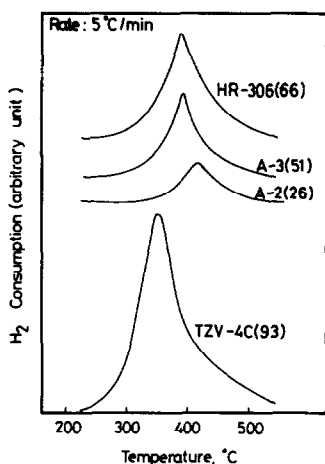
FIG. 4. Temperature-programmed reduction of various catalysts. Hydrogen consumption, μmol/g-cat, in parentheses.

were calculated by dividing the rate constants by the Mo loading, exhibited maxima at 4% MoO_3. This "efficiency maximum" was mentioned as 9.0% on alumina (18) and 7.0% on carbon (19)-supported systems.

Massoth (20) pointed out that HDS activity correlated strongly with the degree of reduction of the surface molybdates. For the alumina-supported catalyst with low Mo loading, the poor HDS activity was due to the difficulty of reducing molybdenum oxide (18). On the other hand, Mo loaded on titania could be reduced to zero-valent state with H_2 (21). We spectulate that Ti/ Zr/V-supported MoO_3 could be reduced easily up to 4%, at which point monolayer coverage was presumably formed hence resulting in high activities. Once the monolayer coverage was exceeded the activities decreased due to the surface molybdate dominated with bulklike MoO_3 (22). To verify this speculation, a temperature-programmed reduction (TPR) technique was applied to several catalysts. The results are given in Fig. 4. Indeed, Ti/Zr/V-supported catalysts showed a lower reduction temperature than alumina-supported catalysts.

Co Promotion on Mo/TiO_2–ZrO_2–V_2O_5

It is well recognized that the addition of cobalt to Mo catalysts enhances HDS and HDN activities (10, 19, 23); however, the mechanism of cobalt promotion is still a subject of controversy. In this study, the cobalt effect was extensively studied with 4 wt% MoO_3 on TiO_2–ZrO_2–V_2O_5. Figure 5 gives the results of cobalt promotion on both HDS and HDN at 350°C. Both curves show maxima at a CoO/MoO_3 ratio of 0.5, whereas the activities are enhanced twofold for HDS and threefold for HDN with respect to unpromoted catalyst. It is accepted that the cobalt promotion in the HDS reaction is strongly affected by the supporting materials. Addition of Co to the Mo/TiO_2 catalyst increased HDS activity 75% (10). However, Duchet et al. (19) reported that the addition of Co to a Mo/carbon catalyst could enhance HDS activity sixfold. Since a Co/carbon catalyst was also active in the HDS reaction, the extremely high activity of Co–Mo/carbon catalyst might be due to the participation of Co as an active phase (19). As shown in Table 3, Co alone on TiO_2–ZrO_2–V_2O_5 showed very low activity with respect to both HDS and HDN.

As shown in Table 3, the catalyst TZV-

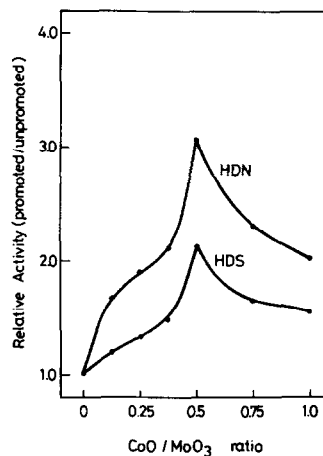FIG. 5. Promotion effect of CoO on MoO_3/TiO_2–ZrO_2–V_2O_5. MoO_3 = 4 wt%, Reaction temperature = 350°C.

TABLE 5

Product Distribution of HDS of DBT[a]

Product selectivity (mol %)	Reaction temperature:	260°C			300°C		
	Catalyst:	TZV-4C	A-2	HR-306	TZV-4C	A-2	HR-306
	Conversion (wt%):	26	25	27.5	86.5	61.5	71.5
Biphenyl		56	90	85	29	85	76
Cyclohexylbenzene		40	7	13	66	12	20
Others		4	3	2	5	3	4

[a] WHSV = 2.0.

4F, prepared by reversing the impregnation order of Mo and Co, showed extremely low activity compared with the catalyst prepared by the standard procedures. This observation did not agree with the results for the titania-supported catalysts (10). We suggest that $TiO_2-ZrO_2-V_2O_5$ contains surface sites that preferentially adsorb the molybdate species which in turn provide adsorption sites for cobalt species. Based on this model, both molybdenum and cobalt could be well dispersed and hence display high activities.

Product Distribution of Hydrotreated Synthetic Feed

Tables 5 and 6 give product distributions for dibenzothiophene desulfurization and aniline denitrogenation at 3.55 MPa, respectively. Both tables show that the Ti/Zr/V-supported catalyst had higher activity

than the alumina-based catalyst, especially at 300°C. The major products of dibenzothiophene desulfurization were biphenyl and cyclohexylbenzene. Biphenyl was found to be the predominant product for alumina-supported catalysts. On the other hand, Ti/Zr/V-supported catalysts gave a much higher selectivity on cyclohexylbenzene. This result was consistent with our previous findings (13) that $TiO_2-ZrO_2-V_2O_5$ itself provided hydrogenation sites.

For aniline hydrodenitrogenation, our results suggest that the benzene ring is hydrogenated prior to C–N bond cleavage as shown in Table 6. Cyclohexylamine was the intermediate product and cyclohexane was the final product, consistent with observations by other researchers (4, 15). In our previous study (13), we found that $TiO_2-ZrO_2-V_2O_5$ provided not only hydrogenation sites but also acid–base sites. The

TABLE 6

Product Distribution of HDN of ANI[a]

Product selectivity (mol %)	Reaction temperature:	260°C			300°C		
	Catalyst:	TZV-4C	A-2	HR-306	TZV-4C	A-2	HR-306
	Conversion (wt%):	27.4	16	15	87.2	46	37.8
Cyclohexylamine		35	42	41	Tr[b]	26	30
Cyclohexane		60	55	56	85	64	60
Methylcyclopentane		3	Tr	Tr	10	5	3
$n-C_6$		Tr	Tr	Tr	3	2	4
Others		2	3	3	2	2	3

[a] WHSV = 2.0.
[b] Trace.

acid–base property of TiO_2–ZrO_2–V_2O_5 would accelerate C–N bond cleavage and C–C bond rearrangement. As shown in Table 6, at 300°C, cyclohexylamine was almost completely removed and a significant amount of methylcyclopentane was formed.

Interaction between HDS of Dibenzothiophene and HDN of Aniline

Satterfield et al. (4) reported that thiophene inhibited the hydrogenation of pyridine to piperidine, the first step in the overall sequence. This effect is a typical example of alumina-supported catalysts. As shown in Table 3, the rate of HDN was far behind that of HDS over alumina-supported catalysts. This might be due to poisoning of hydrogenation sites by S compounds as mentioned above. However, in the case of Ti/Zr/V-supported catalysts the rate of HDN was similar to that of HDS. This means that the carrier itself can provide some aniline hydrogenation sites even though the surface metals are poisoned by the dibenzothiophene.

Many theories have been put forth to explain the poisoning effect of nitrogen compounds on the hydrodesulfurization of dibenzothiophene (5, 6, 25, 26). However, the reaction mechanism in the presence of N-containing compounds is still a subject of disagreement. To elucidate the inhibition effect of N-containing compounds on hydrosulfurization, a feed containing dibenzothiophene only (feed B) was investigated and compared with a feed containing both dibenzothiophene and aniline (feed A), as shown in Table 7. Feed B showed a higher reactivity than feed A when an alumina-supported catalyst (A-2) was used. Above 280°C, the rate constant for HDS of feed B was almost twice as high as that of feed A. This result confirmed that the alumina-supported catalyst could not resist the poisoning of a N-containing compound. For a Ti/Zr/V-supported catalyst, as shown in Table 7, the rate constant for HDS of feed B was higher than that of feed A at lower tem-

TABLE 7

Poisoning Effect of Aniline on the Rate Constants of HDS of DBT

Reaction temperature (°C)	A-2		TZV-4C	
	A[a]	B	A	B
240	0.34	0.39	0.32	0.40
260	0.58	0.79	0.59	0.74
280	1.30	2.25	1.62	1.94
300	1.87	3.17	3.07	3.60
325	2.85	5.18	4.94	6.54
350	4.20	9.68	11.82	12.80

[a] (A) containing dibenzothiophene and aniline; (B) containing dibenzothiophene only.

peratures. However, the acidity of TiO_2–ZrO_2–V_2O_5 itself was strong enough to completely break the C–N bond of cyclohexylamine at higher temperatures, although cyclohexylamine was known to be a stronger poisoning compound than aniline (26). Thus, the rate constant difference decreased with increasing reaction temperature.

Hydrodesulfurization of a Heavy Diesel and a Vaccum Gas Oil

To examine $Co/MO/TiO_2$–ZrO_2–V_2O_5 in a real practice, a heavy diesel and a vacuum gas oil were chosen as feedstocks, and the results are given in Figs. 6 and 7, respectively. Results for both indicate that the Ti/Zr/V-supported catalyst TZV-4C and the commercial alumina-supported catalyst HR-306 had similar activities at low temperatures. However, as the operating temperature increased, the Ti/Zr/V-supported catalyst was more active, as much as twice as high as the commercial catalyst.

CONCLUSIONS

From this study the following conclusions can be drawn.

1. Ti/Zr/V-supported catalysts are more active than alumina-supported catalysts.
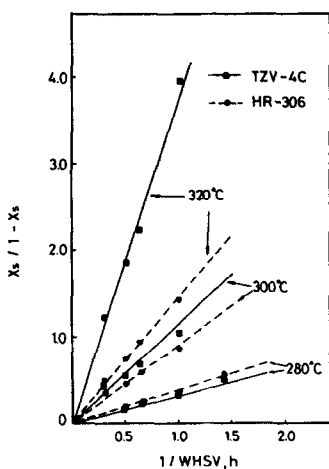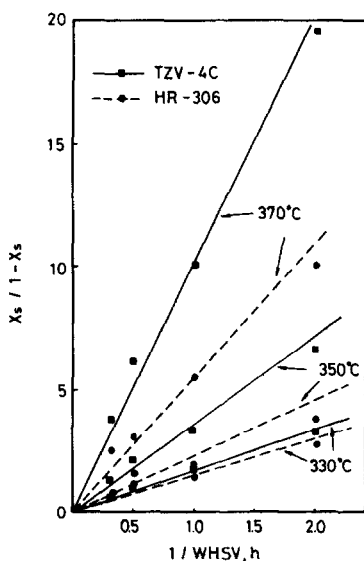2. Co is a promoter that can enhance the HDS and HDN activities of a MoO_3/TiO_2–

FIG. 6. Comparison of second-order kinetics of hydrodesulfurization of a diesel fuel by TZV-4C and HR-306. Pressure: 4.93 MPa. H_2/oil: 2000 SCF/BBL [= 356 m^3 (STP)/m^3].

ZrO_2–V_2O_5 catalyst two- to threefold. The optimal amounts of CoO and MoO_3 on TiO_2–ZrO_2–V_2O_5 are 2 and 4%, respectively.

3. Due to the inevitable fact that N com-

FIG. 7. Comparison of second-order kinetics of hydrodesulfurization of a vacuum gas oil by TZV-4C and HR-306. Pressure: 6.31 MPa. H_2/oil: 3000 SCF/BBL [= 534 m^3 (STP)/m^3].

pounds are contained in the petroleum fractions, the selection of a carrier that can effectively provide hydrogenation sites and break C–N bonds to remove N compounds is rather important in the HDS process. TiO_2–ZrO_2–V_2O_5 itself possesses hydrogenation and C–N bond-cracking activities and hence the Ti/Zr/V-supported catalysts can prevent the mutual inhibition between HDS and HDN.

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