JOURNAL OF CATALYSIS **116**, 600–603 (1989)

The Use of Binary Oxides as Catalyst Supports for Hydrodesulfurization and Hydrodenitrogenation

Previous studies (*1*) of thiophene hydrodesulfurization (HDS) at 1 atm and 573 K have identified a TiO_2–ZrO_2-supported catalyst with an initial HDS activity, on a weight basis, more than twice that of a commercial CoO–MoO_3/Al_2O_3 catalyst. Nitric oxide chemisorption and temperature-programmed desorption results suggested that the higher activity was due to a larger number of more reactive, coordinatively unsaturated Mo sites. This note reports additional efforts to develop more reactive HDS and hydrodenitrogenation (HDN) catalysts using a series of binary oxide supports with a broad range of surface compositions and pore structures.

The binary oxides and their catalysts were prepared as previously described (*1*). Final compositions of the catalysts are based on the concentration of the impregnation solutions.

NO chemisorption/TPD studies were performed as previously described (*2*). Initial thiophene HDS activity results were obtained with a pulse-mode reactor (0.05 cm^3) at 573 K and 1 atm (*1*). Steady-state activity for HDS was also performed with thiophene at 573 K and 1 atm using a fixed-bed (0.5 cm^3), tubular reactor (*3*). In both cases the catalysts were presulfided for 1 h at 673 K in 10 vol% H_2S in H_2. HDN tests were done in a fixed-bed, tubular reactor at 643 K and 85 atm using a vacuum gas oil containing 420 ppm basic nitrogen. A total of 80 cm^3 of catalyst (14 × 18 mesh) was used. Prior to testing the catalyst was presulfided at 593 K for 2 h in 10 vol% H_2S in H_2.

HDS activity test results are reported as relative weight activity (RWA), relative volume activity (RVA), and relative surface area activity (RSA), with American Cyanamid's commercial TRILOBE (Trademark of American Cyanamid) HDS-20 catalyst (5 wt% CoO–16 wt% MoO_3/Al_2O_3) assigned RWA, RVA, and RSA values of 100. HDN activity test results are reported in the same way except that the reference is American Cyanamid's commercial HDN-30 catalyst (5 wt% NiO–21 wt% MoO_3/Al_2O_3) also assigned RWA and RVA values of 100.

Illustrated in Table 1 are the NO chemisorption/TPD results for a series of 5 wt% CoO–16 wt% MoO_3 catalysts made with TiO_2–CeO_2 and TiO_2–MnO materials. The results reveal that the level of NO chemisorbed is affected by the metal : oxide ratio of the support. For TiO_2–CeO_2 the maximum in NO uptake is at a ratio of 3 : 1 based on the bulk composition and for TiO_2–MnO it is at 8 : 1 based on the surface composition as determined by XPS. For TiO_2–MnO-supported catalysts, it was also observed that the surface ratio affected the N_2O/NO TPD ratio. Also, it appeared that the ratio of N_2O/NO on TPD to that of the NO chemisorption value, designated as the R_d value, increased as the ratio of TiO_2 : MnO and, in turn, its calculated electronegativity increased in agreement with previous results (*2*).

The initial HDS activities of a series of binary oxide-supported catalysts are presented in Table 2 along with the NO chemisorption/TPD results. As can be seen, a considerable variation in HDS activity exists with RWA values ranging from 86 for a TiO_2–MnO-supported catalyst to 226 for a TiO_2–CeO_2-supported catalyst. Because the densities of the binary oxides are greater than that of alumina, the RVA values range from 132 to 278.

0021-9517/89 $3.00

TABLE 1

NO chemisorption/TPD Results for Binary Oxide-Supported CoO–MoO$_3$ Catalysts

Catalyst	Support	$TiO_2 : M_xO_y$ molar ratio		Surface area (m^2/g)	NO chemisorption results/TPD results		
		Bulk	XPS		NO uptake (μmol/g)	N_2O/NO	R_d (10^{-3})
A	TiO_2–CeO_2	1 : 1	—	142	171	—	—
B	TiO_2–CeO_2	2 : 1	—	182	319	—	—
C	TiO_2–CeO_2	3 : 1	—	185	391	—	—
D	TiO_2–CeO_2	4 : 1	—	185	376	—	—
E	TiO_2–MnO	1 : 1	1.4 : 1	178	214	—	—
F	TiO_2–MnO	3 : 1	5.5 : 1	145	384	0.75	1.95
G	TiO_2–MnO	6 : 1	8.2 : 1	162	399	0.73	1.83
H	TiO_2–MnO	1 : 1	1.7 : 1	186	229	0.64	2.79
I	TiO_2–MnO	3 : 1	3.3 : 1	125	289	0.62	2.15
J	TiO_2–MnO	6 : 1	5.8 : 1	197	373	0.81	2.17
K	TiO_2–MnO	11 : 1	11.0 : 1	187	216	0.81	3.75
L	TiO_2–MnO	15 : 1	15.1 : 1	197	257	1.03	4.01

Note. Supports for catalysts A–G prepared by homogeneous precipitation using urea. Supports for catalysts H–L prepared by direct addition of NH_4OH.

Previous studies have reported a direct correlation between HDS activity and NO uptake for Al_2O_3-supported CoO–MoO$_3$ catalysts (*4*). For the catalysts described in Table 2, such a correlation does not exist. However, as previously reported (*5*), we have found a correlation based on the assumption that the initial rate of HDS is directly proportional to the level of chemisorbed NO disproportionated to N_2O on TPD. The expression used is

$$K = 2R_d(NO_T)^2/(2R_d(NO_T) + 1) \quad (1)$$

where K is proportional to the amount of N_2O desorbed and R_d is the ratio of the TPD N_2O/NO ratio to the total level of NO chemisorbed, NO_T, expressed per unit surface area of the support. Using this expres-

TABLE 2

NO Chemisorption/TPD and Initial HDS Activity Results for Supported CoO–MoO$_3$ Catalysts

Support	$TiO_2 : M_xO_y$ bulk molar ratio	Surface area (m^2/g)	NO chemisorption results		HDS activity		K^a
			NO uptake (μmol/g)	N_2O/NO	RWA/RVA	RSA	
TiO_2–CeO_2	4 : 1	246	489	1.70	226/258	236	1.54
TiO_2–ZrO_2	1 : 1	218	459	0.81	163/278	192	1.30
TiO_2–MnO	1 : 1	183	350	0.77	86/132	121	0.94
TiO_2–MgO	1 : 1	246	323	0.60	162/261	169	0.94
Al_2O_3	—	258	323	0.23	100/100	100	0.39

[a] $K = 2R_d(NO_T)^2/(2R_d(NO_T) + 1)$.

sion and the data in Table 2, a direct correlation with HDS activity expressed per unit surface area of the support relative to HDS-20 is obtained, as illustrated in Fig. 1.

The correlation presented in Fig. 1 suggests that changes in support chemistry affect not only the number of catalytic sites as measured by the level of NO chemisorbed, but also the specific reactivity of those sites as measured by the R_d value. The changes in specific reactivity are suggested to be in part related to changes in the strength of interaction between the reactant molecule and the catalytic site.

Steady-state activity of these catalysts at 300°C and 1 atm, however, was significantly less than that of the Al_2O_3-supported catalyst (RWA = 100) with RWA values in the range 32–44. For the TiO_2–ZrO_2-supported catalyst we have previously reported (*1*) that the rapid rate of deactivation is related to both carbon deposition and the microporosity of the support. In an effort to further improve the porosity of TiO_2–ZrO_2 while maintaining high surface area, a technique was found (*6*) in which coprecipitation was done at a constant pH or by a swing pH technique (*7*) using NH_4OH, with the resulting hydrogel being calcined at 350°C for 3 h. The properties of two TiO_2–ZrO_2 materials made in these ways are described in Table 3 where they are compared to the properties of a TiO_2–ZrO_2 material made by direct addition of NH_4OH (increasing pH).

TABLE 3

Physical Properties of TiO_2–ZrO_2 Samples

	Sample		
	M[a]	N[b]	O[c]
Surface area (m^2/g)			
N_2 BET	316	312	282
Hg PSD	258	281	139
Pore volume (cm^3/g)	0.62	0.44	0.18
Pore size distribution (vol%)			
<45 Å	4.0	2.0	72.2
45–81 Å	40.1	92.0	10.1
>81 Å	55.9	6.0	17.7
Pore diameter at half volume (Å)	70	61	42
Average pore diameter, 4*V*/*A* (Å)	92	63	50

[a] Constant pH technique.

[b] Swing pH technique.

[c] Increasing pH technique.

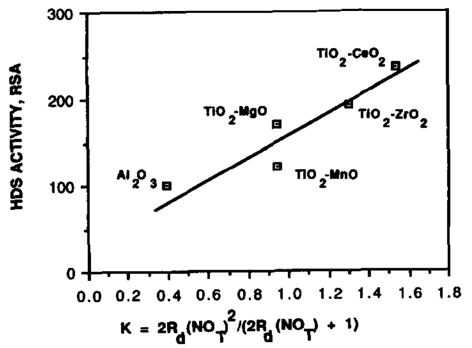

FIG. 1. Correlation of HDS activity with nitric oxide chemisorption/TPD results.

Because of the enhanced porosity of the TiO_2–ZrO_2 materials made by the constant pH and swing pH techniques, 3 wt% CoO–16 wt% MoO_3 and 3 wt% NiO–18 wt% MoO_3 catalysts were made with these materials and tested for HDN activity at 643 K and 85 atm. After 6 h on stream these catalysts were more active than the standard, HDN-30 (RWA/RVA = 100/100), with RWA/RVA values of 144/144 and 116/167, respectively. Unfortunately, these catalysts also exhibited more rapid rates of deactivation than HDN-30, yielding RWA/RVA values of 120/120 and 98/141, respectively, after 60 h on stream.

In conclusion, the results presented show that changes in support chemistry can influence the activity of molybdenum catalysts for both HDS and HDN. It is believed that this effect on catalyst activity is the result of changes in both the number and reactivity of the catalytic sites.

ACKNOWLEDGMENTS

The author thanks Ms. B. Carney and Dr. H. Jung for their assistance in the preparation of catalysts used in the HDN study.

REFERENCES

1. Daly, F. P., Ando, H., Schmitt, J. L., and Sturm, E. A., *J. Catal.* **108,** 401 (1987).
2. Daly, F. P., Schmitt, J. L., and Sturm, E. A., *J. Catal.* **97,** 248 (1986).
3. Jung, H. J., Schmitt, J. L., and Ando, H., *in* "Proceedings, 4th International Conference in the Chemistry and Uses of Molybdenum, Golden, CO, 1982."
4. Topsoe, N-Y., and Topsoe, H., *J. Catal.* **84,** 386 (1983).
5. Daly, F. P., and Ando, H., Schmitt, J. L., and Sturm, E. A., *Stud. Surf. Sci. Catal.* **38,** 553. "Catalysis 1987," Elsevier, Amsterdam, 1988.
6. Daly, F. P., Ando, H., Foley, H. C., and Jung, H. J., U.S. Patent, filed 1987.
7. Ono, T., Ohguchi, Y., and Togari, O., *Stud. Surf. Sci. Catal.* **16,** 631. "Preparation of Catalysts III," Elsevier, Amsterdam, 1983.

F. P. DALY[1]

Chemical Research Division
American Cyanamid Company
1937 West Main Street
P.O. Box 60
Stamford, Connecticut 06904

Received October 4, 1988; revised November 14, 1988

---

[1] Present Address: Degussa Corporation, 104 New Era Drive, South Plainfield, NJ 07080.