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Catalytic Functionalities of Supported Sulfides

V. C–N Bond Hydrogenolysis Selectivity as a Function of Promoter Type

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Two types of γ-Al_2O_3-supported catalysts, containing Group VI–VIII transition metals as active components, were prepared and their selectivities for C–N bond hydrogenolysis determined. These were (a) sulfided MMo catalysts (where M = Fe, Co, Ni, Ru, Rh, Pd, Ir, Pt, Re, or Cr), containing 25 mmol M and 77 mmol Mo/100 g Al_2O_3; and (b) sulfided M catalysts, without Mo, containing 25 mmol M/100 g Al_2O_3. Pseudo-first-order rate constants for two simultaneous, competing reactions, i.e., C–N bond hydrogenolysis of indole (k_1) and ring hydrogenation of naphthalene (k_2), were determined (at 350°C and 137 atm H_2 pressure) for the above catalysts as a function of the periodic table position of M. It was found that the C–N hydrogenolysis vs ring hydrogenation selectivity of the MMo catalysts, as expressed by the k_1/k_2 ratio, was in the order RuMo > IrMo > CrMo > PtMo > CoMo > FeMo > NiMo > ReMo > RhMo > PdMo. The high selectivity of the RuMo, IrMo, and PtMo catalysts is due to a favorable balance of moderate C–N hydrogenolysis activity and very low ring hydrogenation activity. RhMo, NiMo, and CoMo show highest C–N hydrogenolysis activity, but relatively low selectivity due to their high ring hydrogenation activity. The sulfided M catalysts, except Pt and Pd, show markedly lower C–N hydrogenolysis activities than the corresponding MMo catalysts. Comparison of the actual C–N hydrogenolysis activities of MMo catalysts with their "additive" activities (calculated by assuming independent activities of the M and Mo components) shows that Ni, Rh, Co, Fe, and Ru strongly promote, whereas Pt and Pd strongly depress the C–N hydrogenolysis activity of the corresponding MMo catalysts. Similar promoting (or depressing) effects of the M components are also observed in comparing the actual and "additive" ring hydrogenation activities of the MMo catalysts, indicating that C–N hydrogenolysis and ring hydrogenation reactions possibly occur on the same or similar type of active sites. The high C–N hydrogenolysis selectivity of RuMo, IrMo, and PtMo points to the feasibility of their optimization for possible use as improved catalysts in HDN of heavy oils, involving lower hydrogen consumption than that found with conventional Ni- and Co-promoted catalysts. © 1988 Academic Press, Inc.

INTRODUCTION

It was shown previously that the C–O bond hydrogenolysis activity and selectivity of sulfided MMo/γ-Al_2O_3 catalysts (where M = Group VI–VIII transition metals) depend strongly on the promoter (M) type and its periodic table position (*1*). It was anticipated that the promoter could also influence the C–N bond hydrogenolysis activity and selectivity of such catalysts. The study of this subject is of considerable interest in view of the significant concentration of nitrogen in heavy petroleum fractions and residua (usually between 0.1 and 1.0 wt%), as well as in synfuels, e.g., coal-derived liquids (0.4–1.7 wt%) and shale oils (1.3–2.2 wt%) (*2–5*). A major part of the nitrogen in such heavy oils is in the form of condensed aromatic compounds, some of which have been found to undergo hydrodenitrogenation (HDN) at low reaction rates and with high hydrogen consumption

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(*6–12*). Recent kinetic studies of relevant *N*-heterocyclic–carbocyclic model compounds, including 5,6-benzoquinoline, 7,8-benzoquinoline, 3,4-benzoquinoline (phenanthridine), *N*-ethylcarbazole, and 1,10-phenanthroline, have shown that with conventional sulfided CoMo, NiMo, or NiW catalysts the HDN reaction involves extensive hydrogenation of both *N*-heterocyclic and carbocyclic aromatic rings prior to the C–N hydrogenolysis steps (*7, 13*). HDN of bicyclic compounds, e.g., quinoline (*14, 15*) and indole (*16, 17*), shows similar reaction patterns. For tricyclic compounds containing *end*-pyridine rings, e.g., 5,6-benzoquinoline, the HDN reactions involve as a first step fast hydrogenation of the pyridine ring, followed preferentially by hydrogenation of at least one adjacent aromatic ring prior to C–N hydrogenolysis (*7*). For tricyclic compounds containing a *middle-N*-heterocyclic ring, e.g., phenanthridine and carbazole, the HDN reactions preferentially proceed via complete hydrogenation of the condensed carbocyclic–N-heterocyclic ring system prior to C–N bond hydrogenolysis (*7*). In close agreement with these model compound studies, it was recently found that the hydrogen consumption in HDN of a SRC-II middle–heavy distillate and of a synfuel-simulating blend (at 350–375°C; sulfided 3Co8Mo or 3Ni8Mo catalyst) was in the range 8.0–10.3 mol of H_2/N g atom removed, i.e., drastically higher than an ideal hydrogen consumption of 3–4 mol H_2/N g atom removed, calculated on the basis of selective hydrogenation of *N*-heterocyclic rings only, followed by C–N hydrogenolysis (*5*). Rate data obtained in several HDN studies of model compounds, i.e., quinoline (*14, 15*), acridine (*18*), and dilute solutions of benzoquinolines, carbazoles, and 1,10-phenanthroline (*7*), have been found to fit pseudo-first-order kinetics. In other studies, however, authors have proposed Langmuir–Hinshelwood rate expressions, based on self-inhibition of the HDN reactions by the N-containing feeds and consequent deviation from first-order kinetics (*6, 19, 20*). It was found in a detailed HDN study of quinoline solutions that the denitrogenation reaction follows pseudo-first-order kinetics at low nitrogen concentration, but shows non-first-order kinetics at high nitrogen concentration in the feed solution (*20*).

In earlier papers we reported results on the effects of the support and additives upon various catalytic functionalities of supported sulfide catalysts (*21, 22*). Studies of the HDS activities of Group VIII bulk sulfides have shown that first-row metal sulfides, i.e., FeS, Co_9S_8, and Ni_3S_2, are less active for C–S hydrogenolysis of dibenzothiophene than second- and third-row metal sulfides, e.g., those of Ru, Os, Ir, Rh, Pd, and Pt (*23*). Further, it was found recently that the hydrodeoxygenation (HDO) selectivity of a sulfided, Al_2O_3-supported RuMo catalyst was markedly higher than those of supported CoMo and NiMo catalysts (*1*).

In connection with the above results, it was of obvious interest to investigate the HDN activities of Group VI–VIII metals as promoters in Mo-based sulfided catalysts, with the objective of providing data on the feasibility of developing supported catalysts possessing augmented C–N hydrogenolysis vs ring hydrogenation selectivities. The present study reports a systematic study of the C–N hydrogenolysis activities and selectivities of a series of sulfided MMo/γ-Al_2O_3 catalysts, where M = Cr, Fe, Co, Ni, Ru, Rh, Pd, Re, Ir, or Pt. In order to elucidate the role of these transition metals as potential promoters, a series of sulfided M/γ-Al_2O_3 catalysts, not containing Mo, were also prepared and their activities studied. The C–N hydrogenolysis selectivities of all catalysts were determined by an appropriately designed method for kinetic differentiation between their C–N hydrogenolysis and ring hydrogenation activities (see below). The method is based on determination of the rate constants of two simultaneous, competing reactions, i.e., C–N hydrogenolysis of indole and hydrogenation of naphthalene, in the presence of each catalyst, under identical hydrotreating conditions.

EXPERIMENTAL

A. Catalysts

The preparation of catalysts was essentially the same as previously described in connection with our study of hydrodeoxygenation selectivity (*1*). MMo/γ-Al_2O_3 catalysts (where M = Cr, Fe, Co, Ni, Ru, Rh, Pd, Re, Ir, or Pt) were prepared by incipient wetness impregnation, using the following stepwise procedure. The support (Ketjen γ-Al_2O_3; 20–40 mesh; surface area, 209 m^2/g; pore volume, 0.6 cm^3/g) was calcined at 540°C for 16 h and then impregnated by pore volume filling with an aqueous solution of ammonium molybdate. The impregnated sample was oven-dried at 120°C for 16 h and then impregnated with a salt solution containing the promoter (M). The sequentially impregnated catalyst was finally dried at 120°C and calcined at 540°C for 16 h. As previously determined, no losses of the transition metal promoter (M), by volatilization of the corresponding oxides, occur to any appreciable extent under these calcination conditions (*1*). The salts used in the second impregnation step of the above procedure were Cr, Fe, Co, Ni, Rh, and Pd nitrates, Ru nitrosyl nitrate, Ir chloride, ammonium chloroplatinate, and ammonium pherrhenate. All catalysts contained 25 mmol of M and 77 mmol of Mo/100 g of Al_2O_3. M/γ-Al_2O_3 catalysts (without Mo) were prepared by incipient wetness impregnation of the support with solutions of the above salts, followed by drying at 120°C and calcination at 540°C. These catalysts contained 25 mmol M/100 g Al_2O_3. Prior to use, both types of catalysts were presulfided in a flow reactor at 400°C for 2 h under a stream of 10% H_2S–90% H_2 (40 cm^3/min). Sulfur contents of sulfided M/Al_2O_3 catalysts were reported in the preceding paper of these series (*1*).

B. Experimental Procedure

Testing of catalysts was performed in a 150 cm^3 Magnedash autoclave (Autoclave Engineers) equipped with a high-temperature sampling device for periodic withdrawal of small liquid samples during the kinetic experiments. In each run, 100 cm^3 of a feed solution containing 0.5 g each of 99+% pure (Aldrich) indole (IN) and 99+% pure (Aldrich) naphthalene (NP) in *n*-pentadecane (Humphrey Chemicals, purity 99%) was charged to the autoclave and 0.2 g of freshly sulfided catalyst was transferred to the Magnesdash catalyst cage under a small amount of the pure *n*-pentadecane solvent. The autoclave was purged with nitrogen and then hydrogen, pressurized to ~70 atm (1300 psig), and heated quickly (~20 min) without stirring to the desired temperature. At this point the H_2 pressure was adjusted to 137 atm (2000 psig) and the stirring was started. Samples (0.3 cm^3) were withdrawn at intervals of 5 min for the first 20 min and every 10 min afterward for a total period of 1 h, and then analyzed by gas chromatography on a 3 m × 0.3 cm stainless-steel column packed with 10% OV-17 on 100–120 mesh Chromosorb W-HP at a temperature programmed from 100 to 250°C at a rate of 8°C/min.

C. Kinetic Differentiation Method

The kinetic runs were used to determine for each catalyst the rate constants of two simultaneous, competing reactions, i.e., C–N hydrogenolysis of IN (k_1) and ring hydrogenation of NP (k_2), as shown in Fig. 1. Hydrogenolysis of IN, which is in a state of equilibrium with 2,3-dihydroindole (DIN) under the hydroprocessing conditions employed, yields a mixture of *o*-ethylaniline (**1**), ethylcyclohexane (**2**), and ethylbenzene (**3**). Compound **2** is the predominant product, accompanied by smaller amounts of **1** and **3**. Compound **1** is the anticipated initial product formed by C–N hydrogenolysis of the weaker (benzylic) β-bond in DIN. It was previously indicated that **1** undergoes

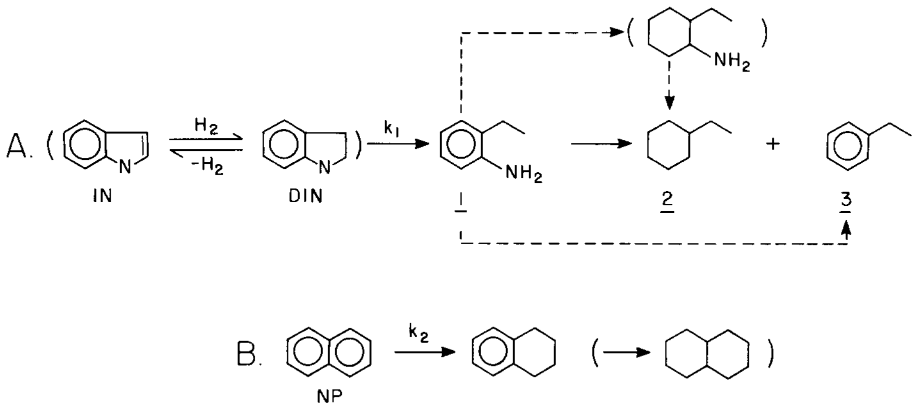

FIG. 1. Scheme for kinetic differentiation of C–N hydrogenolysis vs ring hydrogenation.

fast ring hydrogenation due to the activating effect of the amino group to yield 1-amino-2-ethylcyclohexane (not detected) as a highly reactive intermediate, which is apparently quickly converted to **2** by hydrogenolysis of the (aliphatic) C–N bond (*16*). Direct hydrogenolysis of the (aromatic) C–N bond in **1** to yield **3** is a relatively slower reaction (*16*). Likewise, hydrogenation of **3** to yield ethylcyclohexane (*2*) is a slow reaction which contributes to some extent but cannot account for the formation of **2** as main reaction product, as confirmed by independent runs with **3** as starting compound under otherwise identical hydrotreating conditions (*16*). As indicated in Fig. 1, k_1 is the overall rate constant for the conversion of IN, via DIN, into compounds **1–3** (reaction A). Hydrogenation of NP (reaction B) yields tetralin, which undergoes subsequent hydrogenation to decalin to a low extent (usually <25%). The k_2 rate constant represents the faster hydrogenation of a conjugated ring in the NP system, and not the slower hydrogenation of the residual, viz., single (nonconjugated) aromatic ring. The C–N hydrogenolysis selectivity of the catalysts is provided by the k_1/k_2 ratio.

Reaction data were analyzed on the basis of pseudo-first-order in reactant concentration, viz.,

$$-\ln(1 - x_A) = k_A W f(t/V),$$

where $f(t/V)$ is defined as

$$f(t/V) = \sum_{i=1}^{n} \frac{t_i^c - t_{i-1}^c}{V_{i-1}}.$$

In these equations, x_A is the reactant conversion, k_A is the rate constant, W is the catalyst weight, n is the number of samples taken, t^c is a corrected time, and V is the solution volume left after the ith sample. The corrected time accounts for the amount of reaction which has occurred during heatup to reaction temperature, determined by extrapolating a plot of $-\ln(1 - x_A)$ vs real time to zero conversion. An example of the data fit is shown in Fig. 2. Duplicate runs gave relative errors in k_A values of 3% for C–N hydrogenolysis and 7% for naphthalene hydrogenation.

RESULTS

A. C–N Bond Hydrogenolysis Selectivity of Sulfided MMo/Al$_2$O$_3$ Catalysts

Results on the activities and C–N hydrogenolysis selectivities of the sulfided MMo/Al$_2$O$_3$ catalysts are given in Table 1. The k_1 and k_2 values reflect the C–N hydrogenolysis and ring hydrogenation activities, respectively, while the C–N hydrogenolysis selectivity is given by the k_1/k_2 ratio. As seen, highest C–N hydrogenolysis activity is shown by the RhMo, NiMo, CoMo, IrMo, FeMo, and RuMo catalysts, in that

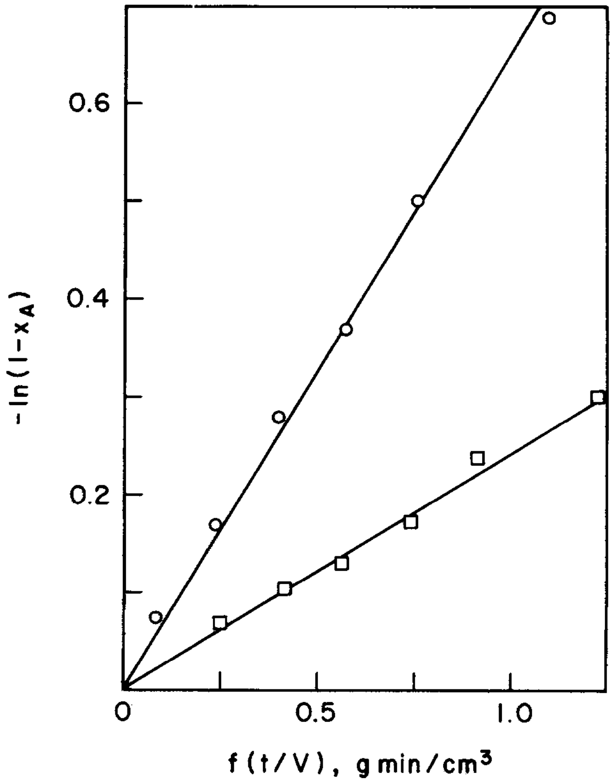

FIG. 2. First-order activity correlation for sulfided RuMo/Al_2O_3 catalyst. Symbols: (○) C–N hydrogenolysis, (□) ring hydrogenation.

order. The RhMo, NiMo, CoMo, and FeMo catalysts, however, also show considerable ring hydrogenation activities, resulting in rather low C–N hydrogenolysis selectivities (1.13, 1.24, 1.55, and 1.38, respectively). Markedly higher selectivities are shown by the RuMo, IrMo, and CrMo catalysts (3.85, 2.86, and 2.59, respectively), due to their very low ring hydrogenation activities. The PtMo and ReMo catalysts show moderate C–N hydrogenolysis selectivity (2.20 and 1.91, respectively), whereas the selectivity of the PdMo catalyst (0.72) is lower than that of the unpromoted Mo catalyst (1.30) and lowest among all MMo catalysts examined. The commercial CoMo catalyst (Ketjen) shows lower activities than the CoMo catalyst prepared in this study, but the selectivities of the two catalysts are similar.

Comparison of the data in Table 1 with results obtained in the previous study of the C–O hydrogenolysis selectivity of the same catalysts (*1*) shows that the ring hydrogenation activities of the catalysts (for hydrogenation of NP) in the presence of indole are drastically lower than those previously found in the presence of diphenyl ether (DPE) (see Discussion).

B. C–N Bond Hydrogenolysis Selectivity of Sulfided M/Al_2O_3 Catalysts

Results on the activities and C–N hydrogenolysis selectivities of sulfided M/Al_2O_3 catalysts (without Mo), where M = Fe, Co, Ni, Ru, Rh, Pd, Ir, Pt, Re, or Cr, are summarized in Table 2. All the catalysts, except Pt and Pd, show markedly lower C–N hydrogenolysis activities than the corresponding MMo/Al_2O_3 catalysts (compare with Table 1). The C–N hydrogenolysis activity of Pt is considerably higher than that of Pd,

TABLE 1

Catalytic Activities and C–N Hydrogenolysis Selectivities of Supported MMo Catalysts as a Function of the Type of Transition Metal (M) Promoter[a–c]

Catalyst[c,d]	Promoter group (row)	k_1 (cm^3/g min), C–N hydrogenolysis	k_2 (cm^3/g min), ring hydrogenation	Selectivity, k_1/k_2
FeMo	$VIII_1$ (1)	2.97	2.15	1.38
CoMo	$VIII_2$ (1)	3.40	2.19	1.55
NiMo	$VIII_3$ (1)	4.25	3.42	1.24
RuMo	$VIII_1$ (2)	2.54	0.66	3.85
RhMo	$VIII_2$ (2)	4.53	4.00	1.13
PdMo	$VIII_3$ (2)	1.27	1.78	0.72
IrMo	$VIII_2$ (3)	3.12	1.09	2.86
PtMo	$VIII_3$ (3)	2.24	1.02	2.20
ReMo	VII (3)	2.10	1.10	1.91
CrMo	VI (1)	1.40	0.54	2.59
-Mo[e]	VI (2)	0.91	0.70	1.30
3Co8Mo (Ketjen)		2.52	1.51	1.67

[a] Kinetic runs performed at 350°C and 137 atm (2000 psig) H_2 pressure.

[b] Feed: solution containing 0.5 wt% each of IN and NP in *n*-pentadecane.

[c] Results are averages of duplicate runs.

[d] All MMo catalysts were prepared by an identical procedure (sequential incipient impregnation) and contained 25 mmol of M and 77 mmol of Mo/100 g Al_2O_3. Catalysts were sulfided prior to use.

[e] Nonpromoted catalyst containing 77 mmol Mo/100 g Al_2O_3.

TABLE 2

Catalytic Activities and C–N Hydrogenolysis Selectivities of Al_2O_3-Supported Transition Metal (M) Catalysts[a,b]

Catalyst[c,d]	Metal (M) group (row)	k_1 (cm^3/g min), C–N hydrogenolysis	k_2 (cm^3/g min), ring hydrogenation	Selectivity, k_1/k_2
Fe	$VIII_1$ (1)	0.71	0.34	2.09
Co	$VIII_2$ (1)	0.77	0.40	1.93
Ni	$VIII_3$ (1)	0.59	0.25	2.36
Ru	$VIII_1$ (2)	1.14	0.33	3.45
Rh	$VIII_2$ (2)	2.07	3.32	0.62
Pd	$VIII_3$ (2)	2.23	2.73	0.82
Ir	$VIII_2$ (3)	2.92	2.63	1.11
Pt	$VIII_3$ (3)	6.38	5.02	1.27
Re	VII (3)	1.15	2.41	0.48
Cr	VI (1)	1.24	0.60	2.07
Mo	VI (2)	0.91	0.70	1.30

[a] Kinetic runs were performed at 350°C and 137 atm (2000 psig) H_2 pressure.

[b] Feed: solution containing 0.5 wt% each of IN and NP in pentadecane.

[c] Results are averages of duplicate runs.

[d] All catalysts were prepared by incipient wetness impregnation and contain 25 mmol of M/100 g Al_2O_3. Catalysts were sulfided prior to use.

whereas the opposite order of activities for C–O hydrogenolysis was previously found for these two sulfided metal catalysts (*1*). Among the catalysts in Table 2, highest C–N hydrogenolysis selectivities are shown by sulfided Ru, Ni, Fe, and Co (in that order) due to their very low ring hydrogenation activities. These high selectivities, however, are of no major practical consequence because of the above-mentioned very low C–N hydrogenolysis activities of these sulfided metals compared with those of the corresponding Mo-based MMo catalysts. The remaining sulfided M catalysts (except Cr), i.e., Rh, Pd, Ir, Pt, and Re, show C–N hydrogenolysis selectivities markedly lower than those of the corresponding MMo catalysts, due in all cases (except Rh) to their higher ring hydrogenation activities than those of the Mo-based catalysts. The hydrogenation activity of Pd, Ir, Pt and Re is only moderate in comparison with the previously observed very high ring hydrogenation activity of the same sulfided metals in the presence of diphenyl ether as an O-containing substrate (*1*). The lower activity of these sulfided metals for ring hydrogenation of NP in the present study could be attributed to the strong competitive adsorption of the N-containing substrate (IN) (see Discussion).

DISCUSSION

C–N Bond Hydrogenolysis

Figure 3A shows the change in C–N hydrogenolysis activity of the sulfided M/Al_2O_3 catalysts as a function of the periodic table position of the transition metal (M). As seen, the first-row Group VIII metals, i.e., Fe, Co, and Ni, show the lowest C–N hydrogenolysis activity. This is qualitatively consistent with results obtained on the C–O hydrogenolysis activity of the same sulfided M/Al_2O_3 catalysts (*1*) and with reported data on the C–S hydrogenolysis activity of bulk sulfides of Group VIII metals (*23*) or of carbon-supported sulfides (*24*). Second-row Group VIII metals, i.e., Ru, Rh, and Pd, show higher C–N hydrogenolysis activity than first-row metals, and the order of activities is Pd > Rh > Ru, which is analogous to that previously found for the C–O hydrogenolysis activities of the same sulfided metals (*1*). This order, however, is different from that reported for C–S hydrogenolysis with bulk sulfides, i.e., Ru > Rh > Pd (*23*), or with carbon-supported sulfides, i.e., Rh > Ru > Pd (*24*). For third-row sulfided metals, the order of C–N hydrogenolysis activities is Pt > Ir > Re. This order is very different from that found for the C–O hydrogenolysis activities of the same metals, i.e., Re > Ir > Pt, and the results may be indicative of different sites for C–N and C–O hydrogenolysis in sulfided, Mo-free, third-row metals, in particular Pt and Re.

Figure 3B shows the change in C–N hydrogenolysis activity of the sulfided MMo/Al_2O_3 catalysts as a function of the periodic table position of the M promoter. It is found that most MMo catalysts have higher C–N hydrogenolysis activities than the corresponding M catalysts (without Mo), except for PtMo and PdMo, which show markedly lower activities, and CrMo, which shows about the same activity, compared with those of the corresponding M catalysts. Further, all MMo catalysts exhibit markedly higher activity than the unpromoted Mo catalyst, except CrMo and PdMo catalysts, which show only slightly higher activities than Mo. First-row Group VIII metals, i.e., Fe, Co, and Ni, which show the lowest C–N hydrogenolysis activity in the absence of Mo, show strong promoting effects (especially Ni) upon hydrogenolysis activity when combined with Mo. This is evidenced by the high C–N hydrogenolysis activity of NiMo (k_1 = 4.25), CoMo (k_1 = 3.40), and FeMo (k_1 = 2.97) in comparison with that of the unpromoted Mo catalyst (k_1 = 0.91). Among second-row metals, Rh (k_1 = 4.53) shows a very strong promoting effect, Ru (k_1 = 2.54) a moderate effect, and Pd essentially no effect upon the C–N hydrogenolysis activity of the corre-

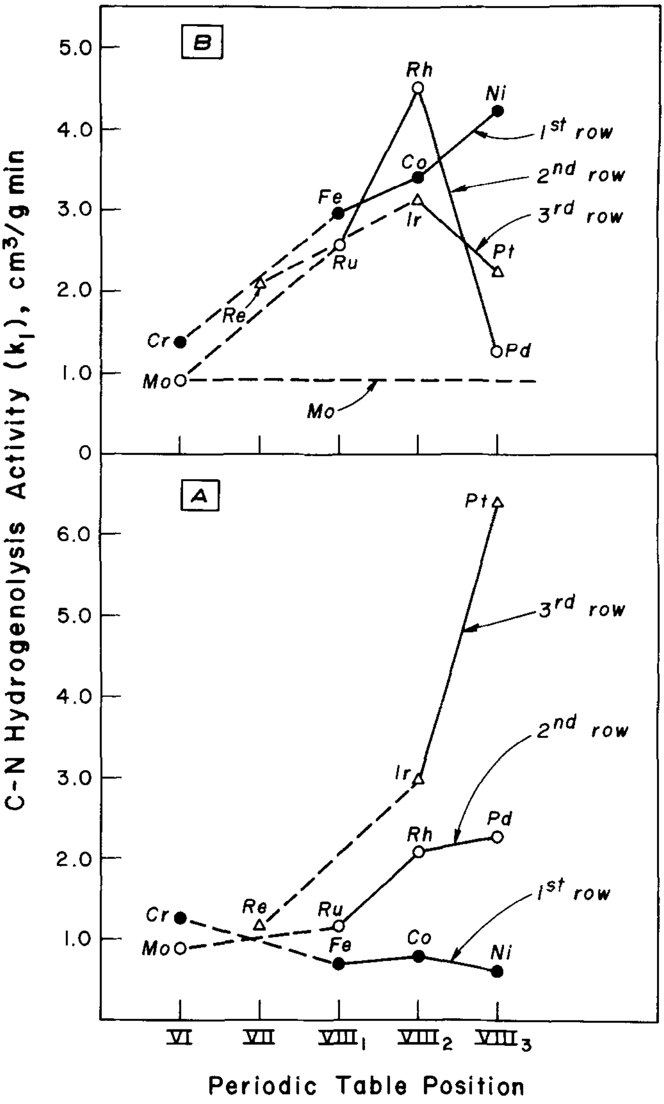

FIG. 3. Variation in C–N hydrogenolysis activity (k_I) for sulfided (A) M/Al_2O_3 and (B) MMo/Al_2O_3 catalysts as a function of the periodic table position of M.

sponding MMo catalyst. Third-row metals, i.e., Re, Ir, and Pt, and especially Ir (k_I = 3.12), show moderately high promoting effects. The moderate C–N hydrogenolysis activity of PtMo is noteworthy since this catalyst showed previously the lowest activity for C–O hydrogenolysis among all MMo catalysts (*1*). Data in Table 1 and Figure 3B also show that among second- and third-row metals maximum activity in each row is exhibited by Mo catalysts with Group $VIII_2$ promoters, i.e., Rh and Ir, respectively. Similar maxima ("volcano" peaks) for second- and third-row Group $VIII_2$ promoters were previously found for C–O hydrogenolysis activity (*1*). However, for first-row metals (Cr, Fe, Co, Ni) the promoting effect upon C–N hydrogenolysis activity increases almost linearly with increases in atomic number reaching a maximum with the Group $VIII_3$ metal Ni (Fig. 3B), while for C–O hydrogenolysis activity

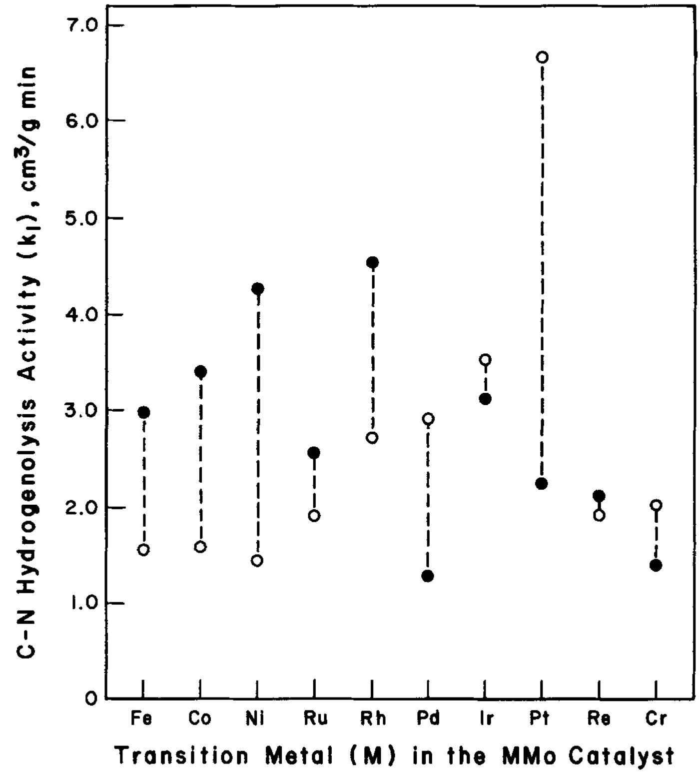

FIG. 4. Differences (---) between actual (●) and additive (○) C–N hydrogenolysis activities of sulfided MMo/Al_2O_3 catalysts.

a clear maximum was reached with Co as promoter (*1*). This is consistent with the observed higher activity of NiMo catalysts than of CoMo catalysts for HDN of heavy oils (*7*).

The effect of the transition metal promoter (M) was further evaluated by comparing the actual C–N hydrogenolysis and ring hydrogenation activities of the composite MMo/Al_2O_3 catalysts with those expected from simple addition of the activities of M/Al_2O_3 and Mo/Al_2O_3, i.e., the resultant activities anticipated if each component (M and Mo) acted independently. The "additive" activities were calculated, based on the equimolar concentration of the M metals (25 mmol/100 g Al_2O_3) in all catalysts and the constant concentration of Mo (77 mol/100 g Al_2O_3) in the MMo/Al_2O_3 catalysts (Tables 1 and 2, footnote *d*). The slight change in the concentrations of the M and Mo components in the composite MMo catalysts was taken into account. The calculated, additive hydrogenolysis activities are compared with the actual C–N hydrogenolysis activities in Fig. 4. The catalysts can be subdivided into the following groups: (i) those showing markedly higher, (ii) those showing slightly or moderately higher, and (iii) those exhibiting lower actual activities than the calculated additive activities. The first group includes catalysts containing Fe, Co, Ni, and Rh, which could be considered strong promoters (especially Ni). The synergistic effect of Co upon the C–S hydrogenolysis activity of the CoMo catalyst has been ascribed to the formation of an active "CoMo–S" phase (*25*). Since the first-row Group VIII metals, i.e., Fe, Co, and Ni, show per se the lowest C–N hydrogenolysis activity (Fig. 3A), it can be deduced that such a low activity is associated with chemical compatibility, viz., with a tendency for interaction of these metals with the Mo component, leading to formation of strongly active catalytic phases. The strong synergistic effect of Ni in the NiMo catalyst is particularly noteworthy and seems to be specific for C–N hydrogenolysis. In contrast, the actual and additive activities of the same catalyst for C–O hydrogenolysis showed essentially no difference (*1*). The CoMo catalyst, on the other hand, shows higher actual than additive activities for both C–O and C–N bond hydrogenolysis, although its activity for the latter is clearly lower than that of the NiMo catalyst, reflecting a relatively lower synergistic effect of Co than of Ni upon C–N hydrogenolysis activity. The second group of catalysts includes RuMo, which exhibits moderately higher, and IrMo and ReMo, which show only marginally higher actual than additive activities. The results with IrMo and ReMo possibly indicate that in these catalysts the M and Mo components either interact in a chemically nonconsequential manner relative to hydrogenolysis activity or, more likely, act and contribute independently to the overall activity observed. The third group of catalysts consists of PdMo and PtMo, which show markedly lower, and CrMo, which exhibits moderately lower actual than calculated additive activities. The very low C–N hydrogenolysis activities of PtMo and PdMo are particularly interesting since the sulfided Pt and Pd metals per se showed (especially Pt) very high hydrogenolysis activities (Fig. 3A). Thus, interaction of these third-row metals with Mo greatly depresses their intrinsic hydrogenolytic activity. Conversely, the promoting effect of these metals upon the hydrogenolysis activity of the corresponding MMo catalysts is very weak, and for Pd the lowest among all transition metals examined (Fig. 3B). The results obtained indicate that third-row metals, and in particular Pt and Pd, interact chemically with Mo in a manner which has a strong negative or "antagonistic" effect upon C–N hydrogenolysis activity. Since this effect is opposite to that of typical promoters (e.g., Ni, Rh, and Co; see above), Pt, Pd, and to a lesser extent Cr, can be described as antagonists of Mo in MMo catalyst systems, as far as C–N hydrogenolysis activity is concerned. Additional characterization of the sulfided PtMo and PdMo catalysts would be necessary in order to determine if their low activities could also be the result of a low degree of dispersion.

Ring Hydrogenation

The ring hydrogenation activities (k_2) of the M/Al_2O_3 and MMo/Al_2O_3 catalysts are plotted in Figs. 5A and 5B, respectively. In general, the hydrogenation activities of both types of catalysts, as determined in the present C–N hydrogenolysis selectivity study, are much lower than those previously observed in a C–O hydrogenolysis selectivity study of the same catalysts, under identical experimental conditions (*1*). As mentioned above, this can be attributed to the stronger inhibition effect of the *N*-heterocyclic feed component (indole) used in the present HDN work than that of the O-containing feed component (diphenyl ether) used in the previous HDO study. Comparison of Figs. 5A with 5B indicates that some of the MMo catalysts (M = Fe, Co, Ni, Rh) possess higher whereas others (M = Re, Ir, Pt, Pd) exhibit lower hydrogenation activities than those of the corresponding M catalysts. Further, comparison of Figs. 5B and 3B reveals considerable similarities in the general patterns of C–N hydrogenolysis and ring hydrogenation activities of the MMo catalysts, as a function of the periodic table position of the M promoter. Thus, for first-row Group VIII metals, both types of activities are in the order Ni > Co > Fe. Likewise, for second-row metals (Ru, Rh, and Pd), a sharp maximum for both types of activities is reached with Rh as promoter. Finally, third-row metals (Re, Ir, Pt) show a maximum in C–N hydrogenolysis activity for Ir as promoter, and a similar but less pronounced pattern is

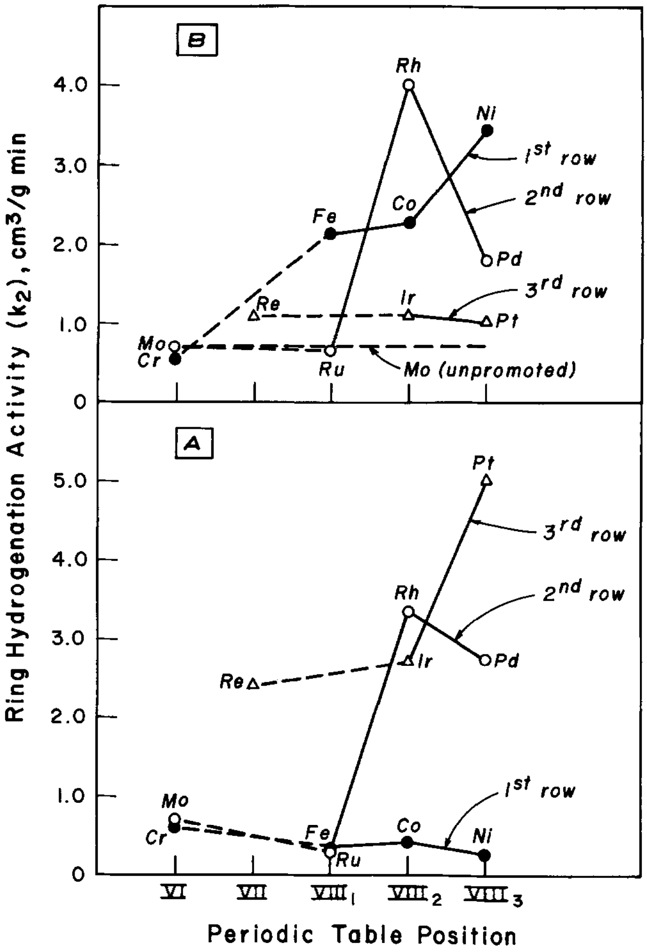

FIG. 5. Variation in ring hydrogenation activity (k_2) for sulfided (A) M/Al_2O_3 and (B) MMo/Al_2O_3 catalysts as a function of the periodic table position of M.

observed for ring hydrogenation activity. Similarities (and some small differences) in the general patterns for C–N hydrogenolysis and ring hydrogenation activities are also observed for the M/Al_2O_3 catalysts (compare Figs. 5A and 3A). In contrast to the above results, major differences in activity patterns were previously observed for C–O hydrogenolysis vs ring hydrogenation (*1*) and for C–S hydrogenolysis vs hydrogenation (*22*). These differences were interpreted as indicating that structurally different active sites are operative for C–O (or C–S) bond hydrogenolysis and ring hydrogenation in sulfided MMo catalysts. On the other hand, the above-described similarities in activity patterns found in the present study would indicate that the active sites for C–N hydrogenolysis and ring hydrogenation in MMo catalysts are of the same or similar type. This is in agreement with previous comparative kinetic studies of HDN vs ring hydrogenation reactions, using sulfided CoMo catalysts on different supports (*16*). Recent stereochemical studies have shown that, in the presence of sulfided NiMo and CoMo catalysts, polycyclic arenes, e.g., naphthalene, phenanthrene, and anthracene, undergo strongly preferential *trans*-hydrogenation at their bridge positions (*26, 27*). Even stronger preference for *trans*-hydrogenation was observed with

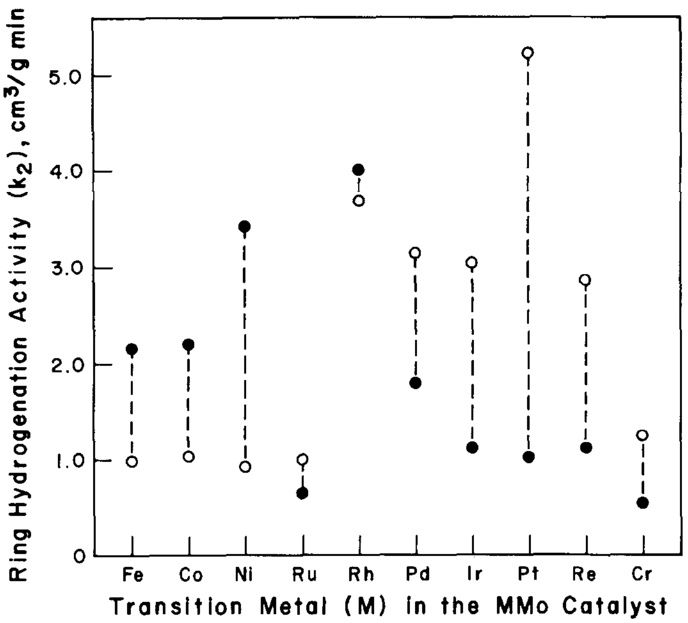

FIG. 6. Differences (---) between actual (●) and additive (○) ring hydrogenation activities of sulfided MMo/Al_2O_3 catalysts.

condensed N-containing compounds, e.g., quinoline and 5,6-benzoquinoline, as feeds (*26, 27*). These results were rationalized by assuming the formation of multiple vacancy ("valley"-like) sites on the catalyst surface, formed by removal of an edge S^{2-} ion plus one or more S^{2-} ions at adjacent basal plane positions. Edgewise penetration and adsorption of the polycyclic arene or *N*-heterocyclic compound in such "valley"-like vacancy sites should be accompanied by hydrogen addition from both sides of the vertically oriented, planar aromatic substrate, leading to *trans*-hydrogenation at bridge positions. For quinoline, which shows a strong tendency for edgewise adsorption via the N atom, the *trans*-hydrogenation is highly stereoselective (*26*) and is accompanied (at 300–370°C) by C–N hydrogenolysis reactions of the hydrogenated N-containing ring (*7*). In the present study, the above-indicated similarity in activity patterns for ring hydrogenation of NP and C–N hydrogenolysis of IN may be due to adsorption and ensuing reactions of both feeds at the same type of multiple vacancy sites. However, the concentration of such sites in different MMo catalysts may change as a function of the M type. The previously observed differences in the activity patterns of MMo catalysts for ring hydrogenation of NP and C–O hydrogenolysis of diphenyl ether (DPE) (*1*) may be related to preferential flatwise adsorption of this aromatic ether on the catalyst surface, due to a lack of favorable geometric factors for its edgewise intrasorption in multiple vacancy sites.

Figure 6 provides a comparison of the actual and additive hydrogenation activities of the MMo catalysts. As seen, for most catalysts there is a similarity in the effect of the M component upon ring hydrogenation and C–N hydrogenolysis (compare with Fig. 4). For the first-row metals (Fe, Co, Ni) and Rh the actual hydrogenation activities of the corresponding MMo catalysts are clearly higher than the additive activities, indicating that these metals are good promoters for ring hydrogenation. On the other hand, the actual hydrogenation activities of PdMo, IrMo, PtMo, and ReMo are markedly lower than their calculated additive activities, indicating that Pd, Ir, Pt, and Re, when combined with Mo, have a strong depressing (antagonistic) effect upon the hydrogenation activity of the corresponding composite catalysts. This is especially pronounced in the case of Pt. The remaining catalysts (RuMo and CrMo) show slightly lower actual than additive hydrogenation activities. The observed similarity in the direction and degree of promotional (or antagonistic) effects of the M component upon the activities for ring hydrogenation and C–N hydrogenolysis of the composite MMo catalysts provides further indication that both types of reactions may occur on the same type of active sites.

C–N Hydrogenolysis Selectivities

As discussed above, C–N hydrogenolysis and ring hydrogenation appear to take place on the same type of sites. Selectivity differences between the various MMo catalysts could possibly be due to differences in relative adsorptivity of IN vs NP on catalysts with different promoters. However, since IN is a very weak base (and NP by virtue of its π-electron system could likewise be considered a very weak base), possible changes in the Lewis acidity of MMo catalyst vacancies, resulting from variation in the M promoter, would be expected to have a rather small effect upon relative adsorptivities. It is, therefore, more likely that the large selectivity differences observed reflect actual changes in intrinsic catalytic activity for C–N hydrogenolysis vs ring hydrogenation due to variations in the promoter type.

The actual hydrogenolysis selectivities of the MMo catalysts, as given by the k_1/k_2 ratio (Table 1), provide a measure for the balance of C–N hydrogenolysis vs ring hydrogenation activities of the catalysts. This balance is very important since it is one of the factors determining the rate of the HDN process and the level of hydrogen consumption (*5*, *7*). For further evaluation of this balance, the additive C–N hydrogenolysis selectivities of the MMo catalysts were also calculated, using the values for additive hydrogenolysis and hydrogenation activities given in Figs. 4 and 6, respectively. The calculated additive selectivities are compared with the actual C–N hydrogenolysis selectivities of the catalysts in Fig. 7. As seen, with Group VIII first-row metals (Fe, Co, Ni) and two of the second-row metals (Rh, Pd) as promoters, there are essentially no differences or only minor differences between the actual and the additive selectivities of the corresponding MMo

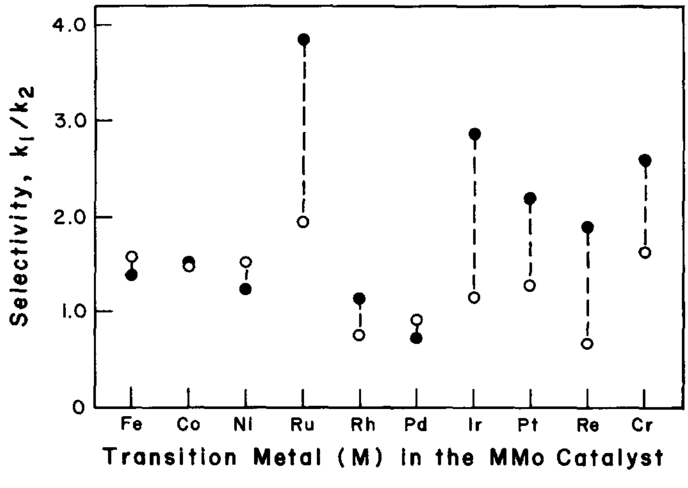

FIG. 7. Differences (---) between actual (●) and additive (○) selectivities of sulfided MMo/Al_2O_3 catalysts.

catalysts. On the other hand, with Ru (second-row) and third-row metals (Ir, Pt, Re) as promoters, the corresponding MMo catalysts show markedly higher actual than additive selectivities. Among the latter group of catalysts, the RuMo, IrMo, and PtMo (and CrMo; Group VI) also show the highest actual selectivities among all MMo catalysts studied.

The observed order of actual C–N hydrogenolysis selectivities of the MMo catalysts is

$$\text{RuMo} > \text{IrMo} > \text{CrMo} > \text{PtMo} > \text{CoMo} > \text{FeMo} > \text{NiMo} > \text{ReMo} > \text{RhMo} > \text{PdMo}.$$

Among the most selective catalysts, RuMo, IrMo, and PtMo are characterized by moderate C–N hydrogenolysis activity, which is favorably balanced by very low hydrogenation activity. HDN reactions with such catalysts could be expected to proceed with lower hydrogen consumption than that with NiMo, CoMo, or RhMo. Further work on the optimization of Mo-based catalysts with promoters, e.g., Ru, Ir, and Pt (and possibly Cr), alone or in combination with promoters having higher C–N hydrogenolysis activity, in particular Ni would be essential for development of improved sulfided catalysts for hydroprocessing of heavy oils.

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