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Catalytic Functionalities of Supported Sulfides

IV. C–O Hydrogenolysis Selectivity as a Function of Promoter Type

JOSEPH SHABTAI,[1] N. K. NAG,[2] AND F. E. MASSOTH[1]

Department of Fuels Engineering, University of Utah, Salt Lake City, Utah 84112

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Two series of γ-Al_2O_3-supported transition metal-containing catalysts were prepared and their functional selectivities for C–O hydrogenolysis determined. These were (a) 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) 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–O bond hydrogenolysis of diphenyl ether (k_1) and ring hydrogenation of naphthalene (k_2) at 350°C and 137 atm H_2 pressure, were determined for the above catalysts in the sulfided form. It was found that the C–O hydrogenolysis selectivity of MMo catalysts, as expressed by the k_1/k_2 ratio was in the order (Mo omitted): Ru > Co > Cr > Ir > Re > Pd > Fe > Rh > Pt > Ni. MMo catalysts showed generally much higher selectivities compared to the corresponding M catalysts. Lowest selectivities among the latter, due to very high ring hydrogenation activities, were exhibited by the sulfided Pd, Pt, Ir, Re, and Rh catalysts. Comparison of the actual C–O hydrogenolysis activities of MMo catalysts with calculated additive activities for these catalysts, assuming independent activities of the M and Mo components, reveals that Ru, Co, and Rh cause a strong promotion, while Pd, Pt, and Re cause a decrease in the hydrogenolysis activity of the corresponding MMo catalysts. Similar comparison of actual and additive ring hydrogenation activities shows that Ni and Rh have a significant promoting effect, while Pd, Ir, Pt, and Re exert a strong depressing effect upon the hydrogenation activities of the MMo catalysts. The observed major differences in the direction and magnitude of the catalytic activities for C–O hydrogenolysis and ring hydrogenation argue strongly for different active sites for these two types of reactions.

INTRODUCTION

Recent hydrodeoxygenation (HDO) studies have demonstrated that conventional sulfided CoMo and NiMo catalysts are not fully effective for exhaustive oxygen removal from coal- and peat-derived liquids, except under drastic operating conditions (*1, 2*). Model compound studies have also indicated that HDO reactions with such catalysts are not sufficiently selective, viz., oxygen removal is accompanied in many cases by side reactions, e.g., excessive hydrogenation of aromatic rings prior to the C–O hydrogenolysis step; and considerable polymerization of reactive intermediates leading to coke formation (*1, 3–13*). Hydrotreatment studies of a coal-derived middle-heavy SRC-II distillate, using new ^{13}C NMR analytical techniques, have shown that HDO of this feed between 260–370°C with sulfided CoMo and NiW as catalysts, is accompanied by extensive ring hydrogenation and dealkylation reactions (*14*). Further, it was indicated that the SRC-II distillate contains a variety of sterically hindered phenols and diaryl ethers, in particular dibenzofuran derivatives, which show considerable resistance to HDO even under drastic processing conditions (*14*). This is in agreement with a recent kinetic study which showed that HDO of dibenzofuran (DBF) is markedly slower than the HDS of dibenzothiophene and that, unlike the latter reaction, it predominantly proceeds with hydrogenation of at least one of the aromatic rings in DBF prior to the heteroatom

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[1] To either of whom correspondence should be addressed.

[2] Present address: Filtrol Division, Harshaw-Filtrol, Los Angeles, CA 90023.

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removal step (*1*). A low selectivity for heteroatom removal vs ring hydrogenation has been observed also in recent kinetic studies of the HDN reactions of 3,4-, 5,6-, and 7,8-benzoquinolines, *N*-ethylcarbazole, and 1,10-phenanthroline (*15*). In view of these findings, preparation of sulfided catalysts with augmented C–O and C–N hydrogenolysis selectivity could be considered as highly desirable. In previous parts of this series we reported results on the effect of the support and additives upon the different catalytic functionalities of sulfided catalysts (*16–18*). Another factor which could be anticipated to influence to a major extent these functionalities and, in particular, the balance of hydrogenolysis vs ring hydrogenation activities, is the nature of the promoter and the method of its incorporation in the catalyst. Recent systematic studies of the HDS activities of groups VI–VIII bulk transition metal sulfides have shown that first-row metal sulfides, e.g., Cr_2S_3, MnS, FeS, Co_9S_8, and Ni_3S_2, are much less active for C–S hydrogenolysis of dibenzothiophene in comparison with second- and third-row metal sulfides, e.g., those of Ru, Rh, Pd, Re, Os, Ir, and Pt (*19*). Among group VIII metals, the bulk sulfides of Ru, Os, Ir, and Rh were found to be markedly more active than those of Pd and Pt. A similar order of HDS activities has been recently reported for carbon-supported transition metal sulfides (*20*). It has been found earlier, however, that for some Al_2O_3-supported sulfided group VIII metals, the activities for HDS of thiophene were in a somewhat different order, i.e., Pt > Pd > Ru > Co > Ni (*21*).

In view of the above studies, it was of obvious interest to investigate the activities of second- and third-row transition metals as possible promoters in supported, Mo-based sulfided catalysts. The present investigation reports a systematic study of the C–O bond hydrogenolysis 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 determine and clarify the role of these transition metals as potential promoters, a series of the corresponding sulfided M/γ-Al_2O_3 catalysts, without Mo, were also prepared and investigated. The C–O hydrogenolysis selectivity of all catalysts was determined by an appropriately designed method for kinetic differentiation between their C–O hydrogenolysis and ring hydrogenation activities (see below). The method involves determination of the rate constants of two simultaneous, competing reactions, i.e., hydrogenolysis of diphenyl ether and hydrogenation of naphthalene, in the presence of each catalyst under identical hydroprocessing conditions.

EXPERIMENTAL

A. Catalysts

MMo/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 sequential 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 a weighed sample was impregnated by pore volume filling using an aqueous solution of $(NH_4)_6Mo_7O_{24}$. The impregnated sample was oven-dried at 120°C for 16 h and then impregnated with a salt solution containing the transition metal promoter (M). The resulting, sequentially impregnated catalyst was dried at 120°C overnight and then calcined in air at 540°C for 16 h. The salts used in the second impregnation step were Cr, Fe, Co, Ni, Rh, and Pd nitrates, Ru nitrosyl nitrate, Ir chloride, ammonium chloroplatinate, and ammonium perrhenate. All catalysts contained 25 mmol of M and 77 mmol of Mo per 100 g of Al_2O_3. M/Al_2O_3 catalysts, containing 25 mmol M/100 g Al_2O_3, were prepared by single-step incipient wetness impregnation of the support with solutions of the above salts, followed by drying at 120°C and calcination at 540°C. Prior to their use, both types of catalysts were presulfided in a flow reactor at 480°C for 2 h under a stream of 10% H_2S–90% H_2 (40 cm^3/min). The sulfur content of the sulfided M/Al_2O_3 catalysts was determined by high-temperature combustion, using a LECO SC-132 sulfur analyzer. Literature data indicate that the volatility of oxide forms of the studied metals is sufficiently low as to avoid losses during calcination up to 540°C (*22*). To confirm this point, samples of freshly calcined (24 h at 540°C) Ru/Al_2O_3 and Pd/Al_2O_3 catalysts, which probably form the most volatile oxides among the examined metals, were analyzed by inductively coupled plasma spectrometry (ICPS). The Ru and Pd contents found for the calcined catalysts were 2.34 and 2.47 wt%, respectively, almost identical within the accuracy of the analytical method with the metal amounts introduced by impregnation in the catalysts, i.e., 2.44 and 2.57 wt%, respectively.

B. Experimental Procedure

Catalysts were tested 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) diphenyl ether (DPE) and 99+% pure (Aldrich) naphthalene (NP) in *n*-pentadecane (Humphrey Chemicals; purity, 99%) was charged to the autoclave, and 200 mg of freshly sulfided catalyst was placed inside the magnedash catalyst cage. To prevent oxidation of the sulfided catalyst, the latter was transferred to the autoclave under a small amount of the pure *n*-pentadecane solvent. The autoclave was purged consecutively with nitrogen and hydrogen, pressurized to ca. 70 atm and quickly heated to 350°C. The pressure was then adjusted to 137 atm, a first sample (corresponding to zero time) taken, and the stirring started. Samples (0.3 cm^3) were withdrawn at intervals of 5 min for the first 20 min and every 10 min afterwards for a total period of 1 h, and analyzed by gas chromatography on a 4 m × 0.3 cm o.d. stainless steel column packed with 10% OV-17 on Chromosorb W-HP, at a temperature programmed from 100–250°C at a rate of 10°C/min.

C. Kinetic Differentiation Method

The above kinetic runs were used to determine the rate constants for two simultaneous, competing reactions, i.e., C–O hydrogenolysis of DPE (k_1) and ring hydrogenation of NP (k_2) in the presence of the various catalysts, as shown in Fig. 1. Hydrogenolysis of DPE (reaction A) yields benzene and phenol, which undergoes fast subsequent hydrogenolysis to yield also benzene. A small amount of cyclohexane is formed by hydrogenation of phenol to cyclohexanol, followed by fast C–O hydrogenolysis of the latter (*1*). Under the conditions of the kinetics runs (350°C, 137 atm) only benzene accompanied by very small amounts of cyclohexane is formed by the above pathway, and very little direct hydrogenation of benzene to cyclohexane is found (*1*). As indicated in Fig. 1, k_1 is the rate constant for the overall (Ar)C–O hydrogenolysis reaction. Hydrogenation of NP (reaction B) yields tetralin, which undergoes subsequent hydrogenation to decalin to a low extent (in most cases <25%). The k_2 rate constant represents the hydrogenation of a conjugated ring in the NP system, and not the hydrogenation of the residual, viz., single (nonconjugated) aromatic ring. The C–O hydrogenolysis selectivity of the catalysts is provided by the k_1/k_2 ratio.

The analysis of the reaction data was

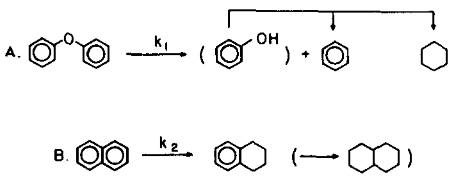

FIG. 1. Scheme for kinetic differentiation of (Ar)C–O hydrogenolysis vs ring hydrogenation.

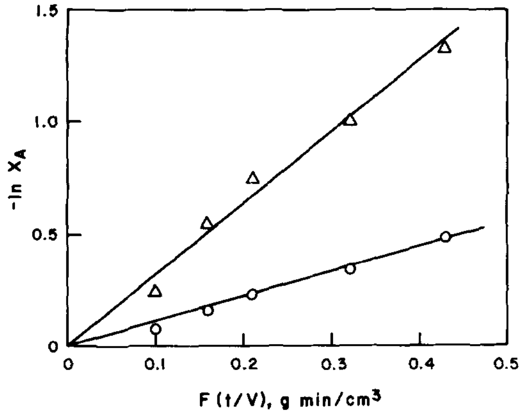

FIG. 2. First-order activity correlation for the sulfided NiMo/Al_2O_3 catalyst. Symbols: (○) C–O hydrogenolysis, (△) ring hydrogenation.

made on the basis of a first-order reaction order in reactant concentration, taking account of zero reaction time after heat up to temperature and depletion of solution volume from sample withdrawals. The integrated equation for a batch reactor is given by

$$-\ln X_A = k_A W f(t/V) \qquad (1)$$

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

$$f(t/V) = \sum_{i=1}^{n} \frac{t_i - t_{i-1}}{V_{i-1}} \qquad (2)$$

In these equations, X_A is the mole fraction of reactant, k_A is the first-order rate constant, W is the catalyst weight, n is the number of samples taken, t 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 heat up to reaction temperature before reaction time is started, and is determined by extrapolating a plot of $-\ln X_A$ versus real time to zero conversion. An example of the data fit to Eq. (1) is shown in Fig. 2 for the NiMo/Al_2O_3 catalyst. Based on duplicate runs with several of the catalysts, the relative error in k values was 4% for C–O hydrogenolysis and 9% for hydrogenation.

RESULTS

A. C–O Bond Hydrogenolysis Selectivity of Sulfided MMo/Al_2O_3 Catalysts

Results on the activities and C–O hydrogenolysis selectivities of the sulfided MMo/Al_2O_3 catalysts are summarized in Table 1. The k_1 and k_2 values reflect the C–O hydrogenolysis and ring hydrogenation activities, respectively, while the C–O hydrogenolysis selectivity is given by the k_1/k_2 ratio. As seen, highest C–O hydrogenolysis activity is shown by the CoMo, RhMo, and RuMo catalysts, in that order. The CoMo catalyst, however, shows also considerable ring hydrogenation activity, resulting in a moderately high C–O hydrogenolysis selectivity of 1.90. Higher selectivity (2.57) is shown by the RuMo catalyst which exhibits relatively low ring hydrogenation activity. A CoMo catalyst containing a double amount of Co, i.e., 50 mmol/100 g Al_2O_3 (footnote *f*) shows considerably lower C–O hydrogenolysis selectivity (1.35), approximately equal to that of a 3Co8Mo commercial (Ketjen) catalyst. The sulfided RhMo catalyst shows high hydrogenolysis activity, but much higher ring hydrogenation activity, resulting in a low C–O hydrogenolysis selectivity (0.72). The sulfided PdMo catalyst shows low activities and a selectivity (0.99) which is only slightly higher than that of the nonpromoted, sulfided Mo/Al_2O_3 catalyst (footnote *e*). Low hydrogenolysis activity and selectivity are shown also by the PtMo catalyst. Lowest selectivity (0.36) is shown by the sulfided NiMo catalyst, which exhibits low hydrogenolysis activity combined with relatively high ring hydrogenation activity.

The sulfided IrMo catalyst shows moderate activities which are clearly higher than those of the nonpromoted Mo catalyst. Furthermore, its selectivity (1.17) is slightly higher than that of the latter catalyst (0.78). The PtMo catalyst shows very low selectivity (0.57), while the ReMo catalyst shows activities comparable to those of the nonpromoted Mo catalyst, but a slightly higher

TABLE 1

Catalytic Activities and C-O Hydrogenolysis Selectivities of Supported MMo Catalysts as a Function of the Type of M (Transition Metal) Promoter[a,b]

Catalyst[c]	Promoter group (row)	k_1 (cm^3/g min), C-O hydrogenolysis	k_2 (cm^3/g min), ring hydrogenation	Selectivity, k_1/k_2
FeMo	$VIII_1$ (1)	6.17	6.88	0.90
CoMo	$VIII_2$ (1)	23.02	12.10	1.90
NiMo[d]	$VIII_3$ (1)	5.42	15.00	0.36
RuMo[d]	$VIII_1$ (2)	9.64	3.75	2.57
RhMo	$VIII_2$ (2)	16.25	22.50	0.72
PdMo[d]	$VIII_3$ (2)	3.30	3.35	0.99
IrMo	$VIII_2$ (3)	7.30	6.25	1.17
PtMo	$VIII_3$ (3)	3.13	5.50	0.57
ReMo	VII (3)	4.50	4.12	1.09
CrMo	VI (1)	3.75	3.00	1.25
−Mo[e]	VI (2)	3.57	4.58	0.78
CoMo[f]		15.50	11.50	1.35
3Co8Mo (Ketjen)		11.50	8.75	1.31

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

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

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

[d] Average of duplicate runs.

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

[f] Contains 50 mmol of Co and 77 mmol of Mo/100 g Al_2O_3.

selectivity (1.09). It is also found that the sulfided CrMo catalyst shows a selectivity (1.25) comparable to that of the commercial (Ketjen) catalyst, although the activities of the former are much lower.

B. C-O Bond Hydrogenolysis Selectivity of Sulfided M/Al_2O_3 Catalysts

Results on the activities and C-O hydrogenolysis selectivities of sulfided M/Al_2O_3 catalysts, where M = Fe, Co, Ni, Ru, Rh, Pd, Ir, Pt, Re, or Cr, are summarized in Table 2. All the catalysts examined except Ni, show much lower C-O hydrogenolysis selectivities in comparison with the corresponding MMo/Al_2O_3 catalysts (compare with Table 1). Among the sulfided M catalysts Fe, Ru, and Cr show highest selectivities (0.77, 0.76, and 0.57, respectively) due to their low ring hydrogenation activities. The selectivities of the Fe and Ru catalysts are approximately equal to that of the sulfided Mo catalyst (0.78). The sulfided Co and Ni catalysts show lower selectivities, i.e., 0.34 and 0.41, respectively, reflecting their very low C-O hydrogenolysis activities in the absence of Mo. The sulfided Pd, Rh, and Re show highest C-O hydrogenolysis activities among the catalysts examined. However, these catalysts exhibit much higher ring hydrogenation activities resulting in very low C-O hydrogenolysis selectivities (0.14 for Pd, 0.27 for Rh, and 0.18 for Re). It is also found that Pd, Ir, Pt, and Re, in the sulfided form, possess relatively much higher hydrogenation activities compared to the corresponding MMo catalysts. In order to confirm that the M/Al_2O_3 catalysts were in the sulfided state, they were analyzed for sulfur (see under Experimental). Table 3 summarizes the sulfur contents and S/M atomic ratios found. The atomic ratios for some of the catalysts, e.g., Rh and Pd, were somewhat higher than

TABLE 2

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

Catalyst, M =	Metal (M) group (row)	k_1 (cm^3/g min), C–O hydrogenolysis	k_2 (cm^3/g min), ring hydrogenation	Selectivity, k_1/k_2
Fe	$VIII_1$ (1)	1.92	2.50	0.77
Co	$VIII_2$ (1)	2.14	6.33	0.34
Ni	$VIII_3$ (1)	1.78	4.32	0.41
Ru[d]	$VIII_1$ (2)	2.37	3.13	0.76
Rh	$VIII_2$ (2)	4.17	15.60	0.27
Pd	$VIII_3$ (2)	4.30	30.47	0.14
Ir	$VIII_2$ (3)	2.94	18.75	0.16
Pt	$VIII_3$ (3)	2.08	13.50	0.15
Re	VII (3)	3.75	20.83	0.18
Cr	VI (1)	1.00	1.75	0.57
Mo	VI (2)	3.57	4.58	0.78

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

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

[c] 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.

[d] Average of duplicate runs.

those reported for stable bulk sulfides (*19*). This was possibly due to the presence of some adsorbed H_2S.

DISCUSSION

C–O Bond Hydrogenolysis

Figure 3A shows the change in C–O hydrogenolysis activity of the sulfided M/Al_2O_3 catalysts as a function of the periodic table position of the transition metal. As seen, the first-row group VIII metals and Cr (group VI) show the lowest C–O hydrogenolysis activity. This is similar to the results reported for C–S hydrogenolysis activity of bulk sulfides of group VI–VIII metals (*19*), and of the same metal sulfides supported on carbon (*20*). However, the order of carbon–heteroatom hydrogenolysis activities for first-row group VIII metals is somewhat different for the bulk vs supported sulfides, i.e., Co > Ni > Fe for C–S hydrogenolysis with bulk sulfides (*19*) as compared with Co > Fe > Ni for C–O hydrogenolysis with the Al_2O_3-supported sulfides (Fig. 3A). Second-row group VIII metals, i.e., Ru, Rh, and Pd, show higher C–O hydrogenolysis activities as compared with the first-row metals of the same group, and the order of activities is Pd > Rh > Ru. This order is different from that found for C–S hydrogenolysis with bulk sulfides, i.e., Ru > Rh > Pd (*19*), or with carbon-supported sulfides, i.e, Rh > Ru > Pd (*20*). Among the third-row sulfided metals examined, the order of C–O hydrogenolysis ac-

TABLE 3

Sulfur Content and S/M Ratios of Sulfided M/Al_2O_3 Catalysts

Catalyst, M =	Sulfur (wt%)	S/M atomic ratio[a]
Fe	1.38	1.3
Co	1.32	1.2
Ni	1.19	1.0
Ru	2.01	2.1
Rh	1.75	1.7
Pd	1.45	1.3
Re	2.05	2.1
Ir	1.03	0.8
Pt	1.00	0.8
Cr	1.54	1.5

[a] The S/M atomic ratios are corrected for the S content of the sulfided Al_2O_3 (Ketjen) support which was found to be 0.4% wt.

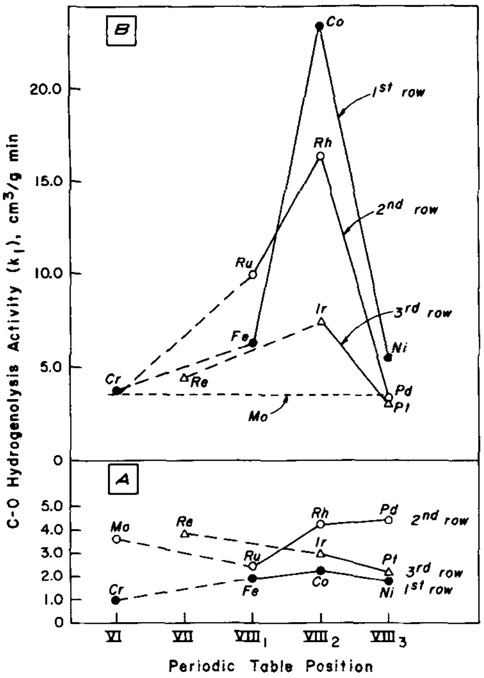

FIG. 3. Variation in C–O hydrogenolysis activity (k_I) for sulfided (A) M/Al_2O_3 and (B) MMo/Al_2O_3 catalysts as a function of the periodic table position of M.

tivity is Re > Ir > Pt. This order is different from that found for C–S hydrogenolysis with bulk and carbon-supported sulfides, i.e., Ir > Re > Pt. The significant differences between the present C–O hydrogenolysis results and those reported for C–S hydrogenolysis argue for the possibility of different sites for these reactions. However, other factors, e.g., bulk vs supported sulfides, alumina vs carbon support, nature of precursor salts, level of metal loading, and reaction conditions, could also contribute to these differences.

Figure 3B shows the change in C–O hydrogenolysis activity of the sulfided MMo/Al_2O_3 catalysts as a function of the periodic table position of the M promoter. All MMo catalysts exhibit higher hydrogenolysis activity than the nonpromoted Mo catalyst, except PdMo and CrMo which show about the same activity as the latter, and PtMo which shows slightly lower activity. The first-row metals, Fe, Co, and Ni, which exhibit the lowest hydrogenolysis activity in the absence of Mo, show a strong promoting effect (especially Co) upon C–O hydrogenolysis activity when combined with Mo. This is seen by comparing the activity of the nonpromoted Mo catalyst (k_I = 3.57) with those of CoMo (k_I = 23.0), FeMo (k_I = 6.17), and NiMo (k_I = 5.42). Likewise, Ru and Rh have a strong promoting effect, as evidenced by the high k_I values found for the RuMo and RhMo catalysts (9.64 and 16.25, respectively). Among the third-row metals only Ir shows a major promoting effect as evidenced by the moderate increase in the hydrogenolysis activity of the IrMo catalyst (k_I = 7.30) relative to that of the nonpromoted Mo. Other metals examined, e.g., Pd and Pt, show no promoting effect on the hydrogenolysis activity of the corresponding MMo catalysts. The low hydrogenolysis activity of the PdMo catalyst is noteworthy since the sulfided Pd metal per se showed the highest C–O hydrogenolysis activity among all metals examined (Table 2). Further, the PdMo is the only catalyst possessing lower C–O hydrogenolysis activity than that of the metal promoter without Mo present. Among group VIII promoters, the $VIII_2$ metals Co, Rh, and Ir show the highest promoting effect among metals in each row.

Although catalyst activities were compared above in terms of a promotional effect of the added metal (M) on the Mo catalyst, it should be realized that the M/Al_2O_3 catalysts themselves exhibit appreciable C–O hydrogenolysis activity (Table 2). Therefore, another way to analyze the data on the composite catalysts is to compare their activities with those expected for simple addition of M/Al_2O_3 and Mo/Al_2O_3 activities, i.e., the resultant activities expected if each component acted independently. The additive activities were calculated on the basis of the equimolar concentrations of the M metals in the MMo/Al_2O_3 and M/Al_2O_3 catalysts, and the constant concentration of Mo in the Mo/Al_2O_3 and MMo/Al_2O_3 catalysts (Tables 1 and 2). The slightly different amounts of

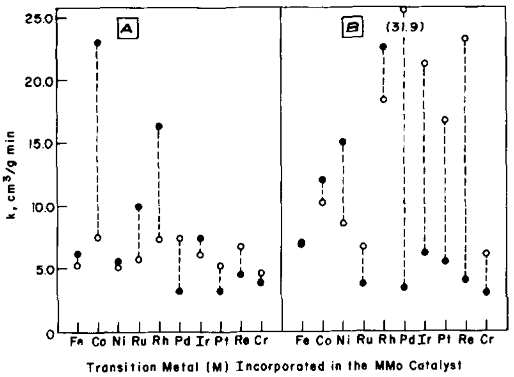

FIG. 4. Differences (–––) between actual (●) and additive (○) activities of sulfided MMo/Al_2O_3 catalysts for (A) C–O hydrogenolysis and (B) ring hydrogenation.

each component in the MMo catalysts were also accounted for in the predicted additive activities. The latter are summarized and compared with the actual C–O hydrogenolysis activities in Fig. 4A. The direction and relative extent of the differences between the actual and additive activities of the examined MMo catalysts are summarized also in Table 4. Three groups of catalysts can be distinguished in Fig. 4A relative to C–O hydrogenolysis: (1) those exhibiting higher, (2) those showing essentially the same, and (3) those having lower activities as compared with the predicted activities. The first group, comprising CoMo, RuMo, and RhMo show a synergistic effect on activity and therefore the metals may be considered as true promoters. The CoMo/Al_2O_3 catalyst has been studied in great detail in the past. The current consensus is that promotion of C–S hydrogenolysis occurs by incorporation of Co at the edges of basic MoS_2 clusters, designated as a "CoMoS" phase (*23*). Only this Co accounts for the promotion, presumably by increasing the intrinsic activity of the active Mo sites rather than increasing the number of active sites. Some of the Co occurs in the alumina phase and some exists as bulk Co_9S_8 (at higher Co levels), both being relatively inactive. It seems reasonable that a similar type of promotion occurs for C–O hydrogenolysis with the RuMo and RhMo catalysts.

The second group of catalysts show only marginal (FeMo, IrMo) or essentially no (Ni, Cr) improvement in C–O hydrogenolysis activity over that of the predicted additive activities. The obvious interpretation is that in these cases the individual components act independently in contributing to the overall activity, although it is possible that some interaction and promotion of the Mo phase by certain M metals could occur, but is counterbalanced by a comparable loss in the activity of the residual M metal. It is noteworthy that the NiMo catalyst failed to show the high promotion observed for the CoMo catalyst, as both catalysts are noted for their enhanced HDS activity (*24*). Apparently, the different promotional effects of Co and Ni for C–O vs C–S hydrogenolysis are related to different types of active sites for these two reactions.

The third group, represented by PdMo, PtMo, and ReMo, show activities approximately equivalent to that of the nonpromoted Mo catalyst and clearly lower than the predicted additive activities. For this

TABLE 4

Direction and Relative Degree of Differences between Actual and Additive Activities and Selectivities of MMo Catalysts

Catalyst, M =	C–O hydrogenolysis[a]	Ring hydrogenation[a]	Selectivity[b]
Fe	0	0	0
Co	↑ ↑ ↑	↑	↑ ↑ ↑
Ni	0	↑	↓
Ru	↑ ↑	↓	↑ ↑ ↑
Rh	↑ ↑	↑	↑
Pd	↓ ↓	↓ ↓ ↓	↑ ↑
Ir	↑	↓ ↓ ↓	↑ ↑
Pt	↓	↓ ↓	↑
Re	↓	↓ ↓ ↓	↑ ↑
Cr	0	↓	↑

[a] Symbols: 0, no difference in activity between actual and additive activities; ↑ (higher) or ↓ (lower), direction of difference; ↑, ↑ ↑, ↑ ↑ ↑ (or ↓, ↓ ↓, ↓ ↓ ↓), relative degree of difference between actual and additive activities.

[b] Differences between actual C–O hydrogenolysis selectivities (Table 1) and additive selectivities calculated from the additive activities of MMo catalysts (Fig. 4).

group of catalysts a loss in activity of the sulfided M component apparently occurs, or, alternatively, there could be a partial loss in both M and Mo activities. A possible explanation for the observed decrease in activity is that the MS_X phase partially covers the active sites of the MoS_2 phase, which could reduce the activity of the latter, and at the same time render the MS_X phase less active through some specific MS_X–MoS_2 interaction. It is noted that the ReMo catalyst is only slightly more active than the Re catalyst, while the PdMo catalyst is actually less active for C–O hydrogenolysis than the Pd catalyst (Fig. 3A and B).

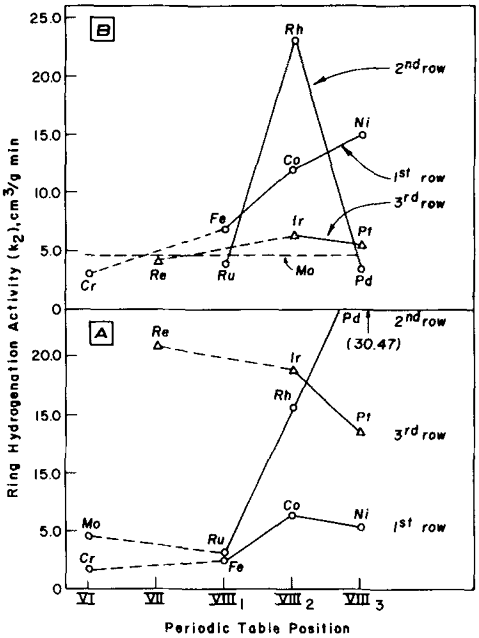

FIG. 5. Variation in ring hydrogenation activity (k_2) for sulfided (A) M/Al_2O_3 and (B) MMo/Al_2O_3 catalysts as a function of the periodic table position of M.

Ring Hydrogenation

The ring hydrogenation activities (k_2) for M/Al_2O_3 and MMo/Al_2O_3 catalysts are plotted in Figs. 5A and B, respectively. Comparison of these figures with the corresponding ones for C–O hydrogenolysis activity (Fig. 3) shows important differences. For example, the observed high hydrogenation activities of sulfided Re, Ir, Pt, and Pd (Fig. 5A), and the higher activity of RhMo as compared with those of CoMo and NiMo (Fig. 5B), are very different from the magnitude and/or order of the C–O hydrogenolysis activities of the same catalysts (Fig. 3). Such radical differences strongly argue for different active sites being responsible for C–O hydrogenolysis and aromatic ring hydrogenation, as has been previously found for C–S hydrogenolysis vs hydrogenation (*25*).

Inspection of Fig. 5A and B shows notable differences between the hydrogenation activities of M and MMo catalysts. Most of the composite (MMo) catalysts (Fig. 5B) are more active than Mo alone, with the exception of Re (same as Mo) and Cr, Ru, and Pd, which show lower activity. Comparison of Fig. 5A and B show that in combination with Mo, hydrogenation activities of the M catalysts (1) increase significantly for first-row transition metals (Fe, Co, Ni) and for Rh, (2) remain with no significant change for Ru and Cr, and (3) decrease strongly for Pd and for third-row metals (Re, Ir, Pt).

Comparison of hydrogenation activities for MMo catalysts with their additive activities are depicted in Fig. 4B. The differences are more pronounced than found for C–O hydrogenolysis, as seen by comparison with Fig. 4A. As in the above discussion of C–O hydrogenolysis activity, effects on hydrogenation activity can be classified in terms of higher, the same, or lower observed activities relative to the predicted additive activities. The first group (CoMo, NiMo, RhMo) show higher activities, and reflect a true promotional effect of the M metals upon catalyst activity for ring hydrogenation, i.e., they exhibit apparent synergism. It has been noted that Co and especially Ni cause an increase in the hydrogenation activity of Mo/Al_2O_3 catalysts, although not as much as in the HDS activity (*26, 27*). The reason for this enhancement has not been explicitly rationalized in terms of changes in active sites. One suggestion is that the M component assists dissociation of H_2 which spills over to the active hydrogenation sites on MoS_2 (*28*) and could thus increase the hydrogenation activity. However, this is not in accord with the observation that some of the sulfided M catalysts that exhibit the highest hydrogenation activity (Pd, Re, Ir) show markedly reduced hydrogenation activity when Mo is present (see Fig. 5A and B). We must conclude that other, as yet unknown factors, are responsible for the hydrogenation promotion. It should also be pointed out that the hydrogenation activities determined are in the presence of DPE, which may have an inhibiting effect via adsorption on hydrogenation sites and, thereby, a bearing on hydrogenation activities.

Only one catalyst (FeMo) is found in the second category which shows no difference in hydrogenation activity as compared with the predicted additive activity. This catalyst was also found to show little difference in actual as compared with the additive C–O hydrogenolysis activity. It thus appears that the FeMo catalyst can be characterized as consisting of essentially separate phases of FeS and MoS_2, each exhibiting its hydrogenolysis and hydrogenation activities independently.

The third category consists of the largest group of MMo catalysts which exhibit lower hydrogenation activities. With the exception of Rh, this includes all second- and third-row metals, as well as Cr. It is notable that Ru is the only metal that showed opposite trends in hydrogenation (lower) and hydrogenolysis (higher), which accounts for its superior selectivity. The drastic lowering in hydrogenation activity of sulfided Pd, Ir, Pt, and Re, when Mo is present, must certainly indicate that the MS_X phase fails to develop in high dispersion over the Mo/Al_2O_3 surface. It is possible that interaction mixed-phase sulfides may be formed, resulting in loss in hydrogenation ability.

Hydrogenolysis Selectivities

As discussed above, the actual C–O hydrogenolysis selectivities of the MMo catalysts (Table 1) directly reflect the balance of their hydrogenolysis vs hydrogenation activities. In order to compare the catalysts' actual and additive selectivities, the latter were also calculated, using the predicted additive hydrogenolysis and hydrogenation activities given in Fig. 4. The additive selectivity values obtained for the MMo catalysts were as follows: M = Fe, 0.77; Co, 0.53; Ni, 0.61; Ru, 0.85; Rh, 0.39; Pd, 0.23; Ir, 0.28; Pt, 0.32; Re, 0.29; Cr, 0.72. The direction and relative degree of differences between the actual and calculated additive selectivities are given in Table 4 (see footnote *b*). The most selective catalysts (Table 1) show generally considerably higher actual selectivities in comparion with the predicted additive selectivities. The order of actual selectivities for these catalysts is

$$\text{RuMo} > \text{CoMo} > \text{CrMo} > \text{IrMo} > \text{ReMo}$$

Thus, the RuMo catalyst is the only one found which has an enhanced C–O hydrogenolysis selectivity over that of the conventional CoMo system. This is different from recent results on the C–N hydrogenolysis selectivities of the same series of MMo catalysts, showing that several catalysts, e.g., RuMo, IrMo, PtMo, and CrMo, are much more selective than CoMo for this type of hydrogenolysis reaction (*29*). A paper describing these results is in preparation.

The interaction of Mo with the examined transition metals, and, consequently, catalyst selectivities, could be expected to depend also on other factors, e.g., concentration level of the promoter, method of catalyst preparation, sulfiding conditions, e.g., temperature and H_2S concentration (*30*), etc. The effect of these factors upon the C–O hydrogenolysis selectivity of sulfided MMo catalysts requires further studies.

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REFERENCES

1. Shukla, Y., Ph.D. thesis, University of Utah, Salt Lake City, Utah, 1985.
2. Ternan, M., and Brown, J. R., *Fuel* **61,** 1110 (1982).
3. Shabtai, J., "Proceedings, International Conference Coal Science, Dusseldorf," p. 502. Verlag Gluckhauf, Essen, 1981.
4. Furimsky, E., *Catal. Rev.-Sci. Eng.* **25,** 421 (1983), and references therein.
5. Haider, G., Ph.D. thesis, University of Utah, Salt Lake City, Utah, 1981.
6. Lee, C. L., and Ollis, D. F., *J. Catal.* **87,** 325 (1984).
7. Krishnamurthy, S., Panvelker, S., and Shah, Y. T., *AIChE J.* **27,** 994 (1981).
8. Odebumni, E. O., and Ollis, D. F., *J. Catal.* **80,** 56, 65, 76 (1983).
9. Nagai, M., and Kabe, T., *J. Catal.* **81,** 440 (1983).
10. Satterfield, C. N., and Yang, S. H., *J. Catal.* **81,** 335 (1983).
11. Lee, C. L., and Ollis, D. F., *J. Catal.* **87,** 332 (1983).
12. Furimsky, E., *Ind. Eng. Chem. Prod. Res. Dev.* **22,** 34 (1983).
13. Weigold, H., *Fuel* **61,** 1021 (1982).
14. Dalling, D. K., Haider, G., Pugmire, R. J., and Shabtai, J., *Fuel* **63,** 525 (1984).
15. Yeh, J. C., Ph.D. thesis, University of Utah, Salt Lake City, Utah, 1985.
16. Muralidhar, G., Massoth, F. E., and Shabtai, J., *J. Catal.* **85,** 44 (1984).
17. Massoth, F. E., Muralidhar, G., and Shabtai, J., *J. Catal.* **85,** 53 (1984).
18. Liu, Y., Massoth, F. E., and Shabtai, J., *Bull. Soc. Chim. Belg.* **93,** 627 (1984).
19. Pecoraro, T. A., and Chianelli, R. R., *J. Catal.* **67,** 430 (1981).
20. Vissers, J. P. R., Groot, C. K., van Oers, E. M., de Beer, W. H. J., and Prins, R., *Bull. Soc. Chim. Belg.* **93,** 813 (1984).
21. Wakabayashi, K., Abe, H., and Orito, Y., *Kogio Kagaku Zasshi* **74,** 1317 (1971).
22. Samsonov, G. V. (Ed.), "The Oxide Handbook." Plenum, New York, 1982.
23. Topsøe, H., Clausen, B. S., Topsøe, N-Y., and Pederson, E., *Ind. Eng. Chem. Fundam.* **25,** 25 (1986).
24. Weisser, D., and Landa, S., "Sulfide Catalysts, Their Properties and Applications." Pergamon, New York, 1973.
25. Massoth, F. E., and Muralidhar, G., *in* "Proceedings, 4th International Conference on Chemistry and Uses of Molybdenum" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 343. Climax Molybdenum Co., Ann Arbor, MI, 1982.
26. Hargreaves, A. E., and Ross, J. R. H., *in* "Proceedings, 6th International Congress on Catalysis," *Chem. Soc. London* **2,** 937 (1977).
27. Massoth, F. E., and Chung, K. S., *in* "Proceedings, 7th International Congress on Catalysis," p. 629. Elsevier, New York, 1981.
28. Delmon, B., *in* "Proceedings, 3rd International Conference on Chemistry and Uses of Molybdenum" (H. F. Barry and P. C. H. Mitchell, Eds.), p. 73. Climax Molybdenum Co., Ann Arbor, MI, 1979.
29. Shabtai, J., Nag, N. K., Balusami, K., Gajjar, B., and Massoth, F. E., *Prepr. Pet. Div. Amer. Chem. Soc.* **31**(1), 231 (1986).
30. Kuo, Y. J., Cocco, R. A., and Tatarchuk, B. J., *Prepr. Pet. Div. Amer. Chem. Soc.* **31**(1), 258 (1986).