Trends for mono-aromatic compounds hydrogenation over sulfided Ni, Mo and NiMo hydrotreating catalysts

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The relative hydrogenation activity in typical hydrotreating conditions of toluene, m-xylene, 1,3,5-trimethylbenzene and 1,2,4,5-tetramethylbenzene was unexpectedly found to decrease over a sulfided NiMo/Al_2O_3 catalyst and to increase over sulfided Ni/Al_2O_3 and Mo/Al_2O_3 catalysts. This change of activity trend is tentatively interpreted by the formation of a mixed NiMoS phase with a different electronic state compared to Ni or Mo sulfide phases. The nature of the aromatic compound influences strongly the magnitude of the promotion effect of Ni on the activity of the Mo in the sulfided NiMo/Al_2O_3 catalyst.

Keywords: aromatic compound, toluene, xylene, trimethylbenzene, tetramethylbenzene, hydrogenation, sulfides, hydrotreating

1. Introduction

The reduction of the aromatics and polyaromatics content in motor fuels (gasoline and diesel) has attracted some attention in the recent years following pending regulations [1–3]. For diesel oil, the hydrogenation of aromatics follows the sequence: tri-aromatics → di-aromatics → mono-aromatics, due to the much faster rate of hydrogenation of the first ring in di- and tri-aromatics compared to the rate of hydrogenation of the last ring [1–8]. It is now well recognized that the hydrogenation of mono-aromatic compounds is the most difficult hydrotreating reaction [5,8].

The most efficient catalysts for aromatic compound hydrogenation in the presence of a high hydrogen sulfide partial pressure are NiMo and NiW sulfide-based hydrotreating catalysts [9–11]. It is also well documented that noble-metal-based catalysts are strongly deactivated in these conditions [2,3]. Although the hydrogenation of various aromatic compounds over sulfided hydrotreating catalysts was studied in the past [1,4,10–19], only a very limited amount of work on the comparison of the reactivity of mono-aromatic compounds over supported sulfides were reported as underlined by recent reviews [1,4]. In contrast, metallic catalysts such as Pt-, Pd-, Ni-based catalysts have received more attention [20–30].

These studies show that the trend for aromatic hydrogenation over pure metallic catalysts with no sulfur in the feed is a decrease of the rate of hydrogenation when the number of substituents on the aromatic ring increases whereas the reverse trend is usually found for sulfided catalysts or noble metal catalysts tested in presence of a sulfur compound [1,15].

From these works, the often reported rule that there is an opposite trend in the relative rates of hydrogenation of alkylbenzene over pure noble metal and metal sulfide catalysts has emerged. This adopted rule may not be fully demonstrated, however, as, noticeably, most of these studies on sulfides or noble metal catalysts were performed in different conditions including mixtures of mono-aromatic compounds versus separate hydrogenation experiments, presence or absence of sulfur in the feed, different types of reactor and different operating conditions and, in particular, reaction temperatures [1,4].

In addition, no comparative studies were reported in the literature on the influence of the nature of mono-aromatic compounds on the hydrogenation activities of sulfided Ni/Al_2O_3, Mo/Al_2O_3 and NiMo/Al_2O_3 catalysts and, therefore, on the promotion effect of Ni on the activity of the Mo catalyst.

In this letter, we address these two questions by comparing the catalytic activity of sulfided Ni, Mo and NiMo supported on alumina catalysts for the separate hydrogenation of toluene, m-xylene, 1,3,5-trimethylbenzene and 1,2,4,5-tetramethylbenzene in typical hydrotreating conditions.

2. Experimental

2.1. Catalysts preparation

The three catalysts tested in this work were prepared by pore filling impregnation of a γ-alumina support (Rhône Poulenc, 263 m^2/g, 0.57 cm^3/g, 1.2 mm extrudates) with aqueous solutions of nickel nitrate (98%, Prolabo) and/or ammonium heptamolybdate (99%, Merck). The wet samples were dried at 120 °C overnight and calcined in air at 500 °C for 3 h. The Ni/Al_2O_3, Mo/Al_2O_3 and NiMo/Al_2O_3 catalysts contained, respectively, 2.6 wt% Ni, 11.4 wt% Mo, and 2.5 wt% Ni and 9.9 wt% Mo, as measured by X-ray fluorescence.

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Table 1
Hydrocarbons, H_2S and H_2 partial pressures.

Aromatic compound	F at LHSV = 1 h^{-1} ($\times 10^{-3}$ mol/h)	Aro (MPa)	CC6 (MPa)	Butane (MPa)	H_2S (MPa)	H_2 (MPa)	Corr. fac.
Toluene	34.3	0.192	1.85	0.042	0.042	3.96	1.0
m-xylene	29.8	0.168	1.86	0.042	0.042	3.98	1.14
1,3,5-trimethylbenzene	26.3	0.149	1.87	0.042	0.042	3.98	1.28
1,2,4,5-tetramethylbenzene	23.6	0.134	1.88	0.043	0.043	3.99	1.43

2.2. Catalytic tests

The catalytic tests were performed in a continuous-flow, high-pressure, fixed-bed reactor using 40 cm^3 of catalyst, i.e., 25.6, 30 and 30.3 g, respectively, for the Ni, Mo and NiMo catalysts. Prior to catalytic testing, the catalysts were sulfided *in situ* using a feed containing 2 wt% dimethyldisulfide (99%, Aldrich) in cyclohexane (99%, Prolabo) at 6 MPa, with liquid hourly space velocity (LHSV) of 2 h^{-1}, H_2/HC = 350 l/l (STP) at 350 °C during 2 h.

After sulfiding, the operating conditions used for the catalytic hydrogenation were a total pressure of 6 MPa, a reaction temperature chosen in the range 300–400 °C, a LHSV chosen in the range 0.25–2 h^{-1} and a ratio H_2/HC = 450 l/l (STP). The liquid feeds were composed of 10 wt% of aromatic compound, 2 wt% of thiophene and 88 wt% of cyclohexane. The mono-aromatic compounds used in this work were toluene (99%, Prolabo), m-xylene (99%, Prolabo), 1,3,5-trimethylbenzene (98%, Aldrich) and 1,2,4,5-tetramethylbenzene (99%, Fluka).

The liquid products of the reactions were analyzed by gas chromatography using a 50 m CPsil5 CB column (film thickness 1.2 μm, internal diameter 0.32 mm) and a flame ionization detector. Temperature programming of the chromatograph was 40 °C for 10 min followed by a temperature increase to 280 °C at 5 °C/min.

The hydrogenation of aromatic compounds into saturated products was measured in a steady state reached generally after 4 h on stream. The conversion is defined by the following formula:

$$X_{\mathrm{HYD}} = \frac{C_0 - C}{C_0}, \tag{1}$$

where C and C_0 are the aromatic compound steady-state concentration and initial concentration, respectively. First-order rates of reaction were computed in mol reactant/mol metal (Ni, Mo or Ni + Mo)/h using the following formula:

$$r_{\mathrm{m}} = -\frac{F}{N}\ln(1 - H_{\mathrm{HYD}}), \tag{2}$$

with F the aromatic compound molar flow rate ($\times 10^{-3}$ mol/h) and N the amount of metal(s) loaded into the reactor in mol of metal(s).

The first-order rates of hydrogenation were then corrected from the variation of the hydrogen and aromatic compound partial pressures induced by their different molar weight and by the thiophene decomposition reaction, as indicated in table 1. The variation in H_2S partial pressure was considered not significant. The correction was made assuming a first order of reaction relatively to H_2 and to the aromatic reactant [10,11,31]. The rates of aromatic hydrogenation reported in this work are therefore corrected relatively to the partial pressures of the toluene hydrogenation experiments using the following formula:

$$r_{\mathrm{mc}} = \frac{P_{\mathrm{tol}} P_{\mathrm{H_2\,tol}}}{P_{\mathrm{aro}} P_{\mathrm{H_2\,aro}}} r_{\mathrm{m}}. \tag{3}$$

The molar flow rates and the values of the correction factors are reported in table 1.

In order to compare the activity of the NiMo catalyst with the activities of the Ni and Mo catalysts, a promotion factor for the hydrogenation activity was defined as

$$q = \frac{r_{\mathrm{mc}}(\mathrm{NiMo})}{\alpha r_{\mathrm{mc}}(\mathrm{Ni}) + (1-\alpha) r_{\mathrm{mc}}(\mathrm{Mo})}, \tag{4}$$

with α the molar fraction of Ni in the NiMo catalyst:

$$\alpha = \frac{\mathrm{Ni}}{\mathrm{Ni} + \mathrm{Mo}}. \tag{5}$$

3. Results and discussion

The activities of the sulfided Ni/Al_2O_3, Mo/Al_2O_3 and $NiMo/Al_2O_3$ catalysts for the hydrogenation of toluene, m-xylene, 1,3,5-trimethylbenzene and 1,2,4,5-tetramethylbenzene are reported in table 2. For the $NiMo/Al_2O_3$ catalyst at 350 °C, the results show a decrease of activity when the number of methyl groups on the benzene ring increases. In order to make sure that the results at 350 °C were not influenced by thermodynamic limitations, the hydrogenation experiments on the NiMo catalyst were repeated at 300 °C. From table 2 it is clearly apparent that the same trend is found.

While these similar trends suggest that there is no major influence of thermodynamic limitations, it was felt that further clarification was needed. In this respect, calculations of the percentage of hydrogenated product at thermodynamic equilibrium were made using the formula

$$X_{\mathrm{thermo}} = \frac{Y_{\mathrm{N}}}{Y_{\mathrm{N}} + Y_{\mathrm{A}}} \times 100 = \frac{K_{\mathrm{a}} P_{\mathrm{H_2}}^{n}}{1 + K_{\mathrm{a}} P_{\mathrm{H_2}}^{n}} \times 100, \tag{6}$$

with Y_{N} and Y_{A} the mole fractions of the naphthene and aromatic species, respectively, K_{a} the equilibrium constant and $P_{\mathrm{H_2}}$ the partial pressure of hydrogen; $n = 3$ for the

Table 2
Hydrogenation of mono-aromatics on sulfided Ni, Mo and NiMo catalysts.[a]

Temperature Catalyst LHSV (h^{-1})	300 °C NiMo 0.25	300 °C NiMo 1	350 °C Ni 0.25	350 °C Mo 0.25	350 °C Mo 1	350 °C NiMo 1	350 °C NiMo 2	400 °C Ni 1
Toluene								
X_{HYD} (%)	nd	33.7	1.8	nd	9.0	84.6	60.7	1.3
r_{mc}	–	320	14	–	91	1455	1455	40
X_{thermo} (%)	100	100	99.3	99.3	99.3	99.3	99.3	87.2
r_{mce}	–	320	14	–	91	1470	1470	45
m-xylene								
X_{HYD} (%)	nd	23.5	5.5	nd	16.3	59.9	nd	3.7
r_{mc}	–	207	42	–	169	705	–	113
X_{thermo} (%)	99.8	99.8	94.9	94.9	94.9	94.9	94.9	48.6
r_{mce}	–	207	45	–	180	774	–	237
1,3,5-trimethylbenzene								
X_{HYD} (%)	nd	18.3	9.3	nd	20.6	40.1	nd	4.5
r_{mc}	–	155	73	–	219	393	–	137
X_{thermo} (%)	99.1	99.1	80.4	80.4	80.4	80.4	80.4	23.4
r_{mce}	–	156	91	–	280	509	–	630
1,2,4,5-tetramethylbenzene								
X_{HYD} (%)	nd	14.7	10.7	nd	21.9	32.0	nd	6.5
r_{mc}	–	121	84	–	233	295	–	199
X_{thermo} (%)	97.2	97.2	56.4	56.4	56.4	56.4	56.4	7.3
r_{mce}	–	125	156	–	463	640	–	6563

[a] nd: not determined; r_{mc} and r_{mce}: in 10^{-3} $\mathrm{mol_{reactant}/mol_{metal}}$ h^{-1}; X_{thermo} (%) calculated from Stull [35].

mono-aromatic compounds considered. Intermediates and isomerized products were not taken into consideration.

Calculation of the equilibrium constant K_a were made using the data from Stull [32]. Data for 1,2,4,5-tetramethylbenzene were extrapolated from values calculated from benzene, toluene, m-xylene and 1,3,5-trimethylbenzene. Values for X_{thermo} are reported in table 2. A comparison with values calculated using the group contribution method of Benson [33] was also performed and showed no major differences. It is, however, recognized that due to the approximations made, these methods may result in more than one order of magnitude error in calculated K_a depending on the compound [4]. Therefore, we have determined the value of X_{thermo} experimentally for toluene hydrogenation. Figure 1 shows the effect of reaction temperature on the toluene hydrogenation activity of the NiMo catalyst. The measurements were performed at two different H_2S partial pressures (0.04 and 0.08 MPa). The curves of figure 1 show that for the NiMo catalyst toluene hydrogenation is under the influence of the thermodynamic equilibrium in a temperature range 350–400 °C. This is dependent on the level of conversion and therefore on the LHSV and H_2S partial pressure. A comparison of experimental data and calculated data using Stull's data leads to a very good fit, as shown in figure 1. In addition, an activation energy of 70 ± 10 kJ/mol was determined in the range 300–340 °C in agreement with values reported in the literature [11,19].

From the thermodynamic values calculated one can determine the kinetic conversion X_{HYDe} using the formula

$$X_{\mathrm{HYDe}} = \frac{X_{\mathrm{HYD}}}{X_{\mathrm{thermo}}} \times 100. \qquad (7)$$

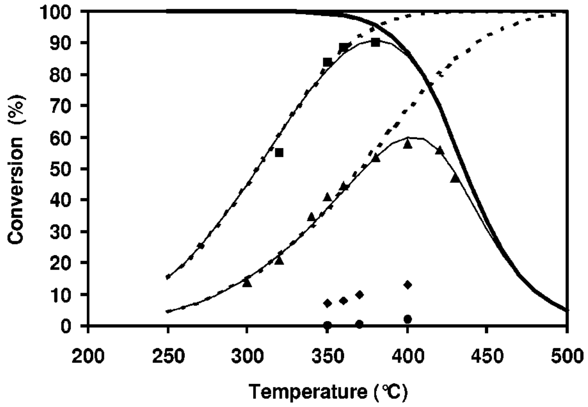

Figure 1. Influence of reaction temperature on the hydrogenation of toluene over sulfided Ni, Mo and NiMo alumina-supported catalysts. (■) NiMo, 0.04 MPa H_2S, (▲) NiMo, 0.08 MPa H_2S, (●) Ni, 0.04 MPa H_2S, (♦) Mo, 0.04 MPa H_2S. Thick line: thermodynamic limit calculated from Stull [35], dotted line: kinetic curve from experimental data, thin line: calculated kinetic and thermodynamic coupled activity curve.

Then the rate constant r_{mce} is computed according to formulae (2) and (3). Values of r_{mce} for the experiments done are also reported in table 2. While toluene and m-xylene are not significantly influenced by thermodynamic limitations between 300 and 350 °C, the 1,3,5-trimethylbenzene and 1,2,4,5-tetramethylbenzene hydrogenation are somewhat influenced. This agrees with the observations generally found in the literature [11]. Nevertheless, both the experimental results and the calculated values suggest that the mono-aromatics activity trend for the NiMo catalyst cannot be explained by a perturbation due to thermodynamic limitations.

The sulfided Ni/Al_2O_3 catalyst was found weakly active at 350 °C, LHSV $= 0.25$ h^{-1} whatever the tested aromatic compound. Figure 1 indicates clearly this large difference for toluene hydrogenation compared with the NiMo catalyst. The hydrogenation activity now increases with the increase of the number of methyl groups on the benzene ring. This trend was confirmed by a set of tests performed at 400 °C, as indicated in table 2, although at this temperature there is a noticeable amount of isomerization and cracking product and a strong influence of thermodynamic limitations. Noteworthy, this trend is clearly different from the trend found for metallic nickel catalysts [28].

The Mo/Al_2O_3 catalyst has also a low activity, as shown in figure 1, for toluene hydrogenation. Tests performed at 350 °C show an increase of hydrogenation activity when the number of methyl groups on the benzene ring increases.

The activation energies for toluene hydrogenation over Ni, and Mo catalysts determined in the temperature range 300–340 °C, were 70 ± 10 kJ/mol for both catalysts. They are in agreement with values reported in the literature [11,19]. Thus, no major differences of activation energy were found between the three different catalysts for toluene hydrogenation.

There is therefore a clear distinction in the hydrogenation activity trends for substituted mono-aromatics between Ni and Mo catalysts on one side, and the NiMo catalyst on the other side, as shown in figure 2. These different trends found between Ni, Mo and NiMo indicate that the NiMo catalysts have a noticeably different reactivity assigned to the presence of a mixed NiMoS phase. Interestingly also, these different trends can be translated into different promotion factors of Ni on the activity of Mo for the hydrogenation of the four different aromatic compounds, as clearly apparent in figure 2. At 350 °C, promotion factors q are 21 for toluene, 5.3 for m-xylene, 2.2 for 1,3,5-trimethylbenzene and 1.6 for 1,2,4,5-tetramethylbenzene.

The trend obtained for the NiMo catalysts is in marked contrast with previous work, as shown by the ranking of relative hydrogenation activity taken from selected literature works and reported in table 3. The first cause of discrepancy might be that some literature experiments were done with mixtures of aromatic compounds, whereas in this work the trends were established for single aromatic compounds. Then the measured activities were free from inhibiting effects from other aromatic compounds although under the influence of the well known inhibiting effect of H_2S (usually considered strong) and of the solvent (which is usually considered mild). Competition for the adsorption of aromatics in a mixture may be a cause of discrepancy especially if one assumes that the more substituted aromatics are the more strongly adsorbed on the adsorption sites then inhibiting more strongly the hydrogenation of the less substituted aromatic compound. Table 3 indicates that other differences render literature data less prone to generalization such as the use of bulk sulfides versus supported sulfides, NiMo versus NiW formula, the use of different testing equipment namely batch reactor versus continuous flow reactor. In addition, the nature of the aromatic compounds was often different.

There appears to be no straightforward interpretation of these different trends. Assuming that the adsorption of the aromatic reactant on the active sites occurs by a π bond-

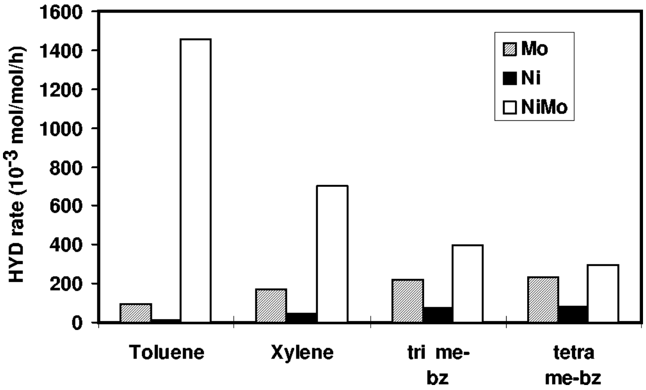

Figure 2. Mono-aromatics hydrogenation activity trends of sulfided Ni, Mo, NiMo/alumina catalysts at 6 MPa, 350 °C.

Table 3
Relative rate constant for the hydrogenation of mono-aromatics over metal and sulfide catalysts.

Catalyst	Pt	Pt	Pd	NiWS	NiWS	NiW	NiW	NiMoS
	SiO_2	Al_2O_3	Al_2O_3	Al_2O_3	Al_2O_3	bulk	bulk	Al_2O_3
Sulfur in feed	no	yes	no	yes	yes	yes	yes	yes
Reference	[25]	[17]	[25]	[15]	[10,11]	[34]	[15]	[this work]
Reactivity ratio								
Benzene	3.3	0.56	1.6	0.63	0.51	0.43	0.70	–
Toluene	1	1	1	1	1	1	1	1
o-xylene	–		0.17	–	–	–	1.34	–
m-xylene	–		0.71	–	–	1.43	–	0.48
p-xylene	0.27	1.18	1.03	1.06	1.12	–	–	
1,3,5-trimethylbenzene	0.03	–	–	–	–	1.87	–	0.27
1,2,4,5-tetramethylbenzene	–	–	–	–	–	–	–	0.20
Pentamethylbenzene	–	–	–	–	–	2.74	–	–
Hexamethylbenzene	–	–	–	–	–	0.65	–	–
Ethylbenzene	–	1.25	–	1.5	–	–	–	–
n-butylbenzene	–	2.9	–	2.19	–	–	1.67	–

ing adsorption, steric effects upon adsorption are likely to operate. However, one cannot explain the change of the activity trends by considering only steric effects, in particular in the case of the Mo and NiMo catalysts which have similar layer structure of the active phase.

One can also exclude an incomplete sulfiding of the studied catalysts as in our conditions these are well sulfided with usually very minor change of morphology of the sulfide particle between Mo and NiMo. Indeed, X-ray photoelectron spectroscopy studies have revealed that in both catalysts the Mo is about 80% sulfided and transmission electron microscopy analyses have shown that the active phase is mainly in the form of single MoS_2 slabs with a mean length of 2.6 ± 0.3 nm [35].

The increase of the number of electron-donating methyl groups on the benzene ring increases the electronic density of the aromatic cycle and, therefore, its basicity. One may speculate that this increase of basicity leads to an increase of the adsorption strength of the aromatic compound on the active surface sites with an electronic transfer from the aromatic cycle to the metal d orbital, as is generally described for metallic catalysts [21–25,36]. This increase of adsorption strength with the number of methyl groups may explain the increase of hydrogenation activity for Ni and Mo catalysts and the decrease of the hydrogenation activity for the NiMo catalyst if one assumes that the aromatic compounds are weakly adsorbed on the Ni and Mo catalysts and strongly adsorbed on the NiMo catalyst. As proposed by Chianelli, the addition of Ni leads to a modification of the electronic state of the MoS_2 phase [37]. This suggests that the modification of the electronic state of MoS_2 by Ni induces a stronger adsorption of mono-aromatics on the “NiMoS” phase adsorption sites and therefore an inversion of the reactivity trend.

While it is possible that kinetic effects or other structural effects may intervene [38,39], the reported results suggest that the inversion of the mono-aromatics activity trend from Ni and Mo to NiMo catalysts is the result of different electronic states of the active sulfide phases. Further work is, however, needed to fully understand these trends. A more detailed comparison of the activity of a larger set of mono-aromatic compounds in different conditions as well as detailed kinetic studies are needed to reach a definitive conclusion.

4. Conclusion

The comparison of the catalytic activity of sulfided Ni/Al_2O_3, Mo/Al_2O_3 and $NiMo/Al_2O_3$ catalysts for the hydrogenation of mono-, di-, tri- and tetramethylbenzene under typical hydrotreating conditions, namely 6 MPa total pressure, 350 °C, and about 0.04 MPa H_2S partial pressure, clearly shows that the more substituted tetramethylbenzene is the more hydrogenated compound over sulfided Ni/Al_2O_3 and Mo/Al_2O_3 catalysts whereas it is the less hydrogenated over the $NiMo/Al_2O_3$ catalyst. As a consequence, the promoter effect of Ni is large for toluene hydrogenation and small for tetramethylbenzene hydrogenation, showing that the magnitude of this effect is largely dependent on the nature of the reactant among other factors. The opposite trend found for the Ni and Mo catalysts on one side and the NiMo catalyst on the other side may be indicative of different electronic states of the active sulfide phases.

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