



Promoting effect of cobalt and nickel on the activity of hydrotreating catalysts in hydrogenation and isomerization of olefins

M. Badawi, L. Vivier*, G. Pérot, D. Duprez

Laboratoire de Catalyse en Chimie Organique UMR CNRS 6503, Faculté des Sciences, Université de Poitiers, 40, avenue du Recteur Pineau, 86022 Poitiers Cedex, France

ARTICLE INFO

Article history:

Received 21 April 2008

Received in revised form 8 July 2008

Accepted 11 July 2008

Available online 23 July 2008

Keywords:

Sulfide catalysts

Promoting effect

Olefin hydrogenation

Isomerization

ABSTRACT

In connection with the specific requirements of the hydrotreating of FCC gasoline, the selectivity of hydrotreating catalysts in hydrodesulfurization with respect to the hydrogenation of olefins has to be controlled and if possible improved. The aim of this study was to compare the reactivities in hydrogenation and in isomerization of various olefins on Mo, CoMo and NiMo catalysts in order to evaluate the promoter effect in both reactions.

It was shown that the promotion effect on the hydrogenation of olefins (150 °C, fixed-bed reactor) was depending on their structure. However, the promotion effect of Ni was higher than that of Co whatever the olefin. This is in accordance with the fact that CoMo catalysts are more efficient in the selective hydrodesulfurization of FCC gasoline than NiMo catalysts. The presence of cobalt favours also the skeletal isomerization of the olefins.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

New restrictions on the sulfur content of the gasoline and diesel fuel were fixed at a maximum content of 10 mg/kg of sulfur as from January 1, 2009 by the directives of the European Parliament and the Council. This is not only because of the harmful emissions of SO_x but also because of the noxious effect of sulfur on the effectiveness of the catalytic technologies used in the post processing of exhaust gases [1]. Thus, hydrotreating has become more and more important in refining with the objective of removing as much as possible of the sulfur impurities from petroleum products [2–8]. Regarding the gasoline pool, the sulfur content depends essentially on the fraction coming from the fluid catalytic cracking (FCC). Consequently, in order to meet the new requirements concerning gasoline, it is necessary to reduce the amount of sulfur impurities in the FCC naphtha drastically. In this particular case, the selectivity of the catalysts in hydrodesulfurization with respect to the hydrogenation of olefins has to be controlled and if possible improved in order to limit the octane rating loss ([8] and references therein). Several factors can influence this selectivity, the presence of Co and Ni promoters in particular [9–12]. The promotion effect of Co or Ni on the activity in HDS of Mo or W sulfide catalysts has been known for many years and various theories were proposed to explain it [10–12]. This effect also exists for the hydrogenation of

olefins [13–17]. However, one could wonder if the promoter effect of Co and Ni in the hydrogenation of olefins is the same or not [16,17] and if it can depend on the olefin structure. Another parameter which could play an important role in the hydrogenation of olefins is their isomerization ([8] and references therein, [18,19]). Actually FCC gasoline contains mostly internal olefins with di-, tri- or tetrasubstituted double bonds (about 75 wt%) [20–23]. These olefins are expected to be much less reactive in hydrogenation than terminal olefins. Therefore, their isomerization into terminal olefins may increase their reactivity in hydrogenation [18,19]. The aim of this work was to compare the reactivity in hydrogenation and in isomerization of olefins with different structures on Mo, CoMo and NiMo catalysts in order to evaluate the promoter effect in both reactions. Three olefins were used in this study: cyclopentene (cC₅⁼), 1-methylcyclopentene (1McC₅⁼), 3,3-dimethylbut-1-ene (33DMC₄¹⁼).

2. Experimental

2.1. Catalysts

The CoMo/Al₂O₃ and NiMo/Al₂O₃ commercial catalysts contained 8.3 wt% Mo with 2.3 wt% Ni and 2.2 wt% Co respectively deposited on alumina (230 m²/g). The Mo/Al₂O₃ catalyst was prepared by incipient wetness impregnation with 8.8 wt% of Mo [24].

The catalysts were presulfided *in situ* with a flow of H₂ (90%) and H₂S (10%) at 400 °C under atmospheric pressure for 15 h. After sulfidation, the catalyst samples (100 to 400 mg of NiMo/Al₂O₃ catalyst

* Corresponding author. Tel.: +33 5 49453479; fax: +33 5 49453899.
E-mail address: laurence.vivier@univ-poitiers.fr (L. Vivier).

or 500 mg of CoMo/Al₂O₃ catalyst and Mo/Al₂O₃ catalyst) were treated under helium at 350 °C for 1 h.

2.2. Transformation of olefins

Cyclopentene (95%) and 1-methylcyclopentene (98%) were purchased from Aldrich, and 3,3-dimethylbut-1-ene (98.5%) and *n*-heptane (99%) from Fluka. They were used without further purification. The transformation of the olefins in solution (16 mol% in *n*-heptane) was carried out in a fixed-bed reactor at 150 °C under atmospheric pressure. The H₂/olefin molar ratio was equal to 36. The molar flow rate of the olefins was varied in order to measure the activity versus residence time which was represented by the inverse of the GHSV at 150 °C under 1 bar. Under these conditions no significant sulphur loss was detected by elemental analysis of the used samples (CE Instruments NA2100 Protein). The reaction products were analyzed on-line by means of a Varian gas chromatograph equipped with an automatic sampling valve, a 50 m CPSil-5 capillary column (film thickness, 0.4 μm) and a flame-ionization detector. The activity of each sample was measured after stabilization (120 min on stream) and under conditions where a linear relationship between conversion and residence time was obtained (conversion lower than 15%). It was checked that the reactor was inactive. Moreover, the solvent (*n*-heptane) has no effect on the considered reactions.

3. Results

From the free energy change calculated with the thermodynamics tables [25], the equilibrium constants were determined for the hydrogenation of the three olefins and were always higher than 5.10⁶ under the conditions used in this study. Therefore, the reactions were not limited by thermodynamics.

3.1. Transformation of cyclopentene

Cyclopentene (cC₅⁼) was hydrogenated into cyclopentane (cC₅) which was the only product obtained with the three catalysts. Under the conditions used in this work the NiMo catalyst was about 20 times more active than the unpromoted catalyst while the CoMo catalyst was only about two times more active than the unpromoted catalyst (Fig. 1). This is in accordance with results reported previously [17].

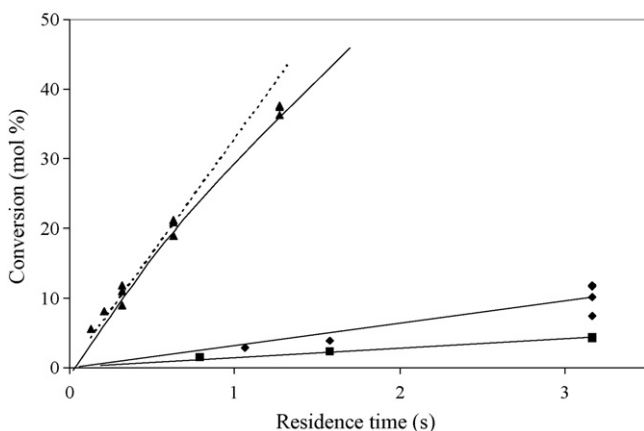
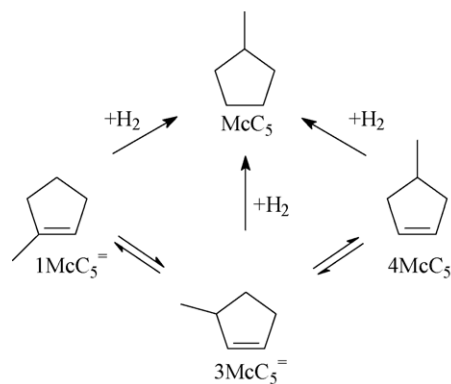


Fig. 1. Conversion of cyclopentene into cyclopentane versus residence time on Mo (■), CoMo (◆) and NiMo (▲) sulfide catalysts at 150 °C.



Scheme 1. Transformation of 1-methylcyclopentene (1McC₅⁼) in 3-methylcyclopentene (3McC₅⁼), 4-methylcyclopentene (4McC₅⁼) and methylcyclopentane (McC₅).

3.2. Transformation of 1-methylcyclopentene

Whatever the catalyst, 1-methylcyclopentene (1McC₅⁼) underwent initially isomerization into 3-methylcyclopentene (3McC₅⁼) and 4-methylcyclopentene (4McC₅⁼) (Scheme 1). The double bond migration was extremely fast so that the distribution of the isomers was the same with all three catalysts and corresponded approximately to the equilibrium distribution at 150 °C [25] (Table 1).

Methylcyclopentane (McC₅) resulting from the hydrogenation of the mixture of the methylcyclopentene isomers was the only hydrogenation product and appeared as a secondary product (Fig. 2).

The NiMo catalyst was 10 times more active in hydrogenation of 1-methylcyclopentene than the unpromoted catalyst (Fig. 3). The CoMo catalyst was only 1.4 times more active than the Mo catalyst. On the other hand, the conversion in isomerization did not depend on the residence time, which confirms that the equilibrium between the methylcyclopentene isomers was obtained very readily.

Table 1
Distribution of the three methylcyclopentene isomers at 150 °C

	Isomers		
	1McC ₅ ⁼	3McC ₅ ⁼	4McC ₅ ⁼
Experimental (mol%)	91	6	3
Calculated (mol%) [25]	96.5	3	0.5

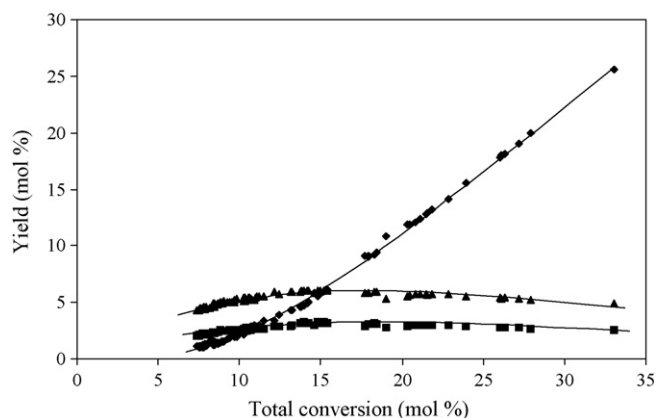


Fig. 2. Transformation of 1-methylcyclopentene into 3-methylcyclopentene (▲), 4-methylcyclopentene (■) and methylcyclopentane (◆) on Mo, CoMo and NiMo sulfide catalysts at 150 °C.

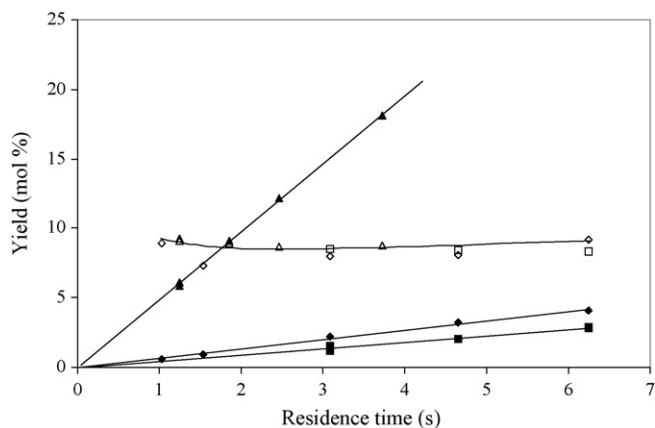


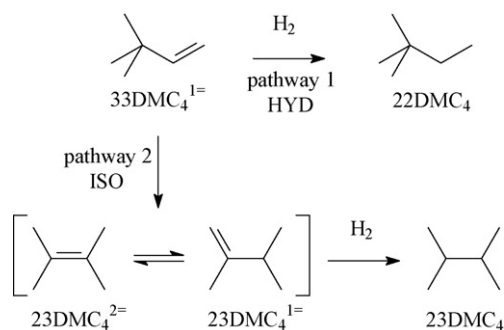
Fig. 3. Hydrogenation and isomerization of 1-methylcyclopentene on sulfide catalysts: yields versus residence time at 150 °C. Hydrogenation: Mo (■), CoMo (◆), NiMo (▲). Isomerization: Mo (□), CoMo (◇), NiMo (△).

3.3. Transformation of 3,3-dimethylbut-1-ene

3,3-Dimethylbut-1-ene ($33\text{DMC}_4^{1=}$) underwent two parallel reactions (Scheme 2): the hydrogenation into 2,2-dimethylbutane (22DMC_4 , pathway 1, HYD) and the skeletal isomerization into 2,3-dimethylbut-1-ene ($23\text{DMC}_4^{1=}$) and 2,3-dimethylbut-2-ene ($23\text{DMC}_4^{2=}$) (pathway 2, ISO). The 2,3-dimethylbutene isomers were in turn hydrogenated into 2,3-dimethylbutane (23DMC_4) as shown by the shape of the curves in Fig. 4. Actually, the amount of 2,2-dimethylbutane makes it possible to measure the hydrogenation activity while the amount of the three other products leads to the isomerization activity.

As shown in Fig. 4, the yields in hydrogenation (formation of 22DMC_4 , pathway 1) and in skeletal isomerization (formation of $23\text{DMC}_4^{2=}$, $23\text{DMC}_4^{1=}$ and 23DMC_4 , pathway 2) were similar with the Mo catalyst. The NiMo catalyst was much more active in hydrogenation than in isomerization (about three times) while it was the reverse for the CoMo catalyst which was twice more active in isomerization than in hydrogenation.

In the hydrogenation of 3,3-dimethylbut-1-ene, the CoMo catalyst presented approximately the same activity as the Mo catalyst while the NiMo catalyst was the most active, it was about 2.5 times more active than the two other catalysts (Fig. 5). In isomerization, the promoter effect was reversed: the CoMo catalyst was about twice as active as the Mo catalyst, while the NiMo catalyst presented a slightly lower activity. It can be noticed that the skeletal isomerization of 3,3-dimethylbut-1-ene was more difficult and much slower than the double bond migration (observed



Scheme 2. Transformation of 3,3-dimethylbut-1-ene ($33\text{DMC}_4^{1=}$) in 2,2-dimethylbutane (22DMC_4), 2,3-dimethylbut-2-ene ($23\text{DMC}_4^{2=}$), 2,3-dimethylbut-1-ene ($23\text{DMC}_4^{1=}$) and 2,3-dimethylbutane (23DMC_4).

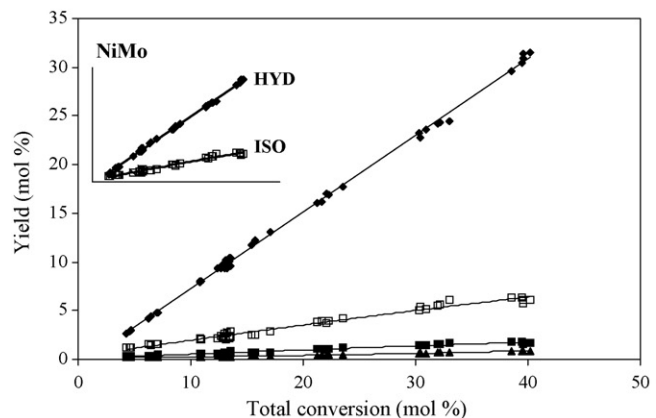
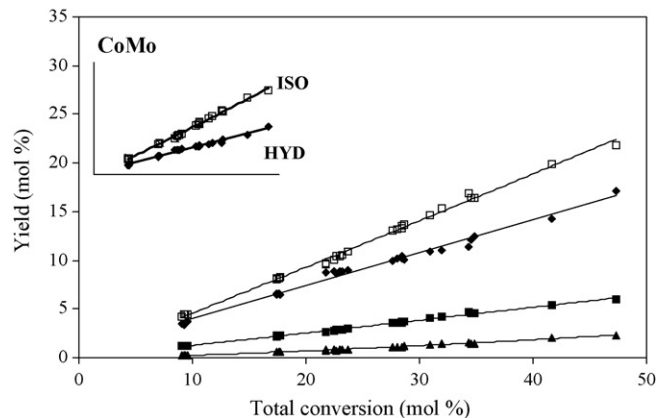
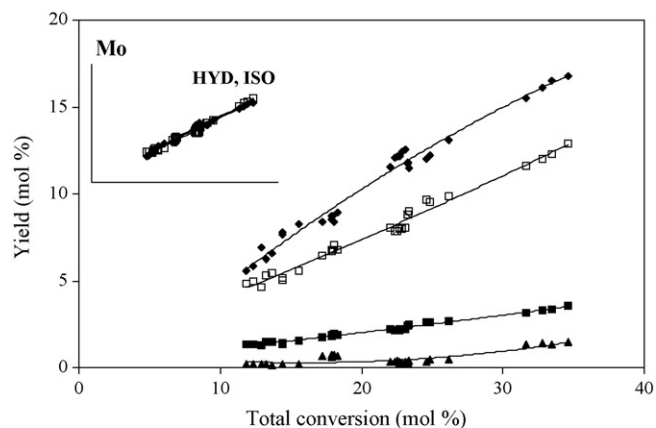


Fig. 4. Transformation of 3,3-dimethylbut-1-ene into 2,2-dimethylbutane (◆), 2,3-dimethylbut-2-ene (□), 2,3-dimethylbut-1-ene (■) and 2,3-dimethylbutane (▲) on Mo, CoMo and NiMo sulfide catalysts at 150 °C.

with 1-methylcyclopentene); it occurred at a rate similar to the hydrogenation (Fig. 6).

4. Discussion

4.1. Effect of the olefin structure

Table 2 summarizes the activities of the Mo, CoMo and NiMo sulfide catalysts in hydrogenation and in isomerization of 1-methylcyclopentene ($1\text{Mc}_5^=$), cyclopentene ($\text{cC}_5^=$) and 3,3-dimethylbut-1-ene ($33\text{DMC}_4^{1=}$) at 150 °C.

With the Mo and CoMo catalysts, the reactivity in hydrogenation of the three olefins increased with the decreasing number of alkyl

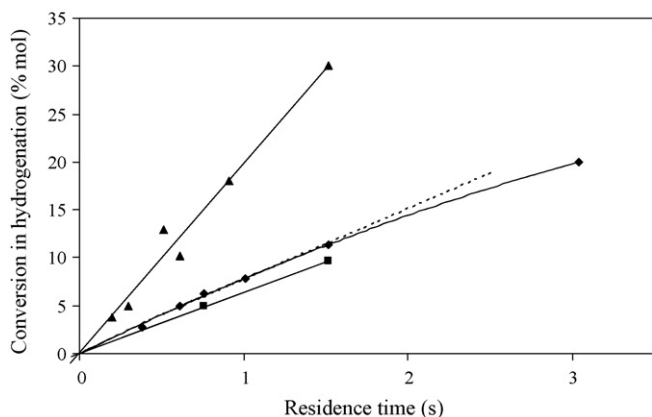


Fig. 5. Conversion in hydrogenation (pathway 1) of 3,3-dimethylbut-1-ene versus residence time on sulfide catalysts on Mo (■), CoMo (◆), NiMo (▲) at 150 °C.

groups attached to the double bond. 33DMC₄¹⁼ was 11 or 13 times more reactive than 1McC₅⁼. This sequence is the one observed in catalysis by metals [26,27] and is generally considered as depending on the adsorption of the reactant molecule, hence on its concentration at the catalyst surface, which in turn depends on the steric hindrance around the double bond. The relative reactivity scale was about the same with these two catalysts:

Mo : 1McC₅⁼(1) < cC₅⁼(2.9) < 33DMC₄¹⁼(12.9);

CoMo : 1McC₅⁼(1) < cC₅⁼(4.6) < 33DMC₄¹⁼(11.2).

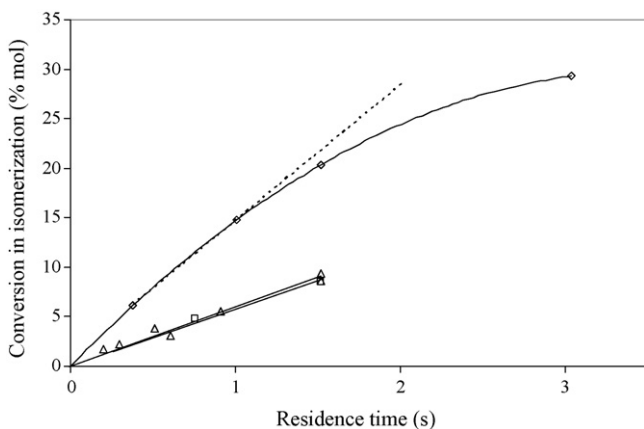






Fig. 6. Conversion in isomerization (pathway 2) of 3,3-dimethylbut-1-ene versus residence time on sulfide catalysts on Mo (□), CoMo (◇), NiMo (△) at 150 °C.

Table 2

Activities of the Mo, CoMo and NiMo sulfide catalysts in hydrogenation and in isomerization^a at 150 °C

Activity (10 ⁻⁴ mol h ⁻¹ g ⁻¹)				
Reactant	1McC ₅ ⁼	cC ₅ ⁼	33DMC ₄ ¹⁼	
				
Products	1McC ₅	cC ₅	22DMC ₄	23DMC ₄ ⁺ + 23DMC ₄
Mo	0.17	0.5	2.2	2.0
CoMo	0.24	1.1	2.7	5.0
NiMo	1.7	11.7	7.0	2.1

^a For 33DMC₄¹⁼.

However, with the NiMo catalyst, cyclopentene was the most reactive and the relative reactivity sequence was the following:

NiMo : 1McC₅⁼(1) < 33DMC₄¹⁼(4.1) < cC₅⁼(6.9).

The relative reactivity of 3,3-dimethylbut-1-ene was unexpectedly low on the NiMo catalyst. As pointed out recently by Toba et al. [19], this means that the reactivity of olefins on sulfur catalysts does not depend only on their own structure but also on the structure of the catalyst and on the configuration of the catalytic centres (see below).

4.2. Effect of the promoter

The promotion effects obtained in the hydrogenation of the olefins (this work), in the isotopic exchange between H₂ and D₂ [28] and in the hydrodesulfurization of dibenzothiophene [24] are represented by the ratios between the activities of the catalysts promoted by nickel or cobalt and the activity of the non-promoted molybdenum catalyst (Table 3).

As already reported [17], the promotion effect on the hydrogenation of olefins was much more significant with the NiMo (up to 23.4 for cyclopentene) than with the CoMo catalyst (not more than about 2). This confirms previous results reported by Candia et al. [16] which indicated that the promotion effect of Ni on the hydrogenation of butene formed during the HDS of thiophene was more significant than the effect of Co and it explains why CoMo catalysts are generally considered as more efficient than NiMo catalysts in the selective HDS of FCC gasoline [8]. The small promotion effect obtained with Co in hydrogenation is also in accordance with the results reported by Hatanaka [23]. Actually, the promotion effects of both metals were similar in the hydrodesulfurization of dibenzothiophene (Table 3) and we can also notice that the promotion effect of nickel in the hydrogenation of cyclopentene was similar to the one obtained in the HDS of dibenzothiophene [24].

A promotion effect was also observed in skeletal isomerization of 3,3-dimethylbut-1-ene but it was less significant than in hydrogenation and, in this case the effect of cobalt was greater than that of nickel which relates to what was obtained in the isotopic exchange between H₂ and D₂ [28]. Even if we suppose that the support plays a role in this reaction, the existence of a promotion effect means that the sulfide phase is also taking part in the process. Actually, if it were not the case, the isomerization activity should be the same with all three catalysts unless the support reacts with Co and Ni promoters to form spinels, which, however, is likely to occur. Nevertheless, it is clear that the sulfide phase can catalyze the isomerization of olefins since unsupported metal sulfides were shown recently to do so [29]. Skeletal isomerization of 3,3-dimethylbut-1-ene is a model reaction used to characterise Brönsted acidic sites on sulfided catalysts [30]. Hence, on this basis, the CoMo catalyst is apparently more acidic than the NiMo catalyst. The involvement of the support in isomerization reaction will be studied in a future paper.

Actually, in connection with the selective HDS of FCC gasoline, the question of whether the hydrogenation of olefins and HDS (or C–S bond cleavage) occur on the same catalytic centres or not is central ([8,17] and references therein) and the role of the promoter seems to be essential in this respect [9]. Since the optimum of promotion effect corresponds to the same promoter/(promoter + molybdenum) atomic ratio in HDS, in hydrogenation of olefins and in isotopic exchange [12,17,24,28], we can suppose that all these reactions take place on the same kind of sites [17]. Consequently, the differences in promotion effect which were observed in the various reactions are very likely to be related to reaction mechanisms and to differences in rate-limiting steps.

Table 3

Promoting effect of nickel and cobalt in molybdenum catalysts observed in hydrogenation of olefins, isotopic exchange and hydrodesulfurization

Promoting effect (activity of CoMo or NiMo over the activity of Mo)	CoMo/Mo	NiMo/Mo	Reference
Hydrogenation of 1-methylcyclopentene at 150 °C	1.4	10	This work
Hydrogenation of cyclopentene at 150 °C	2.2	23.4	This work
Hydrogenation of 3,3-dimethylbut-1-ene at 150 °C	1.2	3.2	This work
Isomerization of 3,3-dimethylbut-1-ene at 150 °C	2.5	1.1	This work
Hydrogenation of propene at 80 °C	1.2	2.2	[17]
Isotopic exchange between H ₂ and D ₂ at 80 °C	5.5	0.8	[28]
Hydrodesulfurization of dibenzothiophene at 400 °C	18	20	[24]

Among the various explanations of the promotion or synergy effect which were proposed in the literature [10–12], the one which, to date, seems to be the most relevant is the one proposed by Topsoe et al. [12] of the existence of a so-called “CoMoS” or “NiMoS” mixed phase. This mixed phase model was interpreted as an illustration of the Sabatier principle by supposing that the catalytic centres are made of sulfur vacancies at the edges of MoS₂ particles where Mo atoms are substituted for promoter atoms in such a way that the latter donates electrons to the main constituent and leads to a weakening of the metal–sulfur bond down to the optimum required for the HDS activity ([31] and references therein, [32]). This interpretation was updated on the basis of *ab initio* calculations using the density functional theory (DFT) and a new metal–sulfur bond energy model was proposed [33]. In line with this theory, it is supposed that the promoter increases the electronic density on the neighbouring sulfur atoms [34], hence their basicity [24].

With this in mind, we can explain the effect of cobalt on both HDS (by assuming that C–S bond cleavage occurs through a β -elimination process [24,35]) and H₂–D₂ exchange (by assuming that the rate-limiting step of the latter is the dissociation of H₂ or D₂ [17,36,37]). Now, to explain the promotion effect in the hydrogenation of olefins, we have to consider other hypotheses. It has been reported that the rate-limiting step of the hydrogenation of aromatics on sulphides was the addition of a proton to the adsorbed substrate having undergone first the addition of a hydride species [38,39]. If it were also the case for olefin hydrogenation, then Co should decrease the rate since the SH groups are expected to be less acidic than on the unpromoted catalyst. However, this effect can be compensated to a large extent by the increase of the number of catalytic centres [40] so that the CoMo catalyst can well be slightly more active than the non-promoted catalyst. The same stands for skeletal isomerization if we suppose that the addition of the proton to the alkene to form the carbenium ion is the rate-limiting step.

The fact that the promotion effects of Ni in the hydrogenation of olefins and in the isotopic exchange between H₂ and D₂ are different from those obtained with Co is more difficult to interpret. In particular, the promotion effect of Ni in the hydrogenation of olefins which is much more significant than that of Co seems to be more complex. Clearly, the adsorption of the reactant does not play the same role as with the Co-promoted catalyst, which means that the steric hindrance around the catalytic centres is probably not the same. Like Co, Ni is supposed to increase the number of catalytic centres and, in line with the proposal of Travert et al. [36], it can also be supposed that the hydrogen species adsorbed on the NiMo catalyst are so unstable that they are very easily captured by any basic substrate such as an adsorbed olefin, which could explain that the promotion effect is particularly important. However, with this reasoning, it is more difficult to explain why skeletal isomerization is not promoted by Ni.

Recent advances using theoretical approaches based on the density functional theory [36,37,41–48] could explain the differences observed between CoMo and NiMo catalysts. Indeed, Raybaud and coworkers [42,43,45,46] showed that the morphology of the active phases is modified by the incorporation of cobalt and nickel

atoms into the MoS₂ structure under sulfo-reductive conditions. The CoMoS phase shows a regular hexagon while the NiMoS phase presents a greater amount of M-edges than S-edges. These findings imply only small modifications of the geometrical model proposed by Kasztelan et al. [49]. Moreover, the cobalt atoms are more stable in substitution at the S-edge while the nickel atoms are localized on both edges. The sulfur coverage at both edges in HDS reaction conditions decrease when Co and Ni are present. Thus, the promoting effect of nickel could be explained by a structural effect: the only promoted metallic edges are the one of the NiMoS. Indeed, the metallic edges of the CoMoS phase would be similar to the one of the unpromoted catalyst. Therefore, the origin of the promoting effect of nickel can be clearly identified. Assuming that hydrogenation reactions take place on the metallic edges, the NiMoS phase is the only one which exhibits a large amount of highly active M-edges.

The sulfo-reductive conditions (molecular ratio H₂S/H₂) appear as a key parameter [41,48,50] and CoMo and NiMo catalysts have not the same sensitivity to H₂S [51–56]. Obviously, the concentration in active catalytic centres depends on the amount of adsorbed H₂S and the magnitude of the promotion effect is also expected to depend on it, which could also explain, at least in part, the differences we obtained between the two catalysts.

5. Conclusion

Except on the NiMo catalyst where cyclopentene was the most reactive, the reactivities in hydrogenation of the olefins decreased with increasing substitution of their double bond, which means in the order:

3, 3-dimethylbut-1-ene > cyclopentene > 1-methylcyclopentene,

The promotion effect of Ni in the hydrogenation of olefins was much greater than that of Co (which is very small), whatever the olefin. This explains why CoMo catalysts are generally considered as more efficient than NiMo catalysts in the selective HDS of FCC gasoline.

Although much less significant, the promotion effect also existed in the skeletal isomerization of 3,3-dimethylbut-1-ene and it was greater with the CoMo than with the NiMo catalyst.

Double bond migration occurred very readily over the three catalysts.

Recent DFT studies on the incorporation of the promoters in the active phase of hydrotreating catalysts are consistent with our experimental results, which shows that both kinds of studies are complementary to each other.

References

- [1] Off. J. Eur. Commun. L76 (22 March 2003) 10.
- [2] T.G. Kaufmann, A. Kaldor, G.F. Stuntz, M.C. Kerby, L.L. Ansell, Catal. Today 62 (2000) 77.
- [3] C. Marcilly, Stud. Surf. Sci. Catal. 135 (2001) 37.
- [4] C. Song, X. Ma, Appl. Catal. B. Environ. 41 (2003) 207.
- [5] I.V. Babich, J.A. Moulijn, Fuel 82 (2003) 607.
- [6] C. Song, Catal. Today 86 (2003) 211.

- [7] F.L. Plantenga, R.G. Leliveld, *Appl. Catal. A. Gen.* 248 (2003) 1.
- [8] S. Brunet, D. Mey, G. Pérot, C. Bouchy, F. Diehl, *Appl. Catal. A. Gen.* 278 (2005) 143.
- [9] J.T. Miller, W.J. Reagan, J.A. Kaduk, C.L. Marshall, A.J. Kropf, *J. Catal.* 193 (2000) 123.
- [10] B. Delmon, *Catal. Lett.* 22 (1993) 1.
- [11] R.R. Chianelli, M. Daage, M.J. Ledoux, *Adv. Catal.* 40 (1994) 177.
- [12] H. Topsøe, B.S. Clausen, F.E. Massoth, *Hydrotreating Catalysis, Catalysis—Science and Technology*, Springer-Verlag, Berlin/Heidelberg, 1996.
- [13] J.F. Le Page, *Catalyse de Contact*, Editions Technip, Paris, 1978, p. 441.
- [14] D. Pirotte, J.M. Zabala, P. Grange, B. Delmon, *Bull. Soc. Chim. Belg.* 90 (1981) 1239.
- [15] B. Delmon, G.F. Froment, *Catal. Rev. Sci. Eng.* 38 (1996) 69.
- [16] R. Candia, B.S. Clausen, J. Bartholdy, N.-Y. Topsøe, B. Lengeler, H. Topsøe, *Proc. 8th Int. Congr. Catal.*, Berlin, Verlag Chemie, Weinheim/Deerfield Beach/Basel, 1984, p. 375.
- [17] M. Brémaud, L. Vivier, G. Pérot, V. Harlé, C. Bouchy, *Appl. Catal. A. Gen.* 289 (2005) 44.
- [18] D. Mey, S. Brunet, C. Canaff, F. Maugé, C. Bouchy, F. Diehl, *J. Catal.* 227 (2004) 436.
- [19] M. Toba, Y. Miki, T. Matsui, M. Harada, Y. Yoshimura, *Appl. Catal. B. Environ.* 70 (2007) 542.
- [20] S. Hatanaka, M. Yamada, O. Sadakane, *Ind. Eng. Chem. Res.* 36 (1997) 1519.
- [21] S. Hatanaka, M. Yamada, O. Sadakane, *Ind. Eng. Chem. Res.* 36 (1997) 5110.
- [22] S. Hatanaka, M. Yamada, O. Sadakane, *Ind. Eng. Chem. Res.* 37 (1998) 1748.
- [23] S. Hatanaka, *Catal. Surv. Asia* 9 (2) (2005) 87.
- [24] J. Mijoin, V. Thévenin, N. Garcia Aguirre, H. Yuze, J. Wang, W.Z. Li, G. Pérot, J.L. Lemberon, *Appl. Catal. A* 180 (1999) 95.
- [25] D.R. Stull, E.F. Westrum Jr., G.C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, John Wiley and Sons Inc., New York, 1969.
- [26] M. Kraus, *Adv. Catal.* 29 (1980) 51.
- [27] J. March, *Advanced Organic Chemistry – Reactions, Mechanisms and Structure*, 4th Ed., Wiley-Interscience Publication, 1992, p. 771.
- [28] A. Scaffidi, L. Vivier, A. Travert, F. Maugé, S. Kasztelan, C. Scott, G. Pérot, *Stud. Surf. Sci. Catal.* 138 (2001) 31.
- [29] A. Daudin, S. Brunet, G. Pérot, P. Raybaud, C. Bouchy, *J. Catal.* 248 (2007) 111.
- [30] S. Karmal, G. Pérot, D. Duprez, *J. Catal.* 130 (1991) 212.
- [31] R.R. Chianelli, *Catal. Rev.-Sci. Eng.* 26 (1984) 361.
- [32] S. Harris, R.R. Chianelli, *J. Catal.* 98 (1986) 17.
- [33] R.R. Chianelli, G. Berhault, P. Raybaud, S. Kasztelan, J. Hafner, H. Toulhoat, *Appl. Catal. A. Gen.* 227 (2002) 83.
- [34] H. Topsøe, B.S. Clausen, N.Y. Topsøe, E. Pedersen, W. Niemann, A. Müller, H. Bögge, B. Lengeler, *J. Chem. Soc. Faraday Trans. 1* 83 (1987) 2157.
- [35] F. Bataille, J.-L. Lemberon, P. Michaud, G. Pérot, M. Vrinat, M. Lemaire, E. Schulz, M. Breyse, S. Kasztelan, *J. Catal.* 191 (2000) 409.
- [36] A. Travert, H. Nakamura, R.A. van Santen, S. Cristol, J.F. Paul, E. Payen, *J. Am. Chem. Soc.* 124 (2002) 7084.
- [37] M. Sun, J. Adjaye, A.E. Nelson, *Appl. Catal. A. Gen.* 263 (2004) 131.
- [38] S. Kasztelan, D. Guillaume, *Ind. Eng. Chem. Res.* 33 (1994) 203.
- [39] S. Blanchin, P. Galtier, S. Kasztelan, S. Kressmann, H. Penet, G. Pérot, *J. Phys. Chem.* 105 (2001) 10860.
- [40] L.P. Nielsen, S.V. Christensen, H. Topsøe, B.J. Clausen, *Catal. Lett.* 67 (2000) 81.
- [41] S. Cristol, J.F. Paul, E. Payen, D. Bougeard, S. Clemendot, F. Hutschka, *J. Phys. Chem. B* 104 (2000) 11220.
- [42] H. Schweiger, P. Raybaud, G. Kresse, H. Toulhoat, *J. Catal.* 207 (2002) 76.
- [43] H. Schweiger, P. Raybaud, H. Toulhoat, *J. Catal.* 212 (2002) 33.
- [44] M. Sun, A.E. Nelson, J. Adjaye, *J. Catal.* 226 (2004) 32.
- [45] P. Raybaud, *Appl. Catal. A. Gen.* 322 (2007) 76.
- [46] A.D. Gandubert, E. Krebs, C. Legens, D. Costa, D. Guillaume, P. Raybaud, *Catal. Today* 130 (2007) 149.
- [47] J.V. Lauritsen, J. Kibsgaard, G.H. Olesen, P.G. Moses, B. Hinnemann, S. Helveg, J.K. Nørskov, B.S. Clausen, H. Topsøe, E. Laegsgaard, F. Besenbacher, *J. Catal.* 249 (2007) 220.
- [48] J.F. Paul, S. Cristol, E. Payen, *Catal. Today* 130 (2008) 139.
- [49] S. Kasztelan, H. Toulhoat, J. Grimblot, J.P. Bonnelle, *Appl. Catal.* 13 (1984) 127.
- [50] M. Breyse, E. Furimsky, S. Kasztelan, M. Lacroix, G. Pérot, *Catal. Rev.* 44 (4) (2002) 651.
- [51] V. Lamure-Meille, E. Schulz, M. Lemaire, M. Vrinat, *Appl. Catal. A. Gen.* 131 (1995) 143.
- [52] J. van Gestel, L. Finot, J. Leglise, J.C. Duchet, *Bull. Soc. Chim. Belg.* 104 (4–5) (1995) 189.
- [53] S. Kasahara, T. Shimizu, M. Yamada, *Catal. Today* 35 (1997) 59.
- [54] S. Texier, G. Berhault, G. Pérot, V. Harlé, F. Diehl, *J. Catal.* 223 (2004) 404.
- [55] M. Egorova, R. Prins, *J. Catal.* 225 (2004) 417.
- [56] V. Rabarihoela-Rakotovo, S. Brunet, G. Pérot, F. Diehl, *Appl. Catal. A. Gen.* 306 (2006) 34.