Journal of Molecular Catalysis A: Chemical 293 (2008) 53–58

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

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 gazes [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 ($cC_5^=$), 1-methylcyclopentene ($1McC_5^=$), 3,3-dimethylbut-1-ene ($33DMC_4{}^{1=}$).

2. Experimental

2.1. Catalysts

The $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ commercial catalysts contained 8.3 wt% Mo with 2.3 wt% Ni and 2.2 wt% Co respectively deposited on alumina (230 m^2/g). The Mo/Al_2O_3 catalyst was prepared by incipient wetness impregnation with 8.8 wt% of Mo [24].

The catalysts were presulfided *in situ* with a flow of H_2 (90%) and H_2S (10%) at 400 °C under atmospheric pressure for 15 h. After sulfidation, the catalyst samples (100 to 400 mg of $NiMo/Al_2O_3$ catalyst

---

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

1381-1169/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2008.07.006

or 500 mg of $CoMo/Al_2O_3$ catalyst and Mo/Al_2O_3 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 H_2/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 significative 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 5.10^6 under the conditions used in this study. Therefore, the reactions were not limited by thermodynamics.

3.1. Transformation of cyclopentene

Cyclopentene ($cC_5^=$) was hydrogenated into cyclopentane (cC_5) 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].

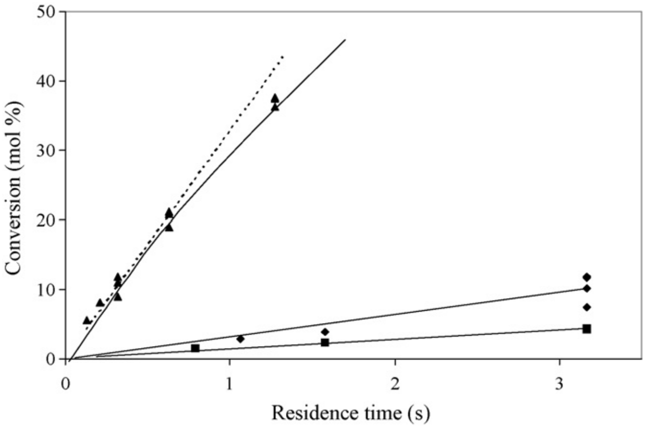
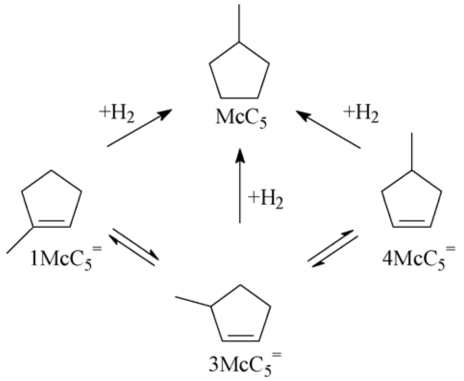


Fig. 1. Conversion of cyclopentene into cyclopentane versus residence time on Mo (■), CoMo (◆) and NiMo (▲) sulfide catalysts at 150 °C.



Scheme 1. Transformation of 1-methylcyclopentene ($1McC_5^=$) in 3-methylcyclopentene ($3McC_5^=$), 4-methylcyclopentene ($4McC_5^=$) and methylcyclopentane (McC_5).

3.2. Transformation of 1-methylcyclopentene

Whatever the catalyst, 1-methylcyclopentene ($1McC_5^=$) underwent initially isomerization into 3-methylcyclopentene ($3McC_5^=$) and 4-methylcyclopentene ($4McC_5^=$) (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 (McC_5) 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

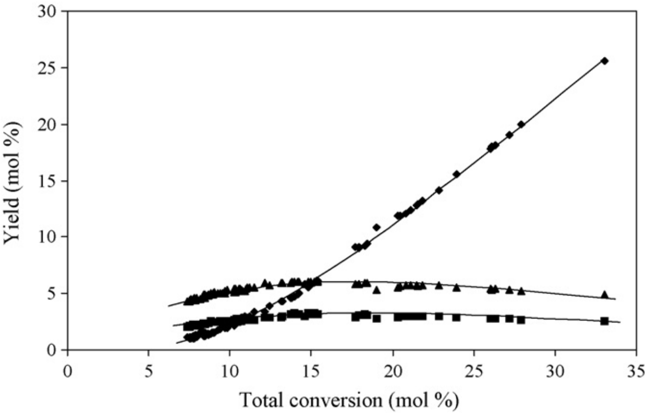


Fig. 2. Transformation of 1-methylcyclopentene into 3-methylcyclopentene (▲), 4-methylcyclopentene (■) and methylcyclopentane (◆) on Mo, CoMo and NiMo sulfide catalysts at 150 °C.

Download English Version:

https://daneshyari.com/en/article/67917

Download Persian Version:

https://daneshyari.com/article/67917

Daneshyari.com