Effect of the catalyst in the BTX production by hydrocracking of light cycle oil

Georgina C. Laredo¹ · José L. García-Gutiérrez¹ · Patricia Pérez-Romo¹ · Eli H. Olmos-Cerda¹

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Abstract

Catalysts to produce the important petrochemicals like benzene, toluene, and xylene (BTX) from refinery feedstocks, like light cycle oil (LCO) are reviewed here by covering published papers using model mixtures and real feeds. Model compounds experiments like tetralin and naphthalene derivatives provided a 53–55% total BTX yield. Higher yields were never attained due to the inevitable gas formation and other C₉₊-alkylbenzenes formed. For tetralin, the best catalysts are those conformed by Ni, CoMo, NiMo, or NiSn over zeolite H-Beta. For naphthalene derivatives, the best catalysts were those conformed by W and NiW over zeolite H-Beta silylated. Real feeds produced a total BTX yield of up to 35% at the best experimental conditions. Higher yields were never reached due to the presence of other types of hydrocarbons in the feed which can compete for the catalytic sites. The best catalysts were those conformed by Mo, CoMo, or NiMo over zeolite H-Beta. Some improvements were obtained by adding ZSM-5 to the support or in mixtures with other catalysts.

Keywords Light cycle oil · Hydrogenation · Hydrocracking · BTX

Introduction

The production of benzene, toluene, and xylene (BTX) from light cycle oil (LCO) has been our matter of interest in the last years [1–4]. LCO, a middle distillate from FCC (fluid catalytic cracking), has lost market as a part of the diesel feedstock due to its inherent low quality (high sulfur, nitrogen, and aromatic contents) [5–7], which makes the resulting fuel difficult to comply with the stringent worldwide environmental regulations [8, 9]. In Mexico, LCO can contain up to 90% of mono-, di- and tri-aromatic compounds [6, 7], being most of these compounds di-aromatic hydrocarbons, i.e. naphthalene derivatives [7]. Among the alternatives for LCO upgrading, the production of BTX after successive hydrotreating (HDT)

and hydrocracking (HCK) procedures (Fig. 1) [1, 2, 10] has been studied either using model mixtures [1, 3] or in a lesser extent using real feeds [2, 4]. Additionally, it is well known [1, 2, 10] that catalysts play a key role in the hydrogenation (partial saturation) of naphthalene followed by the selective cracking of naphthenic structures, producing one-ring-aromatic hydrocarbons with alkyl chains. For this purpose, bifunctional catalysts with acid (support) and metal (hydrogenation-dehydrogenation) functions are frequently used [11, 12]. However, an excess of hydrogenation activity, and strong acidity may crack molecules excessively into light gaseous hydrocarbons and accelerate coke deposition. In this sense, hydrocracking catalysts with metal (groups VI and VIII) sulfides perform, in general, the hydrodehydrogenation, and hydrocracking of heavy oil feedstocks. For this reason, metallic-sulfide-supported catalysts are considered more effective materials than metals [12, 13]. Another key parameter that may influence the activity of bimetallic over the corresponding monometallic catalyst is the ratio of the constituents' metals (e.g. Ni to Co ratio) [14].

Zeolites are widely preferred over other supports because of their stronger acidity, higher thermal, and hydro-thermal stability, higher resistance to sulfur and nitrogen compounds, reduced coke production tendency and higher regeneration capability [12]. Additionally, the porosity of zeolites allows their unique shape selectivity characteristic, i.e. certain

✉ Georgina C. Laredo
glaredo@imp.mx
José L. García-Gutiérrez
garciajl@imp.mx
Patricia Pérez-Romo
pperezr@imp.mx
Eli H. Olmos-Cerda
eholmos@imp.mx

¹ Instituto Mexicano del Petróleo, Lázaro Cárdenas 152,
07730 CDMX Mexico, Mexico

Fig. 1 Reaction scheme for obtaining BTX, LP, and naphtha from naphthalene derivatives in the LCO

reactions are facilitated while others are suppressed. Acidity can significantly influence the selectivity of catalysts, as for example, the distribution of microporous Brønsted acidity seemed to affect the shape-selectivity in a catalyst [15]. Therefore, a balance between acid functions and metal functions may seem to be a requirement for an optimal catalytic performance.

The initial objective of this work is to make a careful revision of the developed catalyst for the BTX production when they were studied using model molecules like tetralin, naphthalene, and naphthalene derivatives, and real feeds such as hydrotreated and non-hydrotreated light cycle oil (HDT LCO and LCO).

Therefore, the main objective of this review is the focusing on the possible correlations between catalyst chemical characteristics strictly in the BTX yield, while previous descriptions [1, 2] were more general as debating catalyst, products, and chemical conditions for petrochemicals, and fuel production from model, and real feeds. The task here was to gather all the information available regarding synthesized single metal, mixed metal, and non-metallic additives catalysts, and their compositions, surface characteristics (total surface and pore volume) and acidic properties (Brønsted/Lewis acidity). With this information available, it was expected to reach a decision regarding the best catalyst up to date to attain scientifically, the highest BTX production through correlations.

Theoretical considerations

Maximum BTX production from model molecules

Tetralin: 1 mol of tetralin (132.2 g) will produce according to previous experiments [3, 4] approximately 0.1, 0.4, 0.18, 0.09 and 0.08 mol of benzene, toluene, p-, m- and o-xylenes, respectively.

After multiplying for their respective molecular weights (78, 92, and 106 g/mol) it was calculated a 63% theoretical conversion.

Naphthalene: 1 mol of naphthalene (128.1 g) will produce according to previous experiments [3, 4] approximately 0.1, 0.4, 0.18, 0.09 and 0.08 mol of benzene, toluene, p-, m- and o-xylenes, respectively. After multiplying for their respective molecular weights (78, 92, and 106) it was calculated a total of 83.5, then a 65% theoretical conversion.

BTX equations used for comparison.

To perform a comparison, the total X yields (X_Y) were calculated when the data was available, by multiplying the hydrocracking conversion (HCK_C) by the X selectivity (X_S) (Eq. 1.) where the X can be: BTX (BTX), light hydrocarbons i.e. paraffin and isoparaffin derivatives (LP), non-aromatic hydrocarbons i.e. naphthenes (HYD), C_{9+} -alkylbenzenes ($C_{9+}ALB$), tetralin and indene type compounds (TI), and heavy hydrocarbons, i.e. naphthalene, phenanthrene derivatives (HH). In some cases, mainly in the real feed studies, the liquid fraction (LF) was also considered (Eq. 2). And a more accurate yield could be obtained (X_{YLF}):

$$X_Y(\%) = HCK_C \times X_S / 100 \quad (1)$$

$$X_{YLF} = X_Y \times LF / 100 \quad (2)$$

Results and discussion

BTX production from tetralin

A summary of the characteristics of the catalyst prepared for BTX production from tetralin is shown in Table 1.

The order of the references depended on the time of publication.

Effect of the acidity of the support

Sato et al. [16, 17] studied the effect of different supports, USY, HY, and mordenite (MOR) on a NiW catalyst. The loading of NiW (NiO-3.5%, WO₃-24.0%) was performed by the usual incipient wetness technique. The testing of the materials was as follows: batch reactor, temperature: 350 °C, reaction time: 1 h, catalyst weight: 0.3 g, tetralin: 5 mL, initial H₂ pressure: 6.1 MPa. The best performance for producing BTX in this work was obtained after using the NiW/USY with a 45% tetralin conversion that provided a 9% total BTX yield, followed by the NiW/HY with a 4% (23% tetralin conversion). The NiW/MOR only provided 1.5% of BTX. Instead of BTX, NiW/USY and NiW/HY produced heavy compounds (HH) as the main product with a 20 and 13% total yield. NiW/MOR due to the extremely low tetralin conversion (10%), formed only, besides BTX, 1.5% of indanes (TI), and 1.5% of heavy compounds (HH). The material on Al₂O₃ did not provide BTX but decalin (41, 95, and 39% for conversion, selectivity, and total yield, respectively). They conclude that the ring-opening (RO) of tetralin needs relatively strong acid sites. Comparing the two zeolites with strong acidity, the acid sites of USY function for hydrocracking of tetralin, whereas those of MOR catalyze isomerization or excess cracking to gaseous products. The high hydrocracking activity of USY may be related to the hydrogen transferability of USY. In tetralin hydrocracking, NiW hydrogenates aromatic compounds which are the result of the tetralin dehydrogenation.

Ferraz et al. [18] prepared three NiMo catalysts by wet impregnation of the following extruded supports: pure alumina (Alu), silica–alumina (SiAl), and Y zeolite (30%, SiO₂/Al₂O₃ = 13.7 mol/mol) on alumina (AluZ). All the extruded supports were previously calcined at 550 °C. Catalysts were prepared by successive molybdenum nickel impregnation with the following metal content: 20% MoO₃ and 4% NiO. First, a solution of (NH₄)₆Mo₇O₂₄ followed by Ni(NO₃)₂·6H₂O. Experimental tests were conducted in a fixed bed reactor at 310 °C, 4 MPa pressure, WHSV of 4 h⁻¹, feed flow rate of 13.5 mL/h, and 600 N mL/min of hydrogen. The observed total BTX yields were 0.2, 2, and 16% for the NiMo/Alu, NiMo/SiAl, and NiMo/AluZ, respectively. They observed an increase in the global conversion of tetralin with increased support acidity. This increase was observed both for the formation of aromatic hydrocarbons and for the hydrogenated compounds (HYD), being the last ones the main products with total yields of 5, 6, and 11 wt.% for the NiMo/Alu, NiMo/SiAl, and NiMo/AluZ, respectively. The higher yield of aromatic

products when acid supports were used was assigned to the protonation of the tetralin molecule, which leads to isomerization, naphthenic ring-opening, and cracking reactions. The yield of cracking products, especially benzene, with the NiMoS/AluZ catalyst increased significantly even in moderate tetralin conversions (19, 28, and 53%).

Laredo et al. [3] prepared mixtures using pellets of a commercial NiMo/Al₂O₃ catalyst with ZSM-5 zeolite that were crushed, sieved to 40/60 mesh, dried in an oven at 120 °C for 2 h, and then tested separately and in mixtures of 20/80, 30/70, and 50/50 NiMo/zeolite wt.% ratios. The total BTX yield went from 10% for the NiMo/Al₂O₃ alone to 59% with the ZSM-5. NiMo/ZSM-5 mixtures provided 35, 45, and 53% for the 50/50, 30/70 and 20/80 mixtures, respectively, at 500 °C, 4.9 MPa, H₂/feed volume ratio of 267 m³/m³, and LHSV of 1.3 h⁻¹. The main secondary product was naphthalene with a presence of 23, 15, and 13%, in the same order. Some hydrogenated products like decalin were produced in the following order: 0, 7, and 4%. As higher was the zeolite content, the higher the Brønsted acidity and the higher the BTX total yield. However, the deactivation of the catalyst due to the lack of metallic function was also faster.

Effect of the support structure

Sato et al. [19] prepared over two kinds of HY zeolites obtained after ion-exchanged cycles using an aqueous solution of ammonium sulfate (3 mol/L) at 95 °C from a commercial NaY(TO) with a framework Si/Al ratio of 2.8, and NaY(CE) with a framework Si/Al ratio of 4.1. The supports were prepared by hydrothermal synthesis using 15-crown-5 as a template. NiMo/HY catalysts (NiO = 1.7%, MoO₃ = 6.7%) by a successive molybdenum nickel impregnation method using aqueous solutions of (NH₄)₆Mo₇O₂₄ and Ni(NO₃)₂·6H₂O, then drying, calcining, and sulfiding prior to the test (400 °C, 5% H₂S/H₂, atmospheric pressure, 2 h). Both zeolites were found to possess similar micropore structures, but different mesopore structures. For both catalysts, the majority of NiMo sulfides were dispersed in the micropores of zeolites. In the NiMo/HY(TO) with mesopores, NiMo sulfides were also located inside the mesopores, whereas in the NiMo/HY(CE), NiMo sulfides were deposited on the external surface of zeolite particles. The hydrocracking of tetralin was carried out in an autoclave with an electric furnace that was waved with a rocking system during the reaction. The experimental conditions were as follows: 5 mL of tetralin, 0.3 g of catalyst, initial hydrogen pressure of 5.9 MPa, reaction temperature of 350 °C, and reaction time of 5–60 min. After the reaction, no significant difference was observed in the catalytic activities of the two NiMo/HY catalysts, being the BTX total yield of 13% for NiMo/HY(TO) and 11% for NiMo/HY(CE). As in their previous works [16, 17] the main product was not

Table 1 Chemical and physical characteristics of the catalyst designed for tetralin hydrocracking

Name	Metal 1	Wt.%	Metal 2	Wt.%	Support	S_{BET} , m^2/g	V_{poro} , cm^3/g	C_L , $mmol/g$	C_B , $mmol/g$	Total acidity, $mmol/g$	Ref
NiW/USY	Ni	2.8	W	16	USY	453.1	0.065	0.56	0.55	1.11	16
NiW/HY	Ni	2.8	W	16	HY	453.7	0.062	0.64	0.22	0.86	
NiW/MOR	Ni	2.8	W	16	Mordenita	320.3	0.023	0.73	0.69	1.42	
NiW/USY	Ni	2.8	W	16	USY	453.1	0.065				17
NiW/Al ₂ O ₃	Ni	2.8	W	16	USY	152.3	0.461				
NiMo/Alu	Ni	3.4	Mo	13.1	Al ₂ O ₃	150	0.4			0.47	18
NiMo/Al-Si	Ni	3.6	Mo	14.2	Al-Si	274	0.45			0.55	
NiMo/AluZ	Ni	3.4	Mo	12.3	Al-Y zeolite	239	0.4			0.7	
NiMo/HY (TO)	Ni	1.3	Mo	4.5	NaY (TO) Si/Al = 2.8	467	0.125				19
NiMo/HY (CE)	Ni	1.3	Mo	4.5	NaY (CE) Si/Al = 4.1	497	0.054				
Mo/BZ (90/10)			Mo	8	Beta/ZSM-5 (90/10)						20
Mo/HY			Mo	8	H-Y	871	0.52				
Ni(2)/H-Beta	Ni	2			H-Beta Si/Al = 75						21
Ni(2)/H-Beta	Ni	2			H-Beta Si/Al = 75						
Ni(1)/H-Beta	Ni	1			H-Beta Si/Al = 75						22
Ni(3)/H-Beta	Ni	3			H-Beta Si/Al = 75						
Ni(5)/H-Beta	Ni	5			H-Beta Si/Al = 75			0.09	0.1	0.19	
Ni(10)/H-Beta	Ni	10			H-Beta Si/Al = 75						
Ni(2)Sn(3)/H-Beta	Ni	2	Sn	3	H-Beta Si/Al = 75						
Ni(5)Sn(3)/H-Beta	Ni	5	Sn	3	H-Beta Si/Al = 75						
Ni(5)Sn(5)/H-Beta	Ni	5	Sn	5	H-Beta Si/Al = 75						
Co(3)Mo(8)/H-Beta	Co	3	Mo	8	H-Beta Si/Al = 75						
Ni(2)Sn(3)/H-Beta	Ni	2	Sn	3	H-Beta Si/Al = 38						
Mo/H-Beta-1			Mo	8.4	H-Beta 1 (Si/Al 25)	536		0.64	0.53	1.17	23
CoMo/H-Beta-1	Co	2.6	Mo	8.3	H-Beta 1 (Si/Al 25)	502		0.66	0.46	1.12	
CoMo/H-Beta-2	Co	2.4	Mo	8.3	H-Beta 1 (Si/Al 75)	480		0.29	0.38	0.67	
CoMo/H-Beta-3	Co	2.5	Mo	8.4	H-Beta 1 (Si/Al 150)	448		0.3	0.12	0.42	
CoMo (0.5)/H-Beta	Co	2.82	Mo	9	H-Beta (Si/Al 25)	502					24
CoMo (1)/H-Beta	Co	4.52	Mo	7.4	H-Beta (Si/Al 25)	511					
CoMo (1.5)/H-Beta	Co	5.79	Mo	6.3	H-Beta (Si/Al 25)	478					
NiSn/H-Beta	Ni	5	Sn	3	Beta			0.12	0.11	0.23	25
NiSn/B Z (10)	Ni	5	Sn	3	Beta/ZSM-5 (90/10)			0.16	0.13	0.29	
NiSn/B Z (20)	Ni	5	Sn	3	Beta/ZSM-5 (80/20)			0.22	0.15	0.37	
NiSn/B Z (30)	Ni	5	Sn	3	Beta/ZSM-5 (61.5/38.5)			0.29	0.17	0.46	
NiSn/Z	Ni	5	Sn	3	ZSM-5			0.69	0.38	1.07	
NiW/H-Beta	Ni	2.7	W	19	Beta						

Table 1 (continued)

Name	Metal 1	Wt.%	Metal 2	Wt.%	Support	S_{BET} , m ² /g	V_{poro} , cm ³ /g	C_L , mmol/g	C_B , mmol/g	Total acidity, mmol/g	Ref
CoMo/H-Beta	Co	3	Mo	8	Beta						
NiMo/H-Beta	Ni	3	Mo	8	Beta						
NiW/B Z (10)	Ni	2.7	W	19	Beta/ZSM-5 (90/10)						
CoMo/B Z (10)	Co	3	Mo	8	Beta/ZSM-5 (90/10)						
NiMo/B Z (10)	Ni	3	Mo	8	Beta/ZSM-5 (90/10)						
NiMo/Al ₂ O ₃	Ni	3.4	Mo	15	Al ₂ O ₃	180–350	0.45–0.65	0.34	0.05	0.39	3
ZSM-5					ZSM-5			0.18	0.17	0.35	
NiMo/Al ₂ O ₃ /ZSM-5 (50/50)	Ni	1.7	Mo	7.5	Al ₂ O ₃ /ZSM-5 (50/50)			0.26	0.11	0.37	
NiMo/Al ₂ O ₃ /ZSM-5 (30/70)	Ni	1.1	Mo	4.5	Al ₂ O ₃ /ZSM-5 (30/70)			0.23	0.14	0.36	
NiMo/Al ₂ O ₃ /ZSM-5 (20/80)	Ni	0.7	Mo	3	Al ₂ O ₃ /ZSM-5 (20/80)			0.21	0.15	0.36	

BTX but heavy compounds (HH), present in amounts of approximately 25 and 23% respectively, while the tetralin conversion was 50 and 45%, in the same order. Apparently, the inherent similarity of microporous structures generates similar catalytic activities [12].

Recently, Oh et al. [20] published the results of the hydrocracking of tetralin using molybdenum (8 wt.%; (NH₄)₆Mo₇O₂₄·4H₂O) on a hybrid zeolite formed by H-Beta (SiO₂/Al₂O₃ = 75) and HZSM-5 (SiO₂/Al₂O₃ = 30) in a 90/10 in weight mechanical mixture, and on an HY (FAU structure, SiO₂/Al₂O₃ = 80) by wet impregnation. They studied these catalysts using tetralin as a model compound to observe the effect of mesoporosity in the hydrocracking process at the following experimental conditions: 450 °C, WHSV = 2.0 h⁻¹, total pressure = 6 MPa, H₂/feed = 1972 mL/mL. A temperature of 450 °C was required for the Mo-S/H-Y catalyst to achieve the near-complete conversion of tetralin because of the low acidity of H-Y. Mo-S/H-Y also produced a much larger yield (11.9%) of alkylbenzenes and a much lower BTX yield (37.3%). Mo-S/BZ(90:10) catalyst produced 53% of BTX plus about 7% of other alkylbenzenes, giving a total of 60% mono-aromatics. On the other hand, the yield of naphtha over the Mo-S/H-Y catalyst reached 20.9%, which was 3.6 times that achieved over the Mo-S/BZ (90:10) catalyst (5.8%). Hence, the mesoporous Mo-S/H-Y catalyst was not an active or selective hydrocracking catalyst compared to Mo-S/BZ (90:10) when tetralin was used as a model feed. As a partial conclusion the authors decided that because actual HDT LCO contains a significant fraction of large tri + ring aromatic molecules, to increase the conversion of large molecules in the LCO and thereby to enhance the BTX yield from real feeds, a small amount of H-Y zeolite (5 or 10%) can be useful. Results regarding this observation will be discussed in the real feed section.

Effect of the metal and content

Choi et al. [21] prepared Ni/H-Beta by wet impregnation of an aqueous solution of nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O) on H-Beta (SiO₂/Al₂O₃ = 75). The Ni loading amount was 2 wt.%. The main product was BTX with 41% maximum total yield obtained at 450 °C WHSV of 2 h⁻¹, 4 MPa, and H₂/tetralin mole ratio of 8. Other products obtained in lesser amounts were non-aromatic hydrocarbons (HYD), C₉₊-alkylbenzenes (C₉₊ALB), and heavy aromatic compounds (HH: i.e. naphthalene derivatives) with total yields of 6.4, 2.5 and 5.5%, respectively.

The same group [22] carried out a more detailing study by changing the nickel contents (1, 2, 5 and 10%) that were prepared by wet impregnation of an aqueous solution of Ni(NO₃)₂·6H₂O on H-Beta with two different SiO₂/Al₂O₃ ratios (38 or 75). They also prepared NiSn/H-Beta catalysts

by a sequential wet impregnation method. The tin precursor solution, which was prepared by dissolving $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 1 M HCl solution, was first impregnated on H-Beta followed by drying, then an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was impregnated on the Sn-impregnated catalyst. For comparison purposes, they also prepared a Co(3)-Mo(8)/H-Beta catalyst by a wet impregnation method with metal precursors $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. The highest BTX total yields of 46, 48, and 47% were obtained with Ni(5)Sn(3)/H-Beta, Ni(5)Sn(5)/H-Beta, and Co(3)Mo(8)/H-Beta, respectively, when reacting at the same experimental conditions: 450 °C WHSV of 2 h^{-1} , 4 MPa, and H_2 /tetralin mole ratio of 8. BTX were the main products of this reaction, some other products found in lesser quantities were light hydrocarbons (LP: 3, 5, and 8%) C_{9+} -alkylbenzenes (C_{9+}ALB : 12, 9, and 12%), tetralin, and indane derivatives (TI: 1, 0.7, and 0.6%), and heavy hydrocarbons i.e. naphthalene derivatives (HH: 1, 6, 4, and 1.6%) for the same catalyst at the same experimental conditions. The effect of the different metal and content was almost negligible.

Upare et al. [23] prepared cobalt promoted Mo/H-Beta catalysts using Beta (β) zeolite with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratios of 25 ($\beta 1$), 75 ($\beta 2$), 150 ($\beta 3$) and mordenite (MOR) with $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 20. The molybdenum catalysts were prepared by incipient wetness impregnation method using appropriate concentrations of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. The cobalt promoted (3.3%) catalysts were prepared by co-impregnation of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ on Beta zeolite supports. The CoMo/H-Beta-1 catalyst gave the highest BTX yield of 42% followed by the Mo/H-Beta-1 with 34% and CoMo/H-Beta-2 with 33% at 380 °C, 8 MPa, 1.6 h^{-1} LHSV, and H_2 flow rate of 100 mL/min, being present in the highest conversion. Other compounds present in lesser amounts were C_{9+} -alkylbenzenes (C_{9+}ALB) being 7, 10, and 10% in the same order. In this case, not only the bimetallic presence was superior in the BTX production than the monometallic catalyst [12, 14], but also the support type (Beta-1 versus Beta-2) mattered, having the former higher Brønsted, Lewis, and total acidities.

Continuing with their study, Upare et al. [24] synthesized the catalysts CoMo (0.5)/H-Beta, CoMo (1.0)/H-Beta, and CoMo (1.5)/H-Beta where the number in parentheses is the cobalt/molybdenum ratio [23] while maintaining the same H-Beta support ($\text{Si}/\text{Al} = 25$). By testing these catalysts for the tetralin hydrocracking at 370 °C, 8 MPa, 1.6 h^{-1} LHSV, and H_2 flow rate of 100 mL/min, they obtained BTX total yields of 42, 36 and 33%, in the order: CoMo (0.5)/H-Beta, CoMo (1.0)/H-Beta, and CoMo (1.5)/H-Beta, respectively. C_4 - C_7 paraffins (LP: 8, 7.4 and 6%), C_{9+} -alkylbenzenes (C_{9+}ALB : 6.6, 6.8 and 6.7%) were also formed in the same

order. This result obviously followed the findings described by Charisiou et al. [14], that the bimetallic ration was also important in the catalytic behavior.

Shin et al. [25] prepared catalysts with various metallic components including Ni, NiSn, CoMo, NiMo, and NiW supported on H-Beta ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 38.0$ or 75.0) and hybrid zeolites by wet impregnation. The hybrid zeolites were prepared by physical mixing of H-Beta and HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) with different HZSM-5 contents and are denoted as BZ(x) hereafter, where x indicates the HZSM-5 content in %. Zeolite-supported Ni and NiSn catalysts with Ni and Sn contents of 5 and 3%, respectively, were prepared with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ as the metal precursors. The NiSn was supported on BZ(x) ($x = 10, 20$, and 38.5) to study the effect of HZSM-5 content in the hybrid zeolites on the tetralin hydrocracking. The sulfide-metal catalysts, CoMo (Co = 3% and Mo = 8%), NiMo (Ni = 3% and Mo = 8%), and NiW (Ni = 3.5% and W = 24%) were supported on H-Beta and BZ(x) by wet impregnation using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, and $(\text{NH}_4)_6\text{W}_{12}\text{O}_{40} \cdot 5\text{H}_2\text{O}$. All the tested catalysts at 425 °C, 4 MPa, and WHSV of 2 h^{-1} produced a rather high total BTX yield between 44 and 53%, providing the best results the NiSn/H-Beta ZSM-5 (90/10) with 52% and NiMo/H-Beta ZSM-5 (90/10) with 53%. Secondary products were naphtha like compounds (HYD) in yields between 1 and 11%, being for NiSn/H-Beta ZSM-5 (90/10) 7.4% and NiMo/H-Beta ZSM-5 (90/10) 6%. Other important secondary products were C_{9+}ALBs in amounts between 2 and 16%. NiSn/H-Beta ZSM-5 (90/10) with 6% and NiMo/H-Beta ZSM-5 (90/10) with 7%. Other products found were indene (TI) and naphthalene derivatives (HH) in lesser amounts. It is inferred that the NiMo/BZ catalyst (10) is a good candidate for use in the selective hydroconversion of polyaromatic hydrocarbons (PAH) to produce high-value BTX, as its metallic, acidic, and structural properties are well balanced.

Partial conclusion

In this work, a relationship between the catalyst characteristics and the BTX total yield was the main task. Figure 2 shows the most important results regarding BTX total yields [3, 20–25]. A total BTX yield higher than 53% was never attained using a hydrocracking catalyst of any type, due to the inevitable gas formation and other C_{9+} -alkylbenzenes formed. The theoretical 63 wt.% BTX conversion was never reached. As it can be seen from the results, BTX was never formed solely but accompanied by hydrogenated hydrocarbons (naphthene compounds) and other alkylbenzenes. The only correlation available in this case, was the relation between the metal content/BET

Fig. 2 Main results for the effect of the catalyst in the BTX total yield from tetralin hydrocracking

surface ratio versus the BTX total yield (wt.%) (Fig. 3), which indicates that the density of metal sites is an important factor in the BTX yield. On the other hand, it seems logical that a better dispersion of the metals contributes to the accessibility of the molecules to the catalytic sites and therefore, increased the selectivity of the reaction [12]. According to Fig. 4, the best catalysts for BTX production were those conformed by Ni, CoMo, NiMo, or NiSn over zeolite H-Beta. Adding a 10 wt.% of ZSM-5 to the H-Beta, the BTX formation can be improved [3, 20, 25]. After dividing the most important BTX yields in groups (Fig. 4) it is noteworthy that the first group, which covers BTX yields from 40–45 wt.%, is not that different from the best performance group (50–53%) of catalysts. It is evident that a balance between metal and acid function are needed to obtain a higher yield and this does not depend on a specific metal or support.

Fig. 3 Effect of the metal content/BET surface ratio on the BTX total yield from tetralin

BTX production from naphthalene and naphthalene derivatives

A summary of the characteristics of the catalyst prepared for BTX production from naphthalene derivatives is shown in Table 2. The order of the references depended on the time of publication.

Effect of the acidity and support structure

Arribas and Martínez [26] prepared Pt/USY catalysts by impregnating the USY zeolites with a 0.2 N HCl solution containing the required amount of hexachloroplatinic acid to obtain a nominal concentration of 1% Pt in the final catalyst and used 1-methylnaphthalene (1-MN) as a representative molecule of the diaromatics present in distillate fuels. Five different USY zeolites were prepared and used as supports: commercial USY-1 (CBV500, NH_4^+ form); USY-3

Fig. 4 Worst to the best catalyst for tetralin hydrocracking for BTX production

(CBV712, NH_4^+ form) and USY-5 (CBV760, H^+ form). The protonic forms of USY-1 and USY-3 were produced by calcination (500 °C, 3 h). USY-2 and USY-4 were prepared by NH_4^+ exchange from a commercial NaY sample, followed by washing until the absence of chlorine, drying at 100 °C overnight, and steamed at 600 and 700 °C for 3 and 5 h, respectively. Finally, the sample USY-4 was further steamed at 760 °C for 8 h. Ammonium exchange treatments were carried out with a 2.5 N aqueous solution of NH_4Cl at 80 °C for 2 h under agitation. Using a fixed bed reactor at the following experimental conditions: 325–355 °C, $\text{WHSV} = 2.0 \text{ h}^{-1}$, total pressure = 4 MPa, H_2/HC of 30 mol/mol, the main products were methyltetralin and dimethylindane with total yields between 41 and 81%, following by decalin derivatives (D, 8 and 28%). The total BTX conversion was only between 6 and 16%. These materials presented the highest BET surface and Brønsted/Lewis ratio. According to the authors, both the framework and extraframework composition of the USY zeolite influenced the acidic and catalytic properties of the Pt/USY catalysts, particularly for those reactions requiring the presence of Brønsted acid sites, i.e. isomerization, ring-opening, cracking, and dealkylation. In general, noble metal catalysts are not preferred for hydrocracking reactions due to their sensibility to sulfur and nitrogen compounds presented in real feeds [2, 10, 14].

Kim et al. [27] studied the hydrocracking of naphthalene to BTX by a Ni_2P /zeolite supported catalyst. The supports used in this study were zeolite Beta, USY, ZSM-5, and SiO_2 .

Supported Ni_2P catalysts were prepared by incipient wetness impregnation of aqueous metal phosphate precursors, followed by temperature-programmed reduction (TPR) in flowing hydrogen. The initial Ni/P ratio in the precursors was fixed at 0.5. The amount of Ni loading was fixed at 1.5 mmol/g of support. The supported nickel phosphate precursor was prepared by incipient wetness impregnation of a solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$, followed by drying and calcination. The $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst was found active only for the hydrogenation of naphthalene, producing tetralin and decalin at 3.0 MPa and 400 °C. BTX formation was provided for the $\text{Ni}_2\text{P}/\text{Beta}$, demonstrating the bifunctional catalytic activity which was attributed to its unique nature of moderate acidity and porosity combined with hydrogenation activity of well-dispersed Ni_2P phase [12]. The authors claimed naphthalene conversions between 90–99% and BTX yield up to 94.4% for the $\text{Ni}_2\text{P}/\text{Beta}$ zeolite, however, due to the shortness of the communication, it was required to add some assumptions for attaining a more realistic value: (1) Even if the naphthalene conversion was 99%, the mass balance will give a liquid yield up to 65% maximum. (2) Usually, not only BTX was formed but other C_{9+} -alkyl-aromatics, therefore the BTX yield of 61% must be taken with caution as the following publications from the same authors probed to be [28–30].

To obtain bi-functional catalysts with high activity for the selective hydrocracking of 1-methylnaphthalene to BTX, Kim et al. [28] prepared a NiW-supported catalyst

Table 2 Chemical and physical characteristics of the catalyst designed for naphthalene derivatives hydrocracking

Name	Metal 1	Wt.%	Metal 2	Wt.%	Co-cat	Wt.%	Support	S _{BET} , m ² /g	V _{poro} , cm ³ /g	C _L , mmol/g	C _B , mmol/g	Total acid-ity, mmol/g	Ref
Pt/USY	Pt	1					USY 1	594	0.4	0.033	0.089	0.122	26
Pt/USY	Pt	1					USY 2	467	0.39	0.009	0.014	0.023	
Pt/USY	Pt	1					USY 3	603	0.47	0.019	0.055	0.074	
Pt/USY	Pt	1					USY 4	425	0.38	0.008	0.010	0.018	
Pt/USY	Pt	1					USY 5	587	0.46	0.011	0.020	0.031	
Ni ₂ P/Beta	Ni	8.8			P	2.3	Beta (Si/Al=12.5)	407	0.31				27
Ni ₂ P/USY	Ni	8.8			P	3.1	USY (Si/Al=40)	620	0.23				
Ni ₂ P/SiO ₂	Ni	8.8			P	3.1	ZSM6 (Si/Al=15)	264	0.07				
Ni ₂ P/ZSM-5	Ni	8.8			P	5.8	SiO ₂	123	0.67				
NiW/Beta(25)	Ni	6.4	W	15.6			Beta (Si/Al=25)	399	0.37			1.081	28
NiW/Beta(38)	Ni	6.4	W	15.6			Beta (Si/Al=38)	426	0.22			0.842	
NiW/Beta(55)	Ni	6.4	W	16.6			Beta (Si/Al=55)	384	0.2			0.776	
NiW/Beta(80)	Ni	6.4	W	15.6			Beta (Si/Al=80)	357	0.19			0.673	
Ni(1)W(1)/HY(12)	Ni	6.4	W	15.6			HY (Si/Al=12)	468	0.27			1.090	29
Ni(1)W(1)/HY(30)	Ni	6.4	W	15.6			HY (Si/Al=30)	575	0.35			0.810	
Ni(1)W(1)/HY(60)	Ni	7.4	W	15.6			HY (Si/Al=60)	491	0.34				
Ni(1)W(1)/HY(80)	Ni	8.4	W	15.6			HY (Si/Al=80)	438	0.28				
K(0.1)Ni(1)W(1)/HY(12)	Ni	6.4	W	16.6	K	0.3	HY (Si/Al=12)	495	0.29			1.080	
K(0.3)Ni(1)W(1)/HY(12)	Ni	6.4	W	15.6	K	0.9	HY (Si/Al=12)	487	0.28			0.910	
K(0.5)Ni(1)W(1)/HY(12)	Ni	7.4	W	16.6	K	1.5	HY (Si/Al=12)	481	0.28			0.730	30
NiW/H-Beta	Ni	6.5	W	20.2			H-Beta (Si/Al 38)						
NiW/H-Beta TMOS	Ni	6.5	W	20.2			H-Beta (Si/Al 38) TMOS						
NiW/H-Beta TEOS	Ni	6.5	W	20.2			H-Beta (Si/Al 38) TEOS						
NiW/H-Beta TBOS	Ni	6.5	W	20.2			H-Beta (Si/Al 38) TBOS						
Ni ₂ P/Beta-N	Ni	8.8			P	9.3	Beta nano sized crystals	407		0.028	0.037	0.065	31
Ni ₂ P/Beta-M	Ni	8.8			P	9.3	Beta micro sized crystals	402		0.03	0.033	0.063	
NiW/Beta-1	Ni	4	W	19.8			Beta-1 (Si/Al=50)	475	0.2	0.14	0.72	0.860	32
NiMo/Beta-1	Ni	4	Mo	16.7			Beta-1 (Si/Al=50)			0.12	0.63	0.750	
CoW/Beta-1	Co	3.9	W	19.8			Beta-1 (Si/Al=50)	480	0.26	0.09	0.4	0.490	
CoMo/Beta-1	Co	3.9	Mo	16.7			Beta-1 (Si/Al=50)			0.11	0.55	0.660	
20 W/Beta-1			W	15.9			Beta-1 (Si/Al=50)			0.11	0.49	0.600	
25 W/Beta-1			W	19.8			Beta-1 (Si/Al=50)	495	0.28	0.09	0.43	0.520	
30 W/Beta-1			W	23.9			Beta-1 (Si/Al=50)			0.07	0.35	0.420	
25 W/Beta-2			W	19.8			Beta-2 (Si/Al=70)	489	0.28	0.04	0.23	0.270	
25 W/Beta-3			W	19.8			Beta-3 (Si/Al=300)			0.24	0.69	0.930	
5 W(1)/Beta	W	4					Beta	504	0.09	0.148	0.296	0.44	33

Table 2 (continued)

Name	Metal 1	Wt. %	Metal 2	Wt. %	Co-cat	Wt. %	Support	S_{BET} , m ² /g	V_{poro} , cm ³ /g	C_L , mmol/g	C_B , mmol/g	Total acidity, mmol/g	Ref
5 W(1)/Beta-0.10 TEOS	W	4					Beta (0.10 TEOS)			0.148	0.294	0.44	
5 W(1)/Beta-0.15 TEOS	W	4					Beta (0.15 TEOS)			0.146	0.293	0.44	
5 W(1)/Beta-0.20 TEOS	W	4					Beta (0.20 TEOS)	506	0.09	0.145	0.291	0.44	
10 W(1)/Beta-0.15 TEOS	W	8					Beta (0.15 TEOS)	478	0.08	0.14	0.282	0.42	
2 W(1)/Beta-0.15 TEOS	W	1.6					Beta (0.15 TEOS)			0.153	0.307	0.46	
CoMo/AY	Co	6.2	Mo	8			HY (Si/Al = 8)/Al ₂ O ₃ (3/2)			0.172	0.12	0.192	35
NiMo/AY	Ni	2.4	Mo	8			HY (Si/Al = 8)/Al ₂ O ₃ (3/2)			0.205	0.127	0.332	

with different acidity. The catalysts were synthesized from $\text{Ni}((\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}, (\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot \text{H}_2\text{O})$, and dealuminated Beta zeolites ($\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio = 25, 38, 55, and 80) by wet impregnation method. 1 g of the catalyst with nickel (Ni, 1 mmol, 6.4%) and tungsten (W, 1 mmol, 15.6 wt.%) on H-Beta was sulfided in H_2S (10%)/ H_2 flow at 350 °C for 3 h. The sulfided catalyst was loaded in the fixed-bed reactor and pretreated in H_2 flow at 400 °C and atmospheric pressure for 8 h. After, the pressure increased to 5 MPa and both the liquid feed of 1-methylnaphthalene (0.037 cm³/min) and H_2 (175 cm³/min) was passed through the catalyst bed. The catalysts with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 25, 38, 55, and 80 showed an acidity of 1.081, 0.842, 0.776, and 0.673 mmol NH_3 /g, respectively. A fair amount of hydrocracking gases was formed with the more acidic catalysis (34–46%). Likewise, catalysts with an acidity of 1.081, 0.842, and 0.776 mmol NH_3 /g offered BTX yields of 33, 39, and 45%, respectively. The catalyst with an acidity of 0.673 mmol NH_3 /g showed a BTX yield of only 9%. Other compounds were formed in lesser amounts: light (LP: 2–7%) and cyclic alkanes (HYD: 1–9%), C_{9+} -alkylbenzenes (C_{9+}ALB : 4–10%), and other heavy hydrocarbons (HH: 4–12%). The obtained results indicated that the acidity of the catalyst has an important role as active sites for the selective ring-opening of 1-methylnaphthalene [3, 12], however, acidity is not directly proportional to the BTX yield.

It is known that the acidity of the catalyst is important for the hydrocracking of multi-ring aromatics [3, 12], therefore, to obtain BTX, Lee et al. [29] submitted 1-methylnaphthalene to a selective ring-opening reaction over KNiW/HY catalysts with different acidity in a fixed-bed flow reactor. The catalysts were prepared by loading HY zeolites ($\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 12 and 30) with 1 mmol/g of nickel (Ni: 6.4%), 1 mmol/g of tungsten (W: 15.6%) and 0.1, 0.3, and 0.5 mmol/g of potassium (K: 0.3, 0.9 and 1.5%) metals via a wet impregnation method. Thus, the hydrogen-form zeolite was impregnated with an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot \text{H}_2\text{O}$, and KNO_3 , and the water was eliminated from the material, dried, and calcinated. The catalyst was sulfided in H_2S (10%)/ H_2 flow at 350 °C for 3 h. Before the reaction test, 1 g of catalyst was reduced using H_2 flow under atmospheric pressure at 400 °C for 8 h. The activity test was carried out using 1-methylnaphthalene (0.037 cm³/min) and H_2 (cm³/min) at 5 MPa and 400 °C. The sequence of the acidity was $\text{Ni}(1)\text{W}(1)/\text{HY}(12) > \text{K}(0.1)\text{Ni}(1)\text{W}(1)/\text{HY}(12) > \text{K}(0.3)\text{Ni}(1)\text{W}(1)/\text{HY}(12) > \text{Ni}(1)\text{W}(1)/\text{HY}(30) > \text{K}(0.5)\text{Ni}(1)\text{W}(1)/\text{HY}(12)$. The acidity decreased with the increase of $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of the HY zeolite and the K in the catalyst. The catalysts with a potassium content of 0.1, 0.3, and 0.5 mmol/g (0.3, 0.9 and 1.5%) showed a BTX selectivity 21.4, 24, and 8% providing a BTX total yield of 21, 23, and 7%, respectively. In this case, other hydrocarbons were produced, in

similar amounts, like light (LP: 16–19%) and cyclic alkanes (HYD: 10–27%), C_{9+} -alkylbenzenes (C_{9+} ALB: 4–17%), and other heavy hydrocarbons (HH: 5–14%). The addition of K to the NiW/HY catalyst improved the catalytic activity for the selective ring-opening of 1-methylnaphthalene due to the optimization of catalyst acidity by the electronic surface modification.

Lee et al. [30] hydrocracked 1-MN using NiW/silylated Beta zeolites. The bifunctional catalysts were prepared as follows. 2 g of H-Beta zeolite, which was obtained by calcination of its NH_4^+ form with SiO_2/Al_2O_3 mole ratio of 38. The silylation was carried out by dissolving the silylation agent (TMOS, TEOS or TBOS) in 50 mL of hexane heated at 70 °C, in the amount required to obtain a loading of 4.0% SiO_2 . After 1 h of reaction, the hexane was eliminated by vacuum, and the solid product was dried and calcined. The H-Beta and the three silylated Beta zeolites were co-impregnated with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ and $(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$ in the amount required to load 1 and 1.1 mmol of Ni and W, respectively, per 1 g of zeolite; subsequently, the water was eliminated by vacuum, and the remaining solid was dried and calcined. In this case, the authors did not define the amount of BTX produced but the amount of ring-opening at 380 °C, 6.0 MPa, and $0.5\ h^{-1}$ LHSV in a continuous-flow reactor. The ring-opening of 1-methylnaphthalene will produce a series of alkyl-benzenes or mono-aromatic compounds among them BTX hydrocarbons form part. Therefore, the best catalyst for RO followed the order: NiW/H-Beta-TBOS (73%) > NiW/H-Beta-TEOS (68%) > NiW/H-Beta (62%) > NiW/H-Beta-TMOS (61%). The BTX yield can be estimated by their previous works [27–29] and considered for comparison purposes to be 20% or lower. The description of other subproducts was not given in this case.

Kim et al. [31] studied the effect of the support on the catalytic properties of Ni_2P /H-Beta nano and mesoporous catalysts on the hydrocracking of 1-MN. The supports used in this study were two kinds of Beta zeolite with different crystal sizes, namely: nano-sized (β -N) and micrometer-sized (β -M), which were loaded with 1.5 mmol of Ni/g of support and mole ratio P/Ni = 2 by incipient wetness impregnation using an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ and $(NH_4)_2HPO_4$, and followed by drying and calcination. Finally, the obtained materials were reduced and passivated using H_2 and 0.1% O_2/He , respectively, under specific conditions. The product distribution after hydrocracking 1-MN at 380 °C, 6.0 MPa, and LHSV of $0.5\ h^{-1}$. Ni_2P /Beta-N provided a higher total BTX production than Ni_2P /Beta-M. (53 vs. 49%). Due to the good BTX target performance, these catalysts produced an array of other subproducts in lesser amounts.

Studies using bifunctional catalysts

Wu et al. [32] studied the selective hydrocracking of 1-methylnaphthalene to BTX using several sulfided transition metals supported on H-Beta catalysts (Metals = NiMo, NiW, CoMo, CoW, Mo, W) in a fixed-bed reactor at 420 °C and 6 MPa. Thus, Na^+ form of Beta zeolite (SiO_2/Al_2O_3 ratio = 50 (Beta-1), 70 (Beta-2), and 30 (Beta-3)) was synthesized from silica gel, sodium hydroxide, and sodium aluminate according to the method reported in the literature. After, the synthesized zeolites were ion-exchanged two times with an aqueous solution of NH_4NO_3 to obtain the H^+ form of Beta zeolite. The catalysts were synthesized by the pore volume impregnation method. Beta zeolite supports were co-impregnated with an aqueous solution of nickel (or cobalt) nitrate, or ammonium molybdate (or tungsten) to prepare NiMo/Beta-1 (or CoMo/Beta-1, NiW/Beta-1, W/Beta-1, Mo/Beta-1, W/Beta-2, W/Beta-3) catalyst. Later, these metal-impregnated zeolites were dried at room temperature for 12 h, dried at 100 °C for 3 h, and calcined at 550 °C for 3 h in air. To achieve an isothermal plug flow fixed-bed reactor, the reactor was loaded with a mixture of catalyst and quartz sand (20–40 mesh) with a mass ratio of 1:6. The catalyst was sulfided in a mixture of 1.5% CS_2 and cyclohexane and treated with H_2 (50 mL/min) at room temperature and 6 MPa. Then, the temperature was increased to 240 °C ($7\ ^\circ C/min$), held at 240 °C for 3 h, increased to 320 °C ($3\ ^\circ C/min$), and held at 320 °C for 3 h. After, 1-methylnaphthalene (0.3 to 3 mL/h) was pumped into the reactor at a WHSV of $0.5\text{--}10\ h^{-1}$, H_2/oil mole ratio of 30, 6.0 MPa, and 420 °C. The 25 W/Beta-1 catalyst showed the best BTX yield (53%) at WHSV = $2\ h^{-1}$, H_2/oil mole ratio of 30, and 1.5 g of the mixture of catalyst and quartz sand. Conversion reached above 98% at WHSV below $1.4\ h^{-1}$, however, the best BTX yields for all the catalysts were obtained between 1.7 and $2.5\ h^{-1}$ of WHSV. At these conditions, the BTX selectivity decreased in the next order: 25 W/Beta-1 (53%) > 20 W/Beta-1, 30 W/Beta-1, 25 W/Beta-3, CoW/Beta-1 > 25 W/Beta-2 > CoMo/Beta-1 > NiMo/Beta-1 > NiW/Beta-1, Mo/Beta-1 (15%). The 20 W/Beta-1 catalyst achieved a higher BTX yield (51%) than the 25 W/Beta-1 (45%) when the WHSV was lower than $2\ h^{-1}$. As the BTX selectivity decreased, more hydrogenated products were obtained, then, the authors concluded that the hydrogenation activity of the catalysts was affected both by the metallic species and their content as well as by the acidity of the Beta support. A strong acidity increased the interaction between the acid centers and the metallic centers, decreasing the hydrogenation activity of the catalysts.

Wu et al. [33] studied in detail the hydrocracking catalysis for BTX production from naphthalene type compounds. To make the catalysis manufacture cheaper, it was prepared

via the $\text{WO}_2(\text{C}_6\text{H}_5\text{NO})_2$ complex, following the next procedure: 15 mL methanol and 0.4 g 2-methoxypyridine were added to a solution of 0.3 g tungsten hexachloride in 15 mL of acetonitrile and then stirring at room temperature for 15 min. The resultant solution was sealed in a Teflon-lined steel autoclave and heated in an oven at 150 °C for 20 h. The red complex was isolated from the product solution by extraction with diethyl ether followed by the removal of the solvent. Regarding the support, Beta zeolite was synthesized by the stream-assisted crystallization method using silica, NaAlO_2 and NaOH as silicon, aluminum, and alkali source, respectively. The obtained zeolite was first modified to its H^+ form via ion-exchange with NH_4NO_3 solution and then treated with the required amount of tetraethoxysilane (TEOS) in hexane. This mixture was stirred at room temperature for 5 h, dried and calcined. The modified zeolites were labeled Beta- x , where $x = 0.10, 0.15$, and 0.20 mL of TEOS/g of zeolite. In this line, the tungsten-based catalysts were synthesized by the incipient wetness impregnation method using the tungsten complex and the modified zeolites prepared previously. The impregnated zeolite was dried both at room temperature and 100 °C, and calcined. The catalysts were named as $y\text{W}(1)/\text{Beta}-x$, where $y = 2, 5$, and 10 wt. % of tungsten. In the same way, a blank catalyst (W/Beta) was prepared using an $(\text{NH}_4)_6\text{W}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ aqueous solution and the H-Beta zeolite unmodified. The experiments were carried out in a fixed bed reactor with WHSV referred to 1-MN, as $0.5\text{--}10\text{ h}^{-1}$, $\text{H}_2/1\text{-MN}$ mole ratio equal to 30, 6.0 MPa pressure, and 420 °C temperature. Conversion reached almost 100% for some catalyst at WHSV below 1.7 h^{-1} , however, the best BTX selectivity was obtained at WHSV between 1.5 and 8 h^{-1} . For the comparison sake, the conversion considered would be when the best BTX yield was obtained. The total BTX yield ranged from 38 to 55%, being the best the obtained with the $5\text{ W}(1)/\text{Beta}-0.15$ (55%), and the worst with the $2\text{ W}(1)/\text{Beta}-0.15$ (38%). When the BTX yields decreased the second kind of compounds produced were hydrogenated hydrocarbons (HYD: 9–13%) and C_{9+} -alkylbenzenes ($(\text{C}_{9+}\text{ALB}$: 8–10%).

Recently, Cao et al. [34] reported the hydrocracking of naphthalene over bi-functional NiMo and CoMo catalysts. These catalysts were prepared by incipient-wetness impregnation method using an aqueous solution of heptamolybdate tetrahydrate, cobalt-nitrate hexahydrate and nickel nitrate hexahydrate as Mo, Co, Ni sources, respectively, and an HY zeolite ($\text{Si}/\text{Al} = 8$)- Al_2O_3 mixture with a ratio of 1.3:2 mass as support. First, the precursor of Mo was impregnated, then the precursor of Ni or Co. The obtained solids were dried at 80 °C and calcined at 500 °C. The catalysts have a mass percentage of 12, 3, and 3% to MoO_3 , CoO, and NiO, respectively. The hydrocracking of cyclohexane solution with 1% naphthalene was carried out in a continuous-flow reactor using 1 g catalyst at 6.0 MPa and an H_2/oil ratio of 200.

Previously, the catalyst was sulfided using a cyclohexane solution with 2.5 vol. % CS_2 at 370 °C for 3 h. The CoMo catalyst showed a higher conversion of naphthalene to BTX than those of NiMo catalyst at 320–420 °C. For both catalysts, the conversions of naphthalene increased with the increasing temperature from 320 to 360 °C. The best mole yields of BTX were 22 and 20% for the CoMo and NiMo catalysts, respectively, at 340 °C. The aim of these authors was not to produce BTX but gasoline, then the BTX yields for this kind of feedstock were low.

Partial conclusion

Figure 5 shows a summary of the total BTX yield from naphthalene derivatives from the principal results [27–33]. The highest total BTX yield was 55% using a hydrocracking catalyst composed of $5\text{ W}(1)/\text{Beta}-0.15$ (TEOS) [33] remarkably like the maximum yield attained when BTX was obtained from tetralin hydrocracking (53%). The 65% theoretical conversion was never reached because not only BTX can be obtained, but also some hydrogenated hydrocarbons and other higher molecular weight alkylbenzenes, besides, with these model molecules (naphthalene and naphthalene derivatives) more hydrogenation and isomerization reactions may compete with the hydrocracking process [12].

In this case, the only relationship attainable for these results were the Brønsted/Lewis ratio versus the BTX total yield (Fig. 6). It seemed that to reach the best hydrocracking performance a balance between Brønsted and Lewis sites is required. According to Wu et al. [33] after carrying out kinetic studies of the 1-methylnaphthalene hydrocracking, they found out that the strong acidity resulted in a strong interaction between acid centers and metal centers, which can decrease the hydrogenation activity of the catalyst. On the other hand, low acidity resulted in high hydrogenation activity (high hydrogenation reaction rates) but low selective-hydrogenation activity, meaning that hydrogenation of the first and second aromatic rings can occur without giving place to hydrocracking by consecutive hydrogenation reactions. Therefore, a moderate acidity showed the highest balance of hydrogenation and cracking activity to achieve the highest BTX yields. Another important point was that the hydrogenating capacity of the metal and their synergistic effect of the promoter when it is used seem to have not significant effect on the BTX total yield. The same authors found out that the hydrogenation rates from the different metals decreased in the following order: $\text{NiW} > \text{NiMo} > \text{CoMo} > \text{CoW}$, and these results were consistent with previous studies. Figure 7 shows from the worst to the best catalyst for the naphthalene derivatives hydrocracking. In this case also, after dividing the most important BTX yields in groups (Fig. 7) it was found that the slope is steeper between the first group that covers the catalysts that

Fig. 5 Main results for the effect of the catalyst in the BTX total yield from naphthalene derivatives hydrocracking

Fig. 6 Effect of the catalysts Brønsted/Lewis ratio on the BTX total yield from naphthalene derivatives hydrocracking

provided the worst BTX yields (35–40 wt.%) and the best performance group (50–55%) of catalysts.

BTX production from real feeds

Effect of the catalyst on the BTX production

A summary of the characteristics of the catalyst prepared for BTX production from real feeds is shown in Table 3. Many of the catalysts tested were derived from previous experiments with model mixtures. However, the major challenge is to convert a real feed like LCO into valuable benzene, toluene, and xylene hydrocarbons, mainly due to the presence of another type of compounds like sulfur, nitrogen, and heavy aromatic hydrocarbons which are going to test the hydrocracking process. Therefore, usually, the real feed

requires to be hydrotreated (HDT) before the next HCK step is going to be taken [2, 4].

Upare et al. [23, 24] developed selective catalysis for the BTX production from pyrolysis fuel oil (PFO). The detailed catalysis synthesis was already described before [22]. In [23] the catalysis tested: Mo/H-Beta, CoMo/H-Beta and CoMo/MOR provided total BTX yields of 11, 20 and 5.3% at 370 °C, 8 MPa H₂, 1250 H₂/feed (v/v), and LHSV of 1.6 h⁻¹. Other products obtained were C₉₊-alkylbenzenes (C₉₊ALB) produced in the following amounts 5, 13, and 2% in the same order.

In the second effort [24], the catalyst tested CoMo(0.5)/H-Beta, CoMo(1.0)/H-Beta and CoMo(1.5)/H-Beta produced a BTX total yield of 34, 35 and 32, respectively, in a fixed bed reactor at 370 °C; 8 MPa H₂, 1250 H₂/feed (v/v); and LHSV of: 0.2 h⁻¹. Other products obtained were light paraffins

Fig. 7 Worst to the best catalyst for naphthalene derivatives hydrocracking for BTX production

(LP: 10, 10, and 15%) and C_{9+} -alkylbenzenes (C_{9+} ALB: 4, 0.5, and 2%) in the same order. Certainly, the differences in LHSV were crucial for the BTX total yield increment in [24]. It is also interesting to observe, that with a real feed, the differences between BTX production were lower among the different catalysts tested, as compared to the experiments carried out with tetralin described in the 3.1 section.

Several metals such as NiMo, CoMo, and Mo were loaded (wet impregnation) onto H-Beta (SiO_2/Al_2O_3 mole ratio = 75) on hybrid zeolites by Oh et al. [34]. The hybrid zeolites were prepared by physically mixing the H-Beta (B) and H-ZSM-5 (Z) (SiO_2/Al_2O_3 mole ratio = 30) zeolites using different H-ZSM-5 amounts and will be referred to as BZ(x), hereafter x indicates the H-ZSM-5 content in %. The zeolite-supported sulfide-metal catalysts were prepared by wet impregnation using $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ as metal sources. The catalysts were tested at several experimental conditions to evaluate the best catalytic mixture and the catalyst that performed the best was tested at 425 °C, 6 MPa, WHSV of 2 h⁻¹, and 1975 H₂/feed volume ratio using a full range distillation hydro-treated light cycle oil (HDT LCO 2/1, Final boiling point (FBP) = 386 °C) and a fractionated hydrotreated light cycle oil (HDT LCO 2/2, FBP 334 °C). When using the HDT LCO 2/1, the BTX total yields were 29% for NiMo/BZ (10) and Mo(8)/BZ (10) catalysts. No naphthalene, tetralin or indene derivatives were obtained at these experimental conditions. Light paraffins (LP: 17 and 29%) and C_{9+} -alkylbenzenes

(C_{9+} ALB: 16 and 16%) were formed. The incorporation of ZSM-5 into the hydrocracking catalyst was observed to increase the BTX yield, which promotes the dealkylation of alkylbenzenes to BTX [12]. When using the HDT LCO 2/2 with the Mo/BZ(10) at the same experimental conditions, the total BTX, light paraffins (LP), and C_{9+} -alkylbenzenes (C_{9+} ALB) yields were 41.4, 14, and 13%, respectively. Obviously, the fractionated LCO provides a better feed for the BTX production due to the reduction of tri-aromatic compounds that do not provide BTX by hydrocracking [7].

Laredo et al. [4] tested a 50/50 in weight mixture of two commercial catalysts: NiMo/ Al_2O_3 and ZSM-5 that were prepared and tested with tetralin in a previous work [3] using, in this case, a fractionated hydrotreated light cycle oil (HDT LCO; FBP = 327 °C). At the best experimental conditions: fixed bed, 425 °C, 7.4 MPa, H₂/feed ratio of 442 m³/m³, the BTX total yield was 31%. Light hydrocarbons (LP: 32.4%) and C_{9+} -alkylbenzenes (C_{9+} ALB: 16%) were also formed. Indene, tetralin, and naphthalene derivatives were completely absent from the product. In this case, only the best catalyst was chosen from the previous experiments with tetralin [3].

Oh et al. [20] published the results of the hydrocracking of a hydrotreated light cycle oil (HDT LCO, FBP 430 °C) with molybdenum (8%, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) on hybrid zeolites formed by H-Beta (SiO_2/Al_2O_3 = 75), HY (FAU structure, SiO_2/Al_2O_3 = 80) and HZSM-5 (SiO_2/Al_2O_3 = 30) in 90/0/10, 85/5/10 and 80/10/10 in weight

Table 3 Chemical and physical characteristics of the catalyst designed for real feeds hydrocracking

Name	Feed	Metal 1	Wt.%	Metal 2	Wt.%	Support	S_{BET} , m ² /g	V_{poro} , cm ³ /g	C_L , mmol/g	C_B , mmol/g	Total acidity, mmol/g	Ref
Mo/H-Beta	PFO			Mo	12.5		536		0.54	0.63	1.17	23
CoMo/H-Beta	PFO	Co	3.3	Mo	12.5	H-Beta (Si/Al 25)	502		0.66	0.46	1.12	
CoMo/MOR	PFO	Co	3.3	Mo	12.5	Mordenite (Si/Al 20)						
CoMo(0.5)/H-Beta	PFO	Co	2.8	Mo	9.0	H-Beta (Si/Al 25)	502					24
CoMo(1.0)/H-Beta	PFO	Co	4.5	Mo	7.4	H-Beta (Si/Al 25)	511					
CoMo (1.5)/H-Beta	PFO	Co	5.8	Mo	6.3	H-Beta (Si/Al 25)	478					
NiMo/B-Z (10)	HDT LCO	Ni	3	Mo	8	Beta/ZSM-5 (90/10)			0.177	0.151	0.33	34
CoMo/B Z (10)	HDT LCO	Co	3	Mo	8	Beta/ZSM-5 (90/10)			0.177	0.151	0.33	
CoMo/B Z (10)	HDT LCO	Co	1.5	Mo	4	Beta/ZSM-5 (90/10)			0.177	0.151	0.33	
Mo/H-Beta	HDT LCO			Mo	8	Beta			0.131	0.131	0.26	
Mo/BZ (10)	HDT LCO			Mo	8	Beta/ZSM-5 (90/10)			0.177	0.151	0.33	
Mo/BZ (10)	FHLCO-1			Mo	8	Beta/ZSM-5 (90/10)			0.177	0.151	0.33	
Mo/BZ (20)	HDT LCO			Mo	8	Beta/ZSM-5 (80/20)			0.207	0.165	0.37	
ZSM-5	HDT LCO					ZSM-5			0.596	0.43	1.03	
NiMo/Al ₂ O ₃ /ZSM-5 (50/50)	FHLCO-2	Ni	1.7	Mo	9.2	Al ₂ O ₃ /ZSM-5 (50/50)			0.26	0.11	0.37	4
Mo/BZ (90/10)	HDT LCO			Mo	8	Beta/ZSM-5 (90/10)						20
Mo/BYZ (85/5/10)	HDT LCO			Mo	8	Beta/HY/ZSM-5 (85/5/10)						
Mo/BYZ (80/10/10)	HDT LCO			Mo	8	Beta/HY/ZSM-5 (80/10/10)						
NiW/	FHLCO-3	Ni	4.7	W	13.5	Al ₂ O ₃ /Beta/HY (30/14/56)	403	0.15	0.38	0.15	0.53	36
NiW/Al ₂ O ₃ -Y	FHLCO-3	Ni	4.7	W	13.5	Al ₂ O ₃ /HY (30/70)	515	0.17	0.41	0.285	0.69	
NiW/Al ₂ O ₃ -B	FHLCO-3	Ni	4.7	W	13.5	Al ₂ O ₃ /Beta (30/70)	325	0.10	0.64	0.4	1.04	

PFO Pyrolysis fuel oil, HDT LCO Hydrotreated light cycle oil. Final boiling point 384 °C, FHLCO-1 Fractionated and hydrotreated light cycle oil. Final boiling point 334 °C, FHLCO-2 Fractionated and hydrotreated light cycle oil. Final boiling point 320 °C, FHLCO-3 Fractionated and hydrotreated light cycle oil. Final boiling point 346 °C

mechanical mixtures, supported by wet impregnation. The addition of the H-Y zeolite came from the conclusion that this mesoporous material can be useful on the hydrocracking of large tri-aromatic molecules than can be present in the HDT LCO. The hydrocracking process of the HDT LCO was carried out at the following experimental conditions: 425 °C, WHSV = 2.0 h⁻¹, total pressure = 6.0 MPa, H₂/feed = 1972 mL/mL. The total BTX yield obtained with the Mo/BZ (90/10), Mo/BYZ (85/5/10), and Mo/BYZ (80/10/10) were 25, 27, and 29%. Other hydrocarbons in the products were, light paraffins (LP: 16, 16, and 14%), C₉₊-alkylbenzenes (C₉₊ALB: 19, 13, and 9%), and some indanes and tetralin derivatives (TI: 1.1, 0.7, and 0.2%). It is noteworthy that the differences in BTX yield between catalysts is not that important. The authors concluded that H-Beta was the most selective component for the hydrocracking of tetralin compounds, which were formed via the hydrotreating of the abundant naphthalene derivatives in LCO. H-ZSM-5, which had the highest acidity and smallest pore size, boosted the BTX yield by promoting the dealkylation/transalkylation of alkylbenzenes (which were co-produced via the hydrocracking of tetralin derivatives over H-Beta) into BTX. And the mesoporous H-Y facilitated the conversion of large molecular-size C₁₁₊ heavy aromatic compounds, which are too large to access the pores of H-Beta or H-ZSM.

Cao et al. [35] also used the CoMo/AY and NiMo/AY prepared catalyst for hydrocracking LCO and combined beds: first NiMo/AY and then CoMo/AY and vice versa. The experimental conditions for the two reactors (R1/R2) were: 385/400 °C, LHSV = 2.0/1.3 h⁻¹, total pressure = 7 MPa, H₂/

feed = 1000 mL/mL. Again, the aim was to produce gasoline and not BTX, the global BTX yields were low (8–13.2%).

Very recent work by Anilkumar et al. [36] presented the results of the hydrocracking of a fractionated hydrotreated light cycle oil (HDT LCO, FBP 346 °C) with a nickel (4.7%) and tungsten (13.5%) bifunctional catalyst obtained by wet impregnation of extrudates formed by the following mixtures: Cat-A (Al₂O₃/Beta/HY (30/14/56)), Cat-B (Al₂O₃/HY (30/70)) and Cat-C (Al₂O₃/Beta (30/70)). Total acidity of the catalyst followed the order (Table 3): Cat-A < Cat-B < Cat-C as well as the monoaromatic hydrocarbons productions: 12, 22, and 44.3 wt% at 350 °C, 6 MPa, H₂/feed ratio of 10 mol/mol and 1 h⁻¹ WHSV. The authors claimed that the combination of dispersed metallic sites and high acidity contributed to the high hydrocracking activity of catalyst-C [1, 2, 10–12, 14]. This data could not be used in the comparison with the other results described in this work, because these authors compiled all the monoaromatic hydrocarbons as one group without differentiating the BTX from the other higher molecular weight C₉₊-alkylaromatics. In this review, only the C₆–C₈₊ (including ethylbenzene) were considered in the comparison.

Partial conclusions

Figure 8 shows some of the more important results. Departing from real feeds a total BTX yield higher than 35% was never attained using a hydrocracking catalyst of any type, due to the presence of another type of competing hydrocarbons [7], and the inevitable gas formation and other C₉₊-alkylbenzenes formed [26]. Considering that all the aromatic compounds (alkylbenzene, tetralin, naphthalene,

Fig. 8 Main results for the effect of the catalyst in the BTX total yield from real feeds hydrocracking

indane, and indene aromatic compounds) may have the capacity to be converted to BTX by hydrocracking and transalkylation reactions [4], and they can be present from 30 to up to 90% in a real feed [7], the theoretical yield should be approximately thirty to eighty percent of the theoretical conversions (63–65%) then equal to 19–55%, depending on the feed. A study regarding feed composition and BTX yield is in progress and it will be presented in the future, however, certainly not all the aromatic compounds available for conversion to BTX are chemically suitable for performing such a task.

The only correlation slightly logic was the effect of the metal content on the catalyst, in the BTX total yield (Fig. 9). In this case, is important to notice the required metal dispersion for carrying on several tasks [12]. It seems that the hydrocracking reaction for the BTX conversion from real feedstocks will require as much as possible from the hydrocracking properties related to the support like acid sites and pore structure rather than the hydrogenation properties related to the supported metals. However, is exceedingly difficult to assess the catalytic performance that requires the combined performance of two active sites (bifunctional catalyst) on the hydrocracking of extraordinarily complex real feedstocks.

Therefore, for the purposes of this work, the best catalysts were those conformed by Mo, CoMo, or NiMo over zeolite H-Beta (Fig. 10). Some researchers [34] found that adding some of ZSM-5 to the H-Beta can improve the BTX formation. A mixture of catalysts in which one of them was ZSM-5 [4] was also useful. Some authors claimed [20] that a small amount of a mesoporous material like H-Y improves the BTX yield by facilitating the diffusion of large molecules, like the tri + aromatic compounds that can be found in real feeds, such as the hydrotreated light cycle oil. Finally, Fig. 10 shows that the slope is steeper between the first group that covers the worst performing catalysts for BTX yield (5–13 wt.%) and the best performance group (30–35%) of catalysts. This behavior means that the catalysts found

using model molecules are not always reliable for their use in a real feed.

Anyhow, there is a strong possibility that this type of feedstocks still will be usable despite of the yield, due to the general trend to convert fossil fuels to petrochemicals.

Reaction scheme, future trends, and economic development of this process

Real feeds upgrading by hydrocracking for obtaining valuable petrochemicals like BTX faces, as far as it was observed, an economic challenge due to the low BTX yield that all types of feeds, catalysts, and experimental conditions seem to provide. Based on the information compiled in this work, a reaction scheme was proposed (Fig. 11). Perhaps, the only possible route for increasing the BTX yield, would be finding a way for increasing disproportionation, and transalkylation reactions [37–40] that increase the formation of BTX from C_{9+} -alkylbenzenes (increasing k_{DT} reaction rate) that according to this scheme, are formed at the same time, and that now are considered by-products. Disproportionation and transalkylation are the two major practical processes for the interconversion of alkylaromatics, especially for the production of dialkylbenzenes [39, 40]. The contribution of these two mechanisms to the overall process depends on the relative stability of the alkylaromatic and bulkier diaryl cationic intermediates and is largely influenced by the reactant size, zeolite pores, and the presence of channel intersections or cavities [41].

However, as the worldwide trend continues in the search for the substitution of crude oil fuels for more environmentally friendly energy sources, the research for petrochemical production from all kinds of crude oils (light or heavy) is going to increase sharply. It is on this demand where low marketable feeds may find a profitable niche. According to Tulio [42], and it is quoted: “The driver this time is the market more than it is cheap raw material supply. By 2030, demand for gasoline and other fuels will be on the decline.

Fig. 9 Effect of the total metal content on the BTX total yield from real feeds hydrocracking

Fig. 10 Worst to the best catalyst for real feeds hydrocracking for BTX production

Fig. 11 Suggested reaction scheme for the HCK of the HDT LCO

The petrochemical sector, in contrast, still has room to grow. Oil companies and engineering firms have noticed. They are installing new equipment and even designing new processes to seize on the trend.”. Therefore, it is hope for this technology even as it is now.

General conclusions

A total BTX yield of 53–55% was obtained by the hydrocracking of tetralin and naphthalene derivatives. Higher yields were never attained due to the inevitable gas formation and other C_{9+} -alkylbenzenes formed. For tetralin, the best catalysts are those conformed by Ni, CoMo, NiMo, or NiSn over zeolite H-Beta. The adding a 10%

in weight of ZSM-5 to the H-Beta, the BTX formation can be improved. For naphthalene derivatives, the best catalysts were those conformed by W and NiW over zeolite H-Beta silylated. While departing from real feeds a total BTX yield higher of 35% was never attained using a hydrocracking catalyst of any type, due to the presence of other types of hydrocarbons from the feed. The best catalysts were those conformed by Mo, CoMo, or NiMo over zeolite H-Beta. The presence of ZSM-5 and H-Y in the support or/as catalyst mixture was claimed to show some improvements in the BTX yield, especially the last one with larger pores, which can facilitate the diffusion of larger molecules like the tri + -ring aromatic molecules which can be present in the real feeds. A balance between acid and hydrogenating function with the right accessibility characteristics to the sites appears to be needed to obtain a high BTX yield.

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Author contributions GCL conceived the review, PPR, JLGG, and EHO revised the information.

Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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