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Applied Catalysis A: General 282 (2005) 45–53

APPLIED CATALYSIS A: GENERAL

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Effect of acidity and metal content on the activity and product selectivity for *n*-decane hydroisomerization and hydrocracking over nickel–tungsten supported on silica–alumina catalysts

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Received 15 August 2004; received in revised form 29 November 2004; accepted 30 November 2004

Abstract

Ni–W/silica–alumina based catalysts with different nickel and tungsten concentration (nickel ranging from 12 to 17% and tungsten ranging from 8 to 30%) were prepared by sol–gel method. The BET, temperature-programmed desorption of ammonia (TPDA) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) techniques were used to characterize the prepared solids. Afterwards, the catalysts were screened for activity and selectivity in the hydroconversion of *n*-decane. Under the experimental conditions, yields of isomers as well as cracking products were a function of both metal content and amount of acid sites. Up to 15% Ni content, nickel increased isomerization selectivity, afterwards, the catalytic selectivity decreased. Moreover, the higher the amount of medium acid sites present on the catalyst, the higher its activity and its deactivation.

After running on stream for 100 min, the catalysts with 15% of nickel and 10% of tungsten (WT(15,10) catalyst) showed the best results (42.3% of conversion and 55% selectivity) at 250 °C.

Keywords: Cracking; Decane; Dewaxing; Hydroconversion; Isomerization; Nickel; Tungsten oxide

1. Introduction

Dewaxing is essential for upgrading lubricant oil, this process is conventionally performed by two methods: solvent and catalytic dewaxing. These are different processes, but basically the first one consists of the elimination of the waxes by extraction with selective solvents, while the catalytic process is carried out chiefly by selective cracking of normal alkanes to lower the amount of molecular weight products which are later removed from the lube by normal distillation [l–4]. There are important differences between both processes and many studies have revealed that catalytic dewaxing has lower operating costs and environmental load than the solvent process, although it usually gives less yield and worse properties of the dewaxed lube [4–6]. In order to improve the performance of the catalytic dewaxing procedure, attempts have recently been made to isomerize normal alkanes to isoalkanes, allowing them to remain in the oils and to produce higher quality oil in higher yield [7–12]. For this purpose, hydroisomerization and selective hydrocracking of long-chain normal paraffins have been intensely studied [13–15] and the difficulty of achieving high isomerization activity has been pointed out [16–18]. Owing to environmental restrictions covered in several legislations throughout the world, non-polluting and atom-efficient catalytic technologies are much sought after. Therefore, efforts have been made to avoid the use of present commercial catalysts for the isomerization of alkanes: HF is particularly dangerous while catalysts containing halids such as $AlCl_3$ or sulfuric acid are corrosive and pose significant environmental challenges including disposal wastes [19]. Recently, there have been efforts by industrial and academic researchers [20–22] to obtain solid acid

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doi:10.1016/j.apcata.2004.11.044

catalysts which are environmentally more suitable for alkane isomerization with minimal cracking. In this context, it was mentioned that an attractive catalytic dewaxing process is usually carried out using a metal/acid bifunctional catalyst, over which the alkanes are dehydrogenated–hydrogenated on metallic sites and then isomerized or cracked on the acid sites through classical or nonclassical ion carbenium chemistry [23–25].

Typical examples of these types of catalysts are noble and group VIII metals (Pt, Pd, Ni, Mo) supported by zeolites and other acidic supports [26–29]. Catalysts loaded with a noble metal (Pt or Pd) show a considerably higher selectivity for hydroisomerization, at medium conversion, with respect to those containing non-noble transition metals such as Ni, Co, Mo and W. However, due to faster cracking of the branched isomers, hydrocracking becomes dominant at high conversion levels. In their turn, composite catalysts (a physical mixture of two catalyst components) have been used only to a limited extent for alkane isomerization [12,30–33], where it was reported that the admixture of a protonated zeolite to a Pt/SiO_2 catalyst enhances its *n*-alkane isomerization activity and it was also assumed that the classical bifunctional mechanism is operative. On the other hand, silicoaluminophosphates (SAPOs) have been studied for *n*-alkane isomerization [34–37]. However, most studies focus on the isomerization of C_6 to C_8 *n*-alkanes.

Previous investigations have reported the high catalytic activity of nickel–tungsten oxide supported on amorphous silica–alumina catalysts for hydrocarbon conversion at mild conditions [38,39]. Fairly high yields of branched isomers have been obtained using these catalysts for the isomerization of C_6 and C_7 normal paraffins.

In the present paper, we report the main results of a study concerning the hydoisomerization/hydrocracking of *n*-decane on Ni–WO_x/SiO_2–Al_2O_3 catalysts. The objective of this work was to investigate the effect of reaction variables on the reactivity and hydroisomerization selectivity.

2. Experimental

The details of the preparation of Ni–WO_x/SiO_2–Al_2O_3 materials, noted ‘‘WT(*x*,*y*)’’ (where *x* and *y* indicate the weight percentage of nickel and tungsten in the catalyst, respectively), have been previously reported [38]. In brief a series of seven WT(*x*,*y*) catalysts, with ‘‘*x*’’ values equal to 12, 15 and 17, ‘‘*y*’’ values equal to 8, 10 and 30 and a constant SiO_2/Al_2O_3 ratio equal to 1.83, were prepared, using the sol–gel method, by mixing the required amounts of aluminum sulfate, sodium tungstanate and nickel nitrate. To the sol obtained, under vigorous stirring, an aqueous solution of sodium silicate was added. To exchange undesirable ions, such as Na^+, the prepared gel was activated, under reflux conditions in a thermostat, with ammonium sulfate (liquid to solid ratio of 30) at 60 °C over a period of 48 h (this unit operation was repeated several times), washed with hot water (60 °C), dried at 120 °C for 4 h and finally calcined at 500 °C for 5 h. A heating rate of 10 °C/min was used.

The surface area was determined by the BET method; we measured the adsorption isotherm of nitrogen at 196 °C. Prior to measuring the adsorption, all samples were degassed at 350 °C for 30 min, and then reduced at 430 °C, with hydrogen, for 1 h. The tungsten and nickel concentration was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

The acidic properties of the samples were measured by using the temperature-programmed desorption of ammonia (TPD of NH_3). Prior to TPD experiments, the sample was pretreated, for 3 h at 500 °C, with an oxygen flow, then purged by flowing helium at 300 °C, and then reduced, at 430 °C for 2 h, in a hydrogen flow. After reduction, the sample was further dried in flowing He at 300 °C for 1 h and then cooled to room temperature. When the system become steady, ammonia was adsorbed at 100 °C for 30 min (using a 10% NH_3/He carrier gas) and then the sample was subsequently purged, at the same temperature, by flowing He (100 ml/min) for 1 h to remove the excess and physically adsorbed NH_3. The TPD spectrum was obtained by heating the sample from 100 to 700 °C at a heating rate of 10 °C/min under a He flow. Evolved NH_3 was monitored with a TCD detector.

An amount of 1 g of catalyst was loaded in a continuous flow fixed-bed quartz reactor, with an inner diameter of 10 mm, operated under isothermal conditions and connected to an on-line gas chromatograph by means of a valve. The test was carried out at atmospheric pressure, a reaction temperature ranging from 150 to 300 °C with a step of 50 °C, a weight hourly space velocity (WHSV) equal to 4 h^{-1} and a hydrogen/hydrocarbon (H_2/*n*-decane) molar ratio equal to 5. Previous to starting the run, the catalyst was kept in a hydrogen stream under 430 °C for 3 h in order to prereduce the metallic function.

Catalytic activity is expressed in term of conversion, which is defined as the fraction of the decane, which has reacted. Selectivity was calculated by dividing the *i*-C_{10} percentage in the products by *n*-C_{10} conversion.

3. Results and discussion

In Table 1, the physico-chemical properties of the solids were summarized. The surface areas of these materials are in the range of 50–84 m^2/g and the sample with the greater amount of tungsten (30%) had the lowest surface area, this effect may be due to a bad tungsten repartition as a multilayer [40]. From the results, it can be observed that the BET specific surface area decreased with increasing nickel and tungsten loading. The effect of tungsten was less pronounced when the nickel content was high; which would favor the idea that nickel ameliorates the tungsten dispersion in catalysts [41].

Table 1
Physico-chemical properties of the different samples

Catalyst	Surface area (m^2/g)	Acid amount (mmol NH_3/g)	
		Weak acid	Medium acid
WT(12,8)	84	0.12	0.15
WT(12,10)	80	0.13	0.11
WT(15,8)	77	0.15	0.17
WT(15,10)	75	0.19	0.11
WT(15,30)	50	0.20	0.05
WT(17,8)	72	0.06	0.24
WT(17,10)	71	0.10	0.26

Table 1 shows clearly that with increasing the nickel amount, the number of the weak acid sites, peak desorption temperature in the TPD curve (not shown) ranging from 150 to 220 °C, present on WT(x,y) samples, increased, passed through a maximum at 15% of Ni then decreased. Besides, the density of weak acid sites increased with increasing the tungsten loading, which means that the tungsten favored the formation of the weak acidity. On the other hand, the amount of medium acid sites, peak desorption temperature in the TPD curve (not shown) ranging from 300 to 315 °C, was enhanced by the increase in the Ni content, whereas increasing the tungsten content had the opposite effect (except catalysts with 17% Ni).

Concerning the chemical composition, the data collected in Table 1 show that, except for WT(15,30) catalyst, the experimental nickel and tungsten content were similar to those expected, suggesting that their was no loss in the amount of both metals during the preparation procedure.

Fig. 1(a) and (b) give the evolution of the conversion with time on stream (TOS). All catalysts showed virtually identical trends with increasing time on stream in that the slopes of the curves became smaller at the high values of TOS and remained steady after 100 min, this feature suggests that the catalytic activity decreased with time on stream, the deactivation being more rapid during the first few minutes, and stationary conversions were obtained after 100 min. Initially, the WT(17,10) catalyst was the most active with 61.2 and 74.9% of conversion at 150 and 300 °C, respectively, and the WT(15,30) one was the least active with 25 and 33.4% of conversion at 150 and 300 °C, respectively, while the conversion over the WT(15,10) catalyst was between those of these two catalysts, but the latter stabilized value was higher than that of WT(17.10), which leads to the fact that the higher the activity showed by the catalyst, more severe is its deactivation. It worthy to note that the deactivation rate was also more pronounced at higher temperatures, the slope in the activity decay was higher at 300 °C (Fig. 1(b)) compared to the one at 150 °C (Fig. 1(a)).

Based on curves of Fig. 1(a) and (b), we could say that the metal addition produced a large increase in the initial catalytic activity (at 20 min). These curves may lead to wrong conclusions on the influence of nickel on the stability of the catalyst, because we cannot assess this effect except when the amount of medium acid sites present on the catalysts are comparable. The WT(12,10) catalyst, with a number of medium acid sites equal to 0.11 mmol NH_3/g, displays much higher deactivation as compared to WT(15,10) having the same amount of medium acid sites, which means that Ni induces a beneficial effect on the stability of the WT(x,y) catalysts. This observation rules out the dependence of the catalysts stability on the density of acid sites and nickel content. Thus, the deactivation may be due to a metallic function poisoning, or to a loss of the support acidity, or finally, to a loss of the hydrogen dissociation capacity of WO_x species, which is rapidly deactivated by coke [42].

In order to verify the above assumptions, cracking, isomerization and hydrogenolysis reactions were thoroughly studied over the seven catalysts. The reaction pathways with respect to these reactions were depicted in Fig. 2(a) and (b).

Under our experimental conditions, WT(17,8) and WT(17,10) showed the highest cracking activity and WT(15,30) the lowest one. During the run, the cracking reactions decreased (Fig. 2(a)), the effect was more drastic during the first few minutes particularly when the number of medium acid sites present on the sample increased (the WT(17,y) catalysts with the highest density of medium acid 0.24 and 0.26 mmol NH_3/g showed the highest decay in the rate of cracking reactions with time on stream). Thus, it seems to be a correlation between the density of moderate acid sites and the cracking activity and we can confirm that the high acidity of the WT(17,y) is also the reason of its rapid deactivation by producing carbonaceous deposits catalyzed by the strong and medium acid sites. Similar observation was reported by Grau et al. [43] during their study on hydoisomerization-cracking of n-octane over Pt/SO_4^{2-}–ZrO_2 catalysts.

With respect to isomerization reactions, the WT(15,30) catalyst, with a density of weak acid sites equal to 0.20 mmol NH_3/g, had the highest value (52.5%) and the WT(17,8) with a density of weak acid sites equal to 0.06 mmol NH_3/g, the lowest one (2.3%), which means that the higher the number of weak acid sites the higher the selectivity toward isomerization. With increasing time on stream, isomerization reactions increased with a significant rise during the first few minutes to reach a steady state after 100 min. This effect was more pronounced in the case of WT(17,10) due to its higher deactivation, which decreased cracking and allowed more isomerization of the adsorbed species.

Concerning hydrogenolysis reactions, no catalyst deactivation was observed during the test period, which suggests that the metallic function was not poisoned. Thus, we can conclude that the WT(x,y) catalyst deactivation should not be attributed to the poisoning of the metallic function, but to a loss of the support acidity or to a loss of the hydrogen dissociation capacity of WO_x species.

The catalytic conversion of n-decane is greatly influenced by reaction temperature and metallic function loading. To

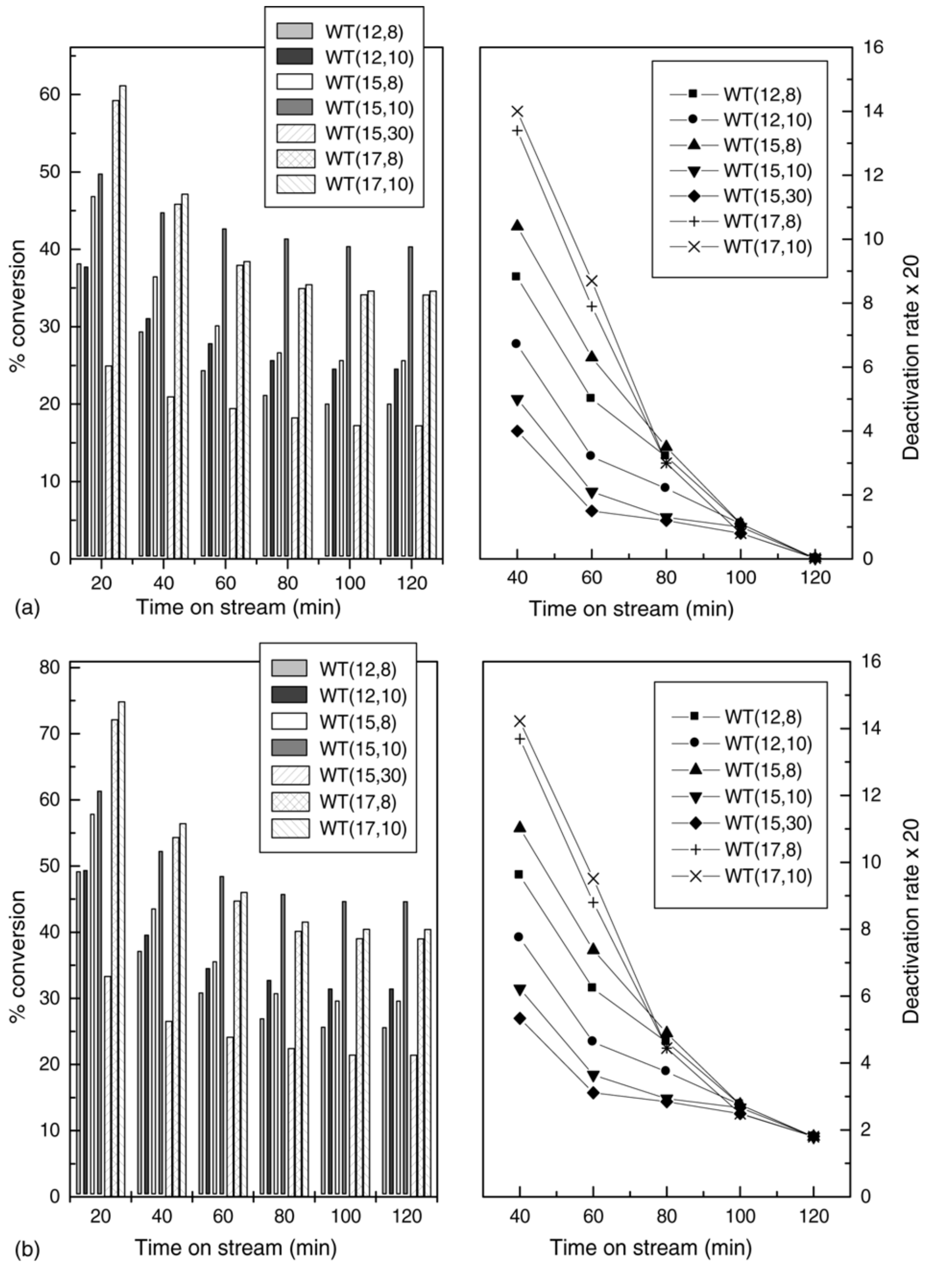

Fig. 1. (a) Conversion and deactivation rate evolution with time on stream at 150 °C. (b) Conversion and deactivation rate evolution with time on stream at 300 °C.

detail these effects, the catalytic performance of the WT(x,y) catalysts was studied after reaching the steady state (results were collected after 100 min on stream), at a reaction temperature ranging from 150 to 300 °C.

Fig. 3(a) and (b) show conversion, hydrogenolysis, cracking, and isomerization reactions as a function of reaction temperature over the various catalysts. Increasing temperature increased conversion, hydrogenolysis and cracking reactions but reduced selectivity to isomers consistent with speeding up both isomerization and cracking, with reduced selectivity resulting from higher activation energy for cracking. Furthermore, conversion and hydrogenolysis reactions increased with increasing nickel content, while selectivity to isomerization increased with nickel content to reach a maximum at about 15% nickel then it decreased monotonically. Such a catalytic behavior can be explained by the fact that in the range 12–15% nickel the value of the metallic site/acid site function ratio is less than the optimal value for isomerization, thus increased metal function of the catalysts (nickel) prompts the formation of isomers via a reduction of the diffusion path between two metallic sites. Hence, the possibility that the intermediate species would encounter acid sites and would be cracked during its migration from one metallic site to another is also less. In contrast, in the range 15–17% nickel there are enough metallic sites to form olefins for feeding all the acid

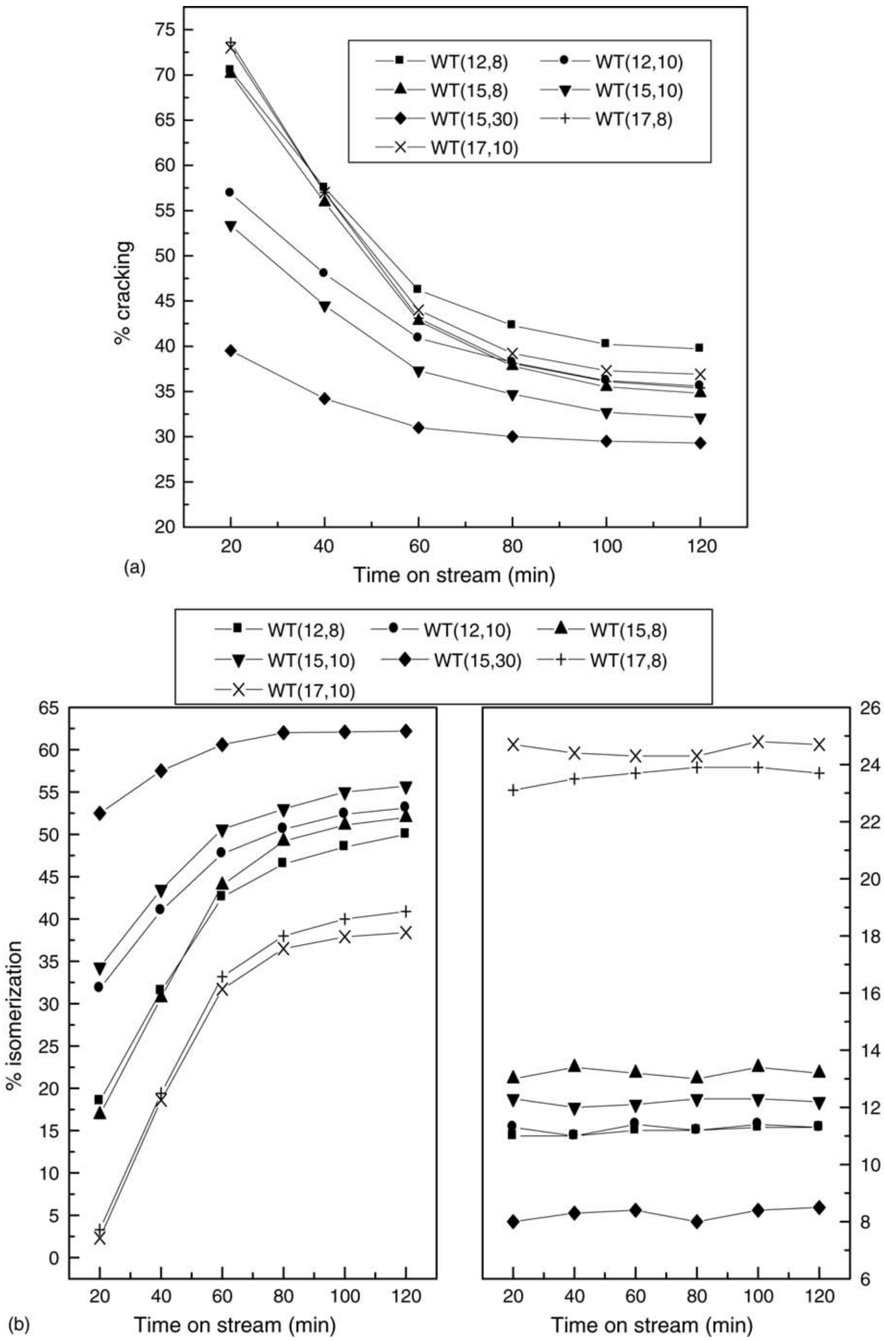

Fig. 2. (a) Evolution of cracking reactions with time on stream at 250 °C. (b) Evolution of isomerization and hydrogenolysis reactions with time on stream at 250 °C.

sites, and further increased metal function prevents the isomerization reaction and increases the rate of cracking and hydrogenolysis reactions (nickel is an active component for the hydrogenolysis reaction [44]). Thus, the observation of a maximum in the nickel content proves that, in our case, the reaction proceeds via a bifunctional mechanism [45]. Another point of view may be taken on account, when the nickel content exceeds a certain threshold (in our case 15%), the amount of hydrogenolysis gas is sufficient to increase the mass transfer resistance, which causes an increase of the intermediate species residence time. Hence, the possibility that these species could be cracked is greater.

On the other hand, increasing tungsten loading induces a decrease in the cracking reactions and an increase in both activity and isomerization selectivity of the catalysts; this increase was more pronounced when the nickel content was high. These effects may be ascribed to the reduced tungsten species activity toward isomerization which can be attributed to their metallic character [46–49] or, if they are large enough, to their ability to stabilize carbenium ion

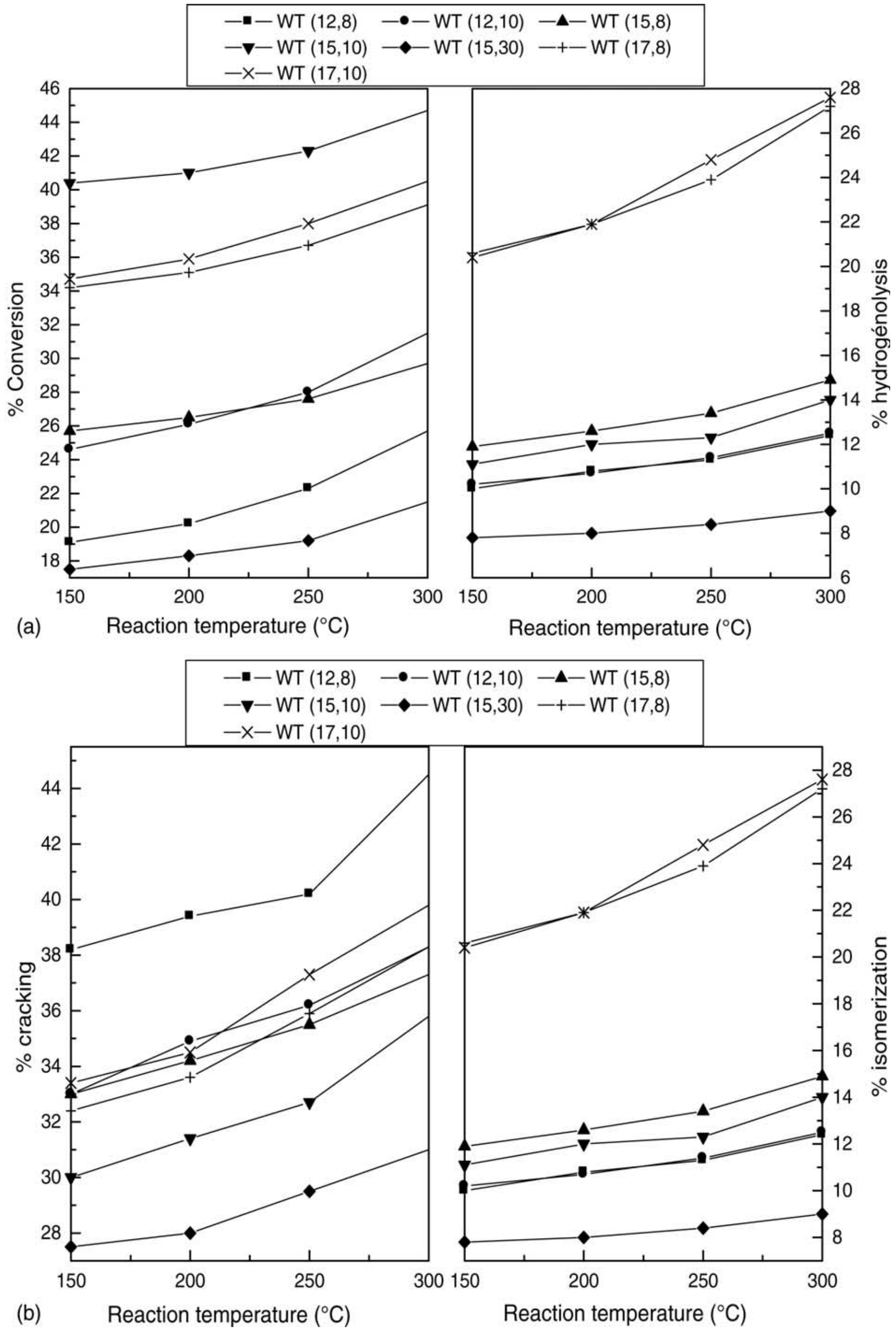

Fig. 3. (a) Effect of reaction temperature on conversion and hydrogenolysis reactions after 100 min on stream. (b) Effect of reaction temperature on cracking and isomerization reactions after 100 min on stream.

intermediates by delocalization of the corresponding negative charge among several oxygen atoms [14,37,38], or to the fact that oxygen atoms of WO_x species could bond dissociated hydrogen atoms formed in H_2 dissociation (by metallic nickel function) or C–H bond activation steps, consequently providing the Brønsted W–O_xH acidic sites and thus enhancing the rate of isomerization reaction [46,50,51]. As suggested by Meijers et al. [52], these results may also be explained by the fact that catalyst activity and stability are related to both Lewis and Brønsted acid sites. Addition of tungsten oxide increases the Brønsted site density at the expense of Lewis sites while maintaining the density of total sites constant [53]. It is known that Lewis sites catalyze favorably cracking reactions associated with the formation of coke [54]; thus addition of tungsten increases the catalyst selectivity to isomerization.

Of the formulations screened in this work, the catalysts with 15 and 17% of nickel and 10% of tungsten showed by far the best performance. Thus, it is interesting to study in more details these systems.

Table 2
Distribution of the monobranched and multibranched isomers over WT(15,10) and WT(17,10) catalysts at various conversions

Conversion (%)	WT(15,10)		WT(17,10)	
	Monobranched	Multibranched	Monobranched	Multibranched
10	94.2	5.8	98.4	1.6
30	93.7	6.3	93.8	6.2
60	90.6	9.4	93.3	6.8
80	84.8	15.2	92.8	7.2

The isodecanes obtained through isomerization of *n*-decane over WT(*x*,10) catalysts can either be monobranched and multibranched. The isomer distribution over WT(15,10) and WT(17,10) was given in Table 2 at various *n*-decane conversions. The transformation of monobranched isomers to multibranched isomers is favored at high conversion. Moreover cracking of multibranched isomers is fast compared with cracking of monobranched isomers. Therefore, the selectivity for monobranched isomers is high over the whole conversion range. In addition, over WT(17,10) catalyst, a low selectivity for multibranched isomers is observed, especially at low conversion, which is presumably a consequence of its high acidity. Same results were reported by Elangovan et al. [55] during their study on the isomerization and hydrocracking of *n*-decane over bimetallic Pt–Pd clusters supported on mesoporous MCM-41 catalysts.

The evolution of the distribution of the methylnonane isomers, over the WT(15,10) and WT(17,10) catalysts, as a function of conversion is shown in Fig. 4. The distribution depend on the conversion of *n*-decane, the considered catalysts favored the formation of 3-methylnonane ($3MC_9$) and 4-methylnonane ($4MC_9$) over 2-methylnonane ($2MC_9$) and 5-methylnonane ($5MC_9$). With increasing conversion, the amounts of $2MC_9$, $4MC_9$, and $5MC_9$ present similar trends over the two catalysts, while the $3MC_9$ increased over WT(15,10) whereas it shows an opposite trend over WT(17,10).

Detailed inspection of the cracked products, at a cracking yield of 25%, reveals that these latter were C_1 to C_9 molecules (Fig. 5(a)), which suggests that cracking mechanism interferes with hydrogenolysis, leading to the high yield of methane. The WT(15,10) catalyst shows a maxima at C_5, while the distribution, over the WT(17,10) catalyst, was skewed toward C_3 and C_4 products because of secondary cracking of some of the C_7 and C_6 fragments (the balance metal-acid is less ideal [56]), similar results were reported by Galperin et al. [57] during their study on the hydroisomerization of *n*-decane over bifunctional Pt-MAPSO-31 catalysts, where they have mentioned that the existence of a maximum at C_4 could be considered as the evidence of a shift in the metal-acid balance, and by Elangovan and Hartmann [58] during their study on the isomerization of *n*-decane over Pt/MCM-41/MgAPO-*n* composite catalysts, where they have stated that secondary

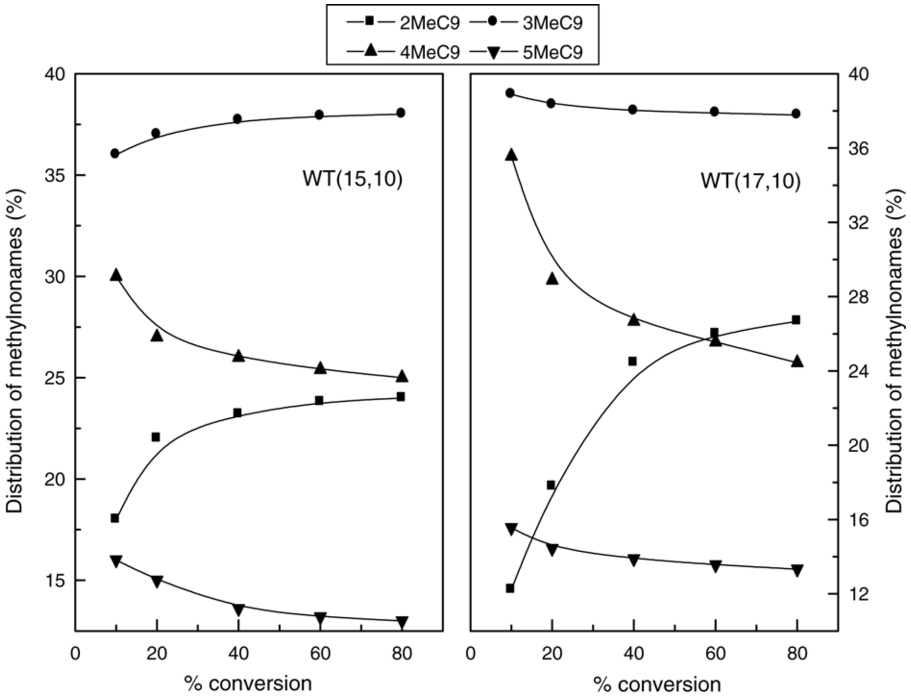

Fig. 4. Distribution of methylnonanes over WT(15,10) and WT(17,10) catalysts at 250 °C.

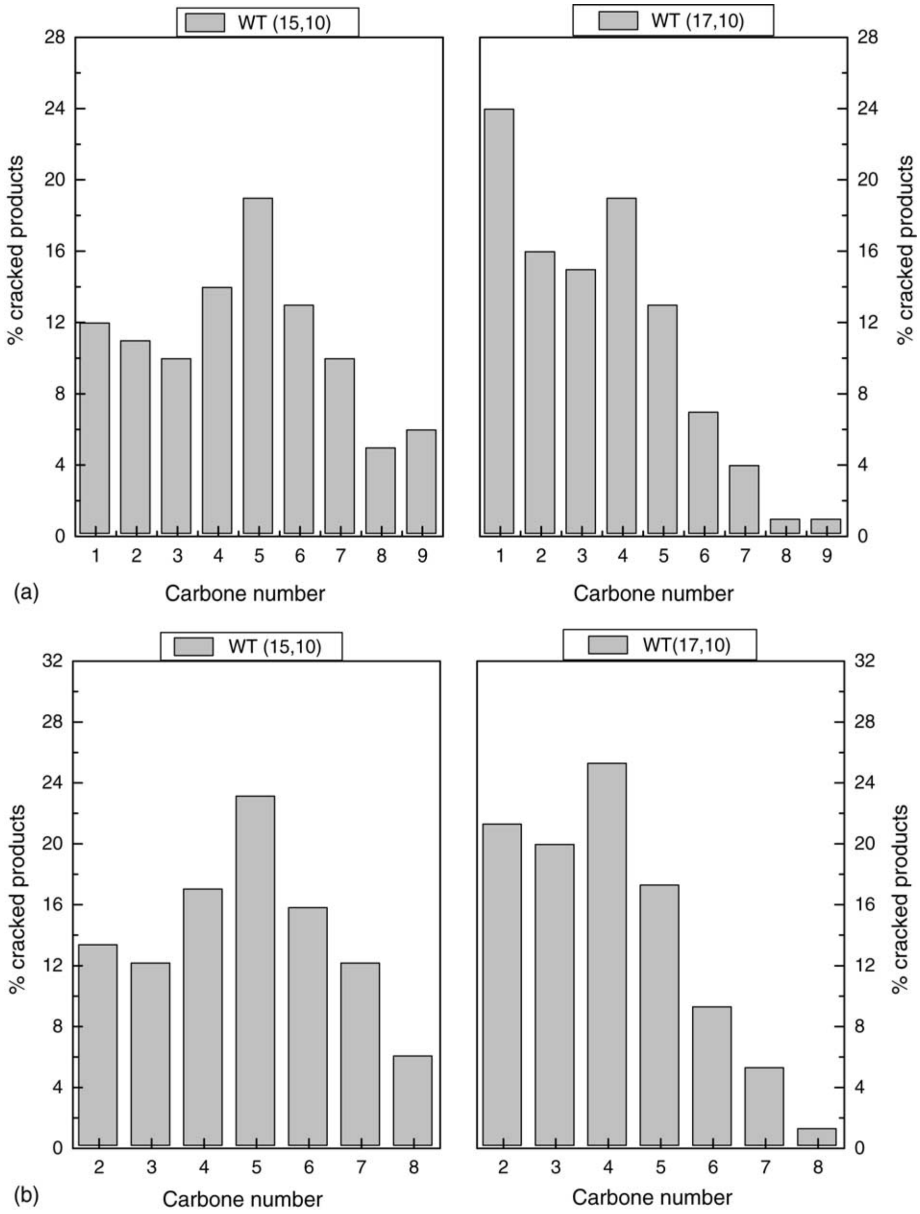

Fig. 5. (a) Distribution of the cracked products over WT(15,10) and WT(17,10) catalysts at 250 °C and a cracking yield of 25%. (b) Distribution of the cracked products (without hydrogenolysis) over WT(15,10) and WT(17,10) catalysts at 250 °C and a cracking yield of 25%.

cracking is often observed over catalysts without well-balanced acid and metal function.

If the hydrogenolysis products were not taken on account, the distribution over WT(15,10) took nearly a Gaussian shape centered on the C_5 molecules (Fig. 5(b)).

4. Conclusions

This study provides supporting evidence that:

- The catalytic performance of WT(x,y) catalysts is strongly correlated with the amount ant the nature of acid sites. Initially, both weak and medium acid sites are suggested to have been present and to have contributed to the isomerization activity. During n-decane hydroisomerization, isomers yields increased with time on stream because of the preferential deactivation of medium acid sites, resulting in increasing amount of isomers desorbed from the catalytic surface instead of undergoing secondary reactions. Furthermore, on WT(x,10) catalysts, multibranched product selectivity decreased with an increase in acid strength (at 80% conversion, the WT(15,10) catalyst, with a density of medium acid sites equal to 0.11 mmol NH_3/g, had a selectivity of 15.2%, while the WT(17,10) catalyst, with a higher density of medium acid sites (0.26 mmol NH_3/g), had a selectivity of 7.2%), and thus cracking is favored at the expense of hydroisomerization at a higher acid strength.

- The WT(*x*,*y*) catalysts deactivation is attributed to a loss of the support acidity or to a loss of the hydrogen dissociation capacity of WO_x species, but not to a poisoning of the metallic function, because in the case of hydrogenolysis reactions (cracking by means of the metallic function), no catalyst deactivation was observed during the period test.
- The amount of metal loading strongly influences the catalytic performance. The activity is improved by a metal rise, while the isomerization selectivity increases with the metal content until sufficient metal site density was reached (15% Ni). If the metal content is too high, the case of WT(17,*y*) catalysts, the selectivity decreases due to the maladjustment in the metal-acid balance. Thus, the combination 15% Ni and 10% W appeared to provide optimal balance between acid and metal function.
- The yield of branched isomers and the distribution of the methylnonane isomers, on the WT(*x*,10) catalysts, are found to be roughly a function of conversion.

For the steady state activity (100 min) and at 250 °C, the WT(15,10) catalyst shows the highest catalytic performance up to 55% selectivity to isomers at 42.3% conversion. Although this beneficial effect on the catalytic performance due to the realization of an excellent balance between acid and metal function, the considered catalyst gives a high hydrogenolysis level (12.3%), this feature suggests that WT(15,10) can exhibit an interesting behavior in catalytic dewaxing if the rate of hydrogenolysis can be diminished.

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