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Dehydrocyclization of n-heptane over Pt catalysts supported on Al- and Si-promoted TiO_2

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ABSTRACT

The effect of content of Si- and Al-promoted TiO_2 catalysts in the dehydrocyclization of n-heptane was studied. The sol–gel method was used to prepare pure TiO_2 and mixed oxides with 1%, 3% and 10% of Al_2O_3 and SiO_2. The structure and surface characterization (XRD, N_2 sorption, H_2 chemisorption, NH_3 uptake) revealed that the promoted cations were dispersed in the TiO_2 lattice, modifying structural and surface properties of catalysts. Dehydrocyclization activity and toluene yields were useful test reaction to detect the effect of content of cations in both acidic and catalytic properties of promoted catalysts. Increase in the TOF was observed as a function of cation content, hand in hand with the increase of overall reaction rate and supported Pt dispersion. The effects in both catalytic activity and deactivation resistance could be explained by the metal-support contact theory, which relates the atomic coordination of promoters with changes in catalytic activity and chemisorption properties of Pt supported on TiO_2.

1. Introduction

It has been demonstrated [1,2] the effects on the strength and distribution of the number of acid sites to promote TiO_2 with Al and Si, modifying its catalytic performance in several reaction systems. Furthermore, Pt/TiO_2 catalyst is a system which exhibits properties of strong metal-support interaction (SMSI), which could be modified to promote cations on the support. It is interesting to explore the application of Pt/TiO_2 catalysts promoted with different contents of Al and Si in reaction systems that are sensitive to both the performance of the metallic phase as the acidic properties of TiO_2 promoted with Al and Si. The general mechanism of n-alkanes dehydrocyclization functionality involves simultaneous metal and acid sites [3–5]. Therefore, the conversion of n-heptane is a sensitive reaction to the morphological properties of the supported metal phase and the acidic properties of the support.

The addition of the Si^{+4} on TiO_2 modifies both structural properties and porosity, enhancing surface area as a function of added Si content [6–10]. The TiO_2–SiO_2 mixed oxide has been studied with various molar ratios in its formulation, and effect of Si content on acid–base properties of surface was observed. It has been found that the combination of SiO_2 and TiO_2 in the synthesis of TiO_2–SiO_2 mixed oxides generates a number of acidic sites per gram of catalyst higher than the number of acidic sites for the respective components as pure oxides (TiO_2 and SiO_2). This phenomenon is similar to that showed in the combination of different pairs of cations as mixed oxides, and it is relate to the formation of an effective charge by the mutual interaction between the charges of the cations which is distributed according to the coordination number [11]. In particular for the mixed oxide of TiO_2–SiO_2, TiO_2 being the major component, the hypothesis predicts forming Brønsted and Lewis acid sites for various combinations of coordination heteroatom bonds. Thus, the catalytic properties of TiO_2–SiO_2 mixed oxide have been exploited in reactions which require the presence of Lewis or Brønsted acidity [6–9,12–15]. In these studies, it was reported that site density (number of acid sites per m^2) decreased due to the simultaneous increase of both acidity and BET surface area as Si was added. At the same time, with the addition of low content of Si into TiO_2, a decrease in the anatase crystal size is detected by X-ray diffraction, involving to crystal edge effects in generation of acid sites.

The addition of Al^{+3} in the TiO_2 matrix for making TiO_2–Al_2O_3 mixed oxides modifies both structural and surface properties, enhancing specific surface area compared with pure components. Addition of Al^{+3} into TiO_2 increase the number of acidic sites per gram greater than the pure components [16]. Unlike to TiO_2–SiO_2 mixed oxide, addition of Al^{+3} generated Lewis acid sites exclusively [15], although it has been reported the presence of Brønsted acidity on TiO_2–Al_2O_3 mixed oxides [17,18] using the adsorption of 2,6-dimethylpyridine (lutidine) as specific molecule to detect Brønsted acidity. There are several research related to study of TiO_2–Al_2O_3 mixed oxides as carriers for catalytic phase, reporting

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that the addition of Al^{+3} into TiO_2 not only improves several properties of catalytic support but also modifies the activity of catalytic supported metal [19].

Several researches related to the application of TiO_2 and TiO_2–SiO_2 and TiO_2–Al_2O_3 mixed oxides as catalytic supports of metals have been reported [10,19–24], being notably greater the number of researches related to M/TiO_2 catalytic system compared to the number of researches related to both M/TiO_2–SiO_2 and M/TiO_2–Al_2O_3, emphasizing the study of the phenomenon of metal-support interaction (SMSI) in M/TiO_2 catalytic system [25–27]. In researches related to M/TiO_2–SiO_2 or M/TiO_2–Al_2O_3, it has been reported that the catalytic performance of supported metal responds to the type and content of added cation and it has been attributed to changes the interaction between the support and the active phase supported [10,24,28–30], resulting a catalyst with enhanced activity in respect to catalysts supported over single oxides. For TiO_2 supported catalysts, the addition of a cation into the TiO_2 lattice may cause changes in the electronic properties of the support, whereas the electronic charge balance between the metal and the support is sensitive to the semiconducting properties of TiO_2 [31]. Thus, electronic interaction of transition metals supported on TiO_2 can be modified by the incorporation of an element that interferes with the original semi conduction properties of pure TiO_2. But in addition to the effects on the interaction between the metal and the support, it also must consider the effects of the addition of Al^{+3} or Si^{+4} in the structural properties, porosity, specific area and surface acidity of TiO_2 [32].

The effects of Al and Si addition in both acidic and catalytic properties of Pt supported on TiO_2 and TiO_2–Al_2O_3 and TiO_2–SiO_2 mixed oxides are studied in this paper. The dehydrocyclization of n-heptane is used as a model test reaction, taking advantage of its reaction scheme that requires the alternating involvement of both catalytic metal activity and the acidic activity to carry out the transformation of the linear alkane. Also, the distribution of the dehydrocyclization reaction products may determine the predominant mechanism, cyclization or isomerization, and point out the influence between metal and acidic functions in catalytic performance.

2. Materials and methods

Pure TiO_2 and TiO_2–Al_2O_3 and TiO_2–SiO_2 mixed oxides were synthesized by sol–gel method, with 1%, 3% and 10% of Al_2O_3 and 1%, 3% and 10% of SiO_2. The synthesis consisted in the simultaneous hydrolysis and condensation of titanium isopropoxide (Aldrich), tri-sec-butoxide (Aldrich) or tetraethyl ortho silicate (Aldrich) in isopropyl alcohol (Baker) as solvent. The hydrolyzing agent was a 0.14 M aqueous solution of HNO_3 (Baker). Excess of solvent was removed by evaporation at room temperature. The xerogel was dried at 110 °C for 12 h, followed by calcination at 500 °C for 4 h in air flow. These oxides were used as a support to prepare 1% weight of Pt catalysts by incipient wetness method, using an aqueous solution of hexachloroplatinic acid (Aldrich).

The BET specific surface area and pore volume of catalyst were characterized by N_2 physisorption at 77 K (Quantachrome), crystal structure was analyzed by X-ray diffraction (D-500, Siemens). The measurement of H_2 uptake was carry out by volumetric method (Micromeritics) for 50 mg samples reduced at 500 °C in 50 cc/min H_2 flow, flushing degasification by high vacuum at 500 °C for 12 h. Samples were cooled and analyzed at 25 °C. The H_2 uptake is reported in µmoles of H_2 per gram of catalyst, and metal supported dispersion (%*D*) is calculated according to the relation of atoms of platinum exposed in the metal crystallite surface (double of H_2 uptake) respect to the total platinum loaded. Samples were reduced at the same temperature of reaction (500 °C)

The effect of Al and Si content in acidic properties were analyzed by ammonia uptake measurements, according to the procedure in a flow analyzer set-up: a sample of 100 mg of catalyst was dried *in situ* in 50 cc/min of helium flow at 400 °C for 1 h. Then, it was cooled at 100 °C and saturated with a calibrated ammonia-helium gas mix (5% mol NH_3 95% mol He, PraxAir) using a gas flow of 20 cc/min for 1 h, followed by gas flushing with helium at the same temperature and flow. The ammonia desorption was carried out heating the sample at 10 °C/min from 100 °C to 500 °C with a helium flow of 100 cc/min. The ammonia uptake was measured by thermal conductivity detector (Gow-Mac).

The catalytic properties of these materials were tested by the dehydrocyclization of n-heptane. The reaction was conducted in an experimental set-up consisting of continuous gas flow microreactor mounted in a tubular furnace with control of temperature (Omega). A Pyrex tubular fixed bed reactor with 7 mm internal diameter was used. Reaction experimental runs were developed as follows: first step consist in the charge of 50 mg of 1% Pt catalyst (100–120 mesh) and reduction at 500 °C for 12 h in a flow of 30 cc/min of H_2 (PraxAir). Second step consist in the feed of a gas current of hydrogen saturated with n-heptane (Aldrich) to the reactor. Operating condition during the reaction experiments were as follows: gas flow = 50 cc/min, temperature = 500 °C, pressure = 585 Torr, hydrocarbon partial pressure = 10.7 Torr, hydrogen–hydrocarbon molar ratio $H_2/HC = 53.5$, WHSV = 345 h^{-1}. The analysis of reaction products stream was made by on-line sampling, which was injected to a gas chromatograph GC (HP5790) with a SE30 Carbowax column (10% weight) and equipped with a thermal conductivity detector (TCD). Differential reactor operation was observed at these conditions, with 10% of conversion or lower, and the reaction rate was calculated according to Eq. (1):

$$r = \frac{F_A \cdot X}{W} \tag{1}$$

where r is the reaction rate (µmol g^{-1} s^{-1}), W is the weight of catalyst (g), F_A is the n-heptane molar flow (mol s^{-1}), and X is the conversion. All reaction experimental runs were conducted on stream for 3 h of continuous time, detecting the deactivation of catalyst. Basic kinetics parameters were calculated according to Eq. (2) for a flow differential reactor with pseudo first order reaction rate and first order deactivation:

$$\frac{W}{v_0} = \frac{X}{k}\exp[-k_D t](1-X) \tag{2}$$

where v_0 is the volumetric flow (L s^{-1}), t is the time on stream (s), k is the first order kinetic constant (L g^{-1} s^{-1}), and k_D is the deactivation constant (s^{-1}). This equation can be written like:

$$-\ln\left[\frac{X}{1-X}\right] = k_D t - \ln\left[\frac{Wk}{v_0}\right] \tag{3}$$

Eq. (3) corresponds to the linear correlation $y = mx + b$. Then, the kinetic constant and deactivation constant can be estimated for each catalyst:

$$k_D = m, \quad k = \frac{v_0\exp(-b)}{W} \tag{4}$$

Turnover frequency is calculated according to the relation of initial reaction rate and the number of metallic active sites, estimated by H_2 uptake and considering a sorption atomic ratio of 1:1 for H:Pt.

3. Results and discussion

Table 1 shows the results in the characterization of 1% Pt catalysts calcined at 500 °C by X-ray diffraction, N_2-physisorption and NH_3 uptake. Table 2 lists the results of characterization by H_2 uptake, overall initial reaction rate and turnover frequency.

Table 1
Effect of content of Al_2O_3 and SiO_2 in anatase crystal size, BET surface area, pore size properties and specific ammonia uptake for catalysts calcined at 500 °C.

Catalysts	%	XRD anatase crystal size (Å)	S_{BET} ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Pore diameter (Å)	NH_3 uptake ($\mu mol\,m^{-2}$)
Pt/TiO_2	–	114	112	0.12	43	3.10
$Pt/TiO_2–Al_2O_3$	1	92	154	0.12	31	2.71
$Pt/TiO_2–Al_2O_3$	3	82	216	0.21	39	2.10
$Pt/TiO_2–Al_2O_3$	10	43	287	0.42	59	1.68
$Pt/TiO_2–SiO_2$	1	101	163	0.22	54	2.54
$Pt/TiO_2–SiO_2$	3	94	217	0.23	42	2.44
$Pt/TiO_2–SiO_2$	10	55	290	0.28	38	2.14

Table 2
Effect of content of Al_2O_3 and SiO_2 in H_2 uptake per gram of catalyst, metal supported dispersion, overall initial reaction rate and TOF for catalyst reduced at 500 °C.

Catalysts	%	H_2 uptake ($\mu mol\,g^{-1}$)	%*D*	Initial reaction rate ($\mu mol\,g^{-1}\,s^{-1}$)	TOF (s^{-1})
Pt/TiO_2	–	6.8	27	3.10	0.017
$Pt/TiO_2–Al_2O_3$	1	11.5	41	2.71	0.024
$Pt/TiO_2–Al_2O_3$	3	15.0	43	2.10	0.022
$Pt/TiO_2–Al_2O_3$	10	13.4	48	1.68	0.028
$Pt/TiO_2–SiO_2$	1	7.3	34	2.54	0.032
$Pt/TiO_2–SiO_2$	3	12.6	41	2.44	0.036
$Pt/TiO_2–SiO_2$	10	16.8	49	2.14	0.022

The effect of content of Al and Si in the anatase crystal size of TiO_2 indicates that the addition of cation into the TiO_2 crystal lattice modify the structural conformation of anatase, diminishing the mean crystal size as the cation content increase. At the same time, an increase in the BET surface area is observed as a consequence of the cation addition, and more sensitive than the changes observed in pore size properties (pore volume and pore diameter). These results indicate that the addition of Al or Si in the synthesis of TiO_2 correspond to the synthesis of mixed oxide with cations disperse into the crystal lattice, modifying the structural and textural properties of these materials. The H_2 chemisorption is also modified by the addition of Al and Si, showing a noticeable increase in the H_2 uptake per gram of catalyst as a function of Al and Si content. It is an important fact indicating that the addition of cations to the support not only modifies the structural properties of anatase but also the H_2 uptake of supported metal is increased as a function of cation content in support, and therefore, its catalytic performance. It is expected that hand in hand with the change in H_2 uptake properties, the hydrogenation and dehydrogenation activities can be modifying by the addition of cations to the support. These effects on H_2 uptake can be related with changing in the Pt crystallite size, associated with the increase in the metal supported dispersion (%*D*) according to the increase in BET surface area. However, additional to the increase in Pt dispersion, change in H_2 chemisorption could be associated with an effect in the inherent semiconductor properties of TiO_2 by addition of cations, changing the electronic exchange in the metal-support interface as a function of Al or Si content. An interesting results has been reported by Escobar et al. [32] related to the effect of $Al_2O_3–TiO_2$ mixed oxides supports in the metal supported dispersion, showing that the SMSI state can be extensively modified by the interaction between Al and Ti.

Another interesting result is the decrease in the specific uptake of NH_3 ($\mu mol\,m^{-2}$) by the content of cations in support, showing that the acidic density is also affected by addition of cations. This behavior can be explained according to the action of two simultaneous effects: decreasing of anatase crystal size and increasing of specific surface area. The increase of surface acidity (NH_3 per gram) by addition of cations has their origin mainly by two contributions: anatase crystal edge effects and heteroatom bond formation on oxide surface (Ti—O—Al, Ti—O—Si). On the other hand, increase of surface area can be related to interaction of cations into anatase crystal structure. It results in a decrease of specific number of acid sites as a function of Al and Si content, showing that these cations have the capacity to modify the electronic balance on the surface of mixed oxides, and therefore, changing their acidic properties. These results in acidic density can be also explained according to the effect of coordination Al and Si on the catalytic surface, and also it would be possible an associated effect with changes in the semiconductor properties of TiO_2.

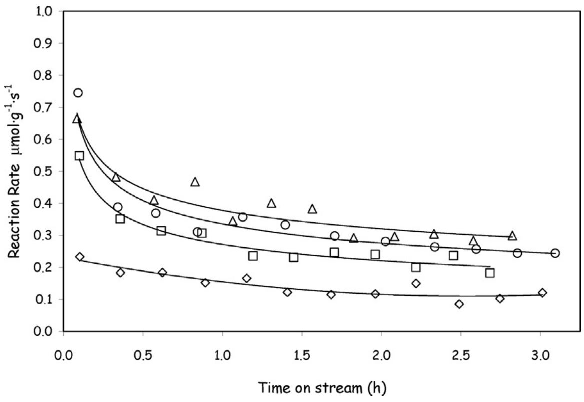

Fig. 1. Effect of Al addition on the reaction rate on 1% Pt/TiO_2 catalysts. (◇) 0%, (□) 1%, (△) 3%, (○) 10% Al_2O_3.

In Table 2, the overall initial reaction rate per gram of catalyst to n-heptane dehydrocyclization and the catalytic activity per site (TOF) are listed. These results indicate that there is a noticeable improvement in the overall initial reaction rate as the Al and Si content is increased, achieving threefold activity for catalyst with 10% Al_2O_3 and 10% SiO_2, respect to the catalyst supported on pure TiO_2. In contrast, the addition of Al and Si generates moderate increase in TOF according to the low structure sensitivity of hydrogenation and dehydrogenation reactions. However, it is significant to observe that the increase in TOF is lower for Al-promoted catalysts than Si-promoted ones, achieving a twofold increase for 3% SiO_2 catalyst, showing that the increase in catalytic activity responds to the type of promoted cation. Although the moderate TOF increase, it is important to emphasize that these results demonstrate that is possible to detect a modification in the metallic activity by the addition of Al and Si into TiO_2. In others words, adding of cations into the TiO_2 support not only modify the structural and textural properties, but also has effect in the catalytic performance of supported metal [32].

Figs. 1 and 2 illustrate the effects of the content of Al and Si in the overall reaction rate of n-heptane dehydrocyclization, showing

Table 3
Effect of content of Al_2O_3 and SiO_2 in first order kinetic constant (k) and deactivation constant (k_D) for catalyst reduced at 500 °C.

Catalysts	%	Kinetic constant $k \times 10^{-3}$ ($L\,g^{-1}\,s^{-1}$)	Deactivation constant $k_D \times 10^{-3}$ (s^{-1})
Pt/TiO_2	–	0.357	0.070
Pt/TiO_2–Al_2O_3	1	0.742	0.089
Pt/TiO_2–Al_2O_3	3	0.979	0.075
Pt/TiO_2–Al_2O_3	10	0.870	0.074
Pt/TiO_2–SiO_2	1	0.556	0.077
Pt/TiO_2–SiO_2	3	1.027	0.164
Pt/TiO_2–SiO_2	10	1.324	0.113

Table 4
Selectivity of n-heptane dehydrocyclization products on 1% Pt/TiO_2 catalysts, T_{REAC} = 500 °C, at time on stream t = 0.

Catalysts	%	C_1–C_6 (%)	Cyclo alienes (%)	Benzene (%)	iC_7 (%)	C_7 = (%)	Toluene (%)
Pt/TiO_2	–	5.2	–	–	–	4.0	90.8
Pt/TiO_2–Al_2O_3	1	13.5	3.0	3.7	7.4	9.6	62.8
Pt/TiO_2–Al_2O_3	3	11.3	2.3	3.6	5.6	11.0	66.2
Pt/TiO_2–Al_2O_3	10	4.3	6.9	1.6	4.9	9.1	73.2
Pt/TiO_2–SiO_2	1	3.6	2.4	–	4.1	11.8	78.2
Pt/TiO_2–SiO_2	3	7.7	10.0	7.6	–	5.7	69.0
Pt/TiO_2–SiO_2	10	14.3	3.3	–	5.0	10.3	67.1

Table 5
Selectivity of n-heptane dehydrocyclization products on 1% Pt/TiO_2 catalysts, T_{REAC} = 500 °C, at time on stream t = 3 h.

Catalysts	%	C_1–C_6 (%)	Cyclo alienes (%)	Benzene (%)	iC_7 (%)	C_7= (%)	Toluene (%)
Pt/TiO_2	–	–	–	–	–	15.8	84.2
Pt/TiO_2–Al_2O_3	1	3.8	–	–	7.9	15.2	73.1
Pt/TiO_2–Al_2O_3	3	2.8	–	–	5.2	14.1	77.9
Pt/TiO_2–Al_2O_3	10	–	–	–	–	11.7	88.3
Pt/TiO_2–SiO_2	1	–	–	–	–	15.3	84.7
Pt/TiO_2–SiO_2	3	–	–	–	–	21.8	78.2
Pt/TiO_2–SiO_2	10	5.3	–	–	6.1	13.2	75.4

both deactivation by the time on stream, and improving of reaction rate as a function on cations content. Kinetic and deactivation constants are listed in Table 3. It is noticeable to observe that adding of cations has an improvement in the catalytic activity, showing an increase in kinetic constant as a function of Al and Si content, but also the resistance to deactivation responds according to the type of cation. It is important to observe that the Al-promoted catalysts have no significant change in deactivation constant, in contrast to the Si-promoted ones, showing a noticeable increase in k_D with the Si content. The deactivation of these catalysts is usually associated with the acidic density, according to the fact that the deactivation by carbon deposition is promoted by acid sites of catalyst. However, in this case, there is not a direct relationship between the change in acidic density observed for these catalysts and deactivation resistance by promotion of cation, showing that deactivation resistance is noticeable different according to the type of promoted cation. In other words, these results show that deactivation resistance in n-heptane dehydrocyclization is sensitive to the type of promoted cation because the difference in atomic coordination in the catalytic surface. Furthermore, the catalytic effects observed by addition of cations can be associated with electronic transfer effects, according to the results in the selectivity (Tables 4 and 5). The main product is toluene for all samples, followed by hydrocracking production (C_1–C_6), isomerization (iC_7), cyclization and benzene selectivities. These results indicate that dehydrocyclization is the predominant reaction mechanism. At time on stream t = 0, hydrocracking reaction has an important activity, it associated with initial high activity of Pt, which is diminished by deactivation by coke deposition (Table 5). The same way happened with cycloalkane, benzene and isomerization selectivity.

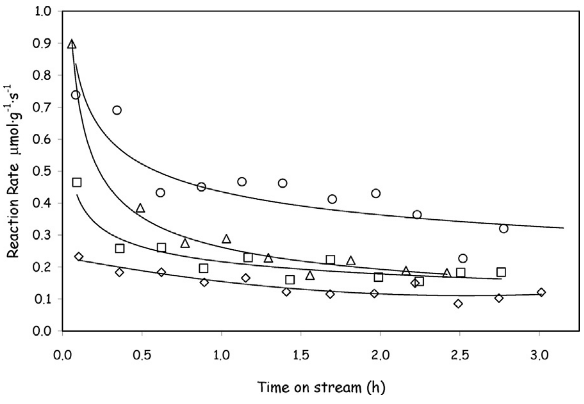

Fig. 2. Effect of Si addition on the reaction rate on 1% Pt/TiO_2 catalysts. (◇) 0%, (□) 1%, (△) 3%, (○) 10% SiO_2.

Changes in the activity of dehydrogenation, cyclization and aromatization can be associated to the effect of the support functionality in the metallic phase [5], without ruling out the conversion of n-heptane depends on the combination of both metal and acid sites [3,4]. This results in selectivity are indicative of moderate acidic strength that promotes toluene selectivity by the dehydrogenation of n-heptane with the alkene formation as a first step (metallic function), and cyclization by the action of moderate acidic function as a second step. A third step by the metallic function is needed to complete the toluene formation. Then, the addition of cations has an important role in the metallic role of the catalyst, not only increasing the TOF as a function of cation content but also promoting the toluene selectivity.

The model of metal-semiconductor contact theory has been proposed to explain the changes in the TOF of the Pt supported on Al- and Si-promoted TiO_2. Ioannides and Verykios [31] have suggested that the catalytic activity of metal supported on TiO_2 depends on the electronic properties of the support, in particular of electronic interaction in the metal-support inter-phase, which is feasible to modify by addition of cations inside the crystal lattice of TiO_2 (cation doping) in order to handle the electronic transfer between the metal and the support. According to this theory, the valence of the cation added to the support plays a major role in electronic balance between metal and support, since both the value of the valence and cation content modified potential electronic charge transfer (work function the support, Φ_S), being the difference between the charge transfer potential of the metal and the support (work function metal and support $\Phi_M - \Phi_S$) the driving force for the electronic transfer from the metal to support or vice versa.

The addition of cation into the network of TiO_2, with different valence to +4 (Al^{+3}, W^{+6}) means an aggregate number of species in the donor or recipient charging, creating donors or recipients levels of potential between the conduction bands and valence (band gap) and causing a shift in the electrochemical potential of the support (energy or Fermi level, E_F). The charge transfer potential of a solid ($\Phi_M - \Phi_S$) is determined as the difference between the electrostatic potential (potential energy of a free electron) and the electrochemical potential of the electrons inside the solid (Fermi level) [33] therefore $\Phi_M - \Phi_S$ is the measure of the energy required to transport charge of the solid (or metal support) and transported in the form of free electrons. By modifying the value of the work function of support Φ_S with the addition of cations, the transfer potential between the pair of metal support $\Phi_M - \Phi_S$ is also changed, resulting in an offset charge from the metal to the support or vice versa, depending on the valence of the cation content and added. The theory predicts that the addition of cations into the support of M/TiO_2 system with a valence higher than the valence of Ti^{+4} (like W^{+6}) results in a greater difference between $\Phi_M - \Phi_S$ in comparison with the addition of a cation equal or lower valence (Si^{+4}, Al^{+3}) to the valence of Ti^{+4}, so that the effects of charge shift between the metal-support inter-phase. In support of this theory, the authors report the results for Pt catalysts supported on TiO_2 which is observed in the decline in both catalytic activity and hydrogen chemisorption using a promoter with higher valencies than +4, while these properties are concerned with the addition of promoters with lower valences than +4. It means that the charge transfer at the metal-support inter phase can be changed by modifying the electronic structure of supported metal crystallites, and thereby promote or inhibit both the catalytic properties and hydrogen chemisorption. Then, the effects of Al and Si addition in both H_2 uptake and the catalytic activity of Pt/TiO_2 catalysts could be explained by the metal-semiconductor contact theory, showing that the changes in the toluene yield and TOF are promoted by changes in the electronic interaction between metal and support inter phase. Additionally and according to the effect in supported Pt pointed out above, the differences in deactivation resistance observed for these catalysts can be related to the type of atomic coordination of promoters in the TiO_2, showing that the deactivation constant is more sensitive for Si-promoted catalyst than the Al-promoted ones [34].

4. Conclusions

The addition of Al^{+3} and Si^{+4} into TiO_2 lattice increase the overall catalytic activity of n-heptane dehydrocyclization for Pt catalysts supported on TiO_2–Al_2O_3 and TiO_2–SiO_2 mixed oxides, with toluene as a main product, showing that the metallic function is promoted over the acidic function. The increase in dehydrogenation and aromatization activity by the addition of Al and Si is associated with a moderate acidic activity of support since the low hydrogenolysis and isomerization selectivity. Moderate increase in the TOF is observed as a function of cation content, hand in hand with the increase of the H_2 uptake (Pt dispersion) and a noticeable increase in overall reaction rate. This effect in TOF could be explained by the metal-support contact theory, which explains the effects in the catalytic activity and H_2 uptake properties of Pt supported on TiO_2 by changes in the electronic transfer between metal and support due the addition of cation into the TiO_2 crystal lattice. Also, the distinctive effect of promoters in deactivation resistance can be associated with the difference in atomic coordination of Al and Si on the catalytic surface.

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