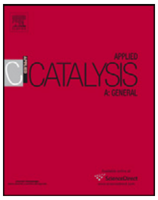
Applied Catalysis A: General 408 (2011) 156–162

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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



Metal-doped carbon aerogels as catalysts for the aromatization of n-hexane

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ARTICLE INFO

Article history:
Received 16 June 2011
Received in revised form
16 September 2011
Accepted 18 September 2011
Available online 22 September 2011

Key words:
n-Hexane aromatization
Carbon aerogels
Active phase
Acidity
Pre-treatments

ABSTRACT

Metal (Cr, Mo, W) – doped carbon aerogels were synthesized from resorcinol–formaldehyde polymerization, characterized textural and chemically and used as aromatization catalysts. Catalytic performance depended on the thermal treatments applied to the samples and on the nature of the metal phases formed (pure carbon is inactive). Only cracking and aromatization reactions were detected and benzene was produced by dehydrogenation and direct 1–6 ring closure. The partial reduction of the metal oxides led to less acidic surfaces enhancing the aromatization versus cracking. Benzene selectivity of 60% without deactivation was obtained. However, when Ni and Co were reduced to the zero valence, strong interactions with the hexane led to a 100% selectivity to methane.

1. Introduction

The preparation of aromatic compounds from alkanes by catalytic reforming is an interesting reaction from an economic point of view because they are used as feedstock in many industrial synthetic processes. Platinum is the typical active metal in naphtha reforming catalysts used in the production of high-octane gasoline. Industrial catalysts are normally based on Pt, mainly supported on chlorinated alumina [1] and great efforts have been made to improve their performance [2–4]. Alternative catalysts are also being sought using mainly different types of zeolites as Pt-supports [5–11].

Many papers have tried to explain the exceptional behaviour of PtKL catalysts first reported by Bernard [5]. The debate on the performance of this catalyst traditionally centres on its porous and chemical characteristics. The main hypotheses proposed to explain the properties of the Pt clusters on basic supports are (i) the role of the basicity of the support and of the metal–support interactions (ii) the influence of the geometry of the channels leading to the concepts of the molecular die and of the structural recognition and preorganisation of the alkane molecule, and (iii) the platinum cluster size. However, as Meriaudeau pointed out in a classical review of aromatization [6] none of these hypotheses by itself can fully explain this effect and the exceptional Pt/KL catalytic performance for aromatization remains a matter of debate. Thus, it was proposed recently that the catalysts control is due to the entry of hexane into the lobes of the L-zeolite containing the active sites [7].

In previous papers [8–11], we showed how the ionic exchange of beta zeolite with alkaline metal simultaneously modifies the acidity, the porosity, the ability to obtain very small Pt-clusters, and the interaction of these clusters with the neighbouring alkaline atoms of the zeolite. Pt/KL was used as a reference. The Pt/Csbeta and Pt/KL samples show similar catalytic performance, which strongly differs from that of the Pt/Nabeta. The steric constraints induced by the increase in the size of the alkali result in a decrease in both the Pt content and the adsorption capacity of the support. The acidity also decreases as the cation size increases. The acidity favours undesired reactions such as cracking and isomerisation, also inducing coke deposition. This not only leads to the loss of valuable products, but can also cause catalyst deactivation [8,9]. Furthermore, the alkali metal strongly affects the size of the Pt particles and their electronic behaviour as shown following the adsorption of CO by FTIR. Smaller Pt particles are obtained in the presence of the heavier alkali metals, suggesting that the more basic supports stabilize the smaller Pt species. The similar behaviour of the Pt/Csbeta and Pt/KL catalysts emphasizes the combined roles of the alkali and their porous environment in determining the acid–base properties of the zeolitic support, the stabilization of the Pt species, and the catalytic behaviour.

However, very high aromatization selectivity was also described for other catalytic systems, offering attractive alternatives to the Pt/zeolites catalysts. Ciuparu [12] obtained values of almost 90% for aromatization selectivity using Pd supported on MgO–ZrO_2 composites. This is favoured by the basicity of the MgO, while on a ZrO_2 rich support isomerization increases at the expense of

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0926-860X/$ – see front matter
doi:10.1016/j.apcata.2011.09.021

aromatization. Aromatization catalysts based on transition metal oxides were also developed. Al-Kandari [13] studied the correlation between the catalytic activity and the surface structure of molybdenum-based catalysts. Different active Mo-phases were obtained by reduction as a function of temperature and the n-hexane aromatization to benzene was shown to be related to the formation of metallic Mo^0. Molybdenum carbide (Mo_2C) is also a traditional alternative to the Pt-catalysts as an aromatization catalyst and research in this field is continuously appearing [14,15]. The n-octane aromatization selectivity reaches in this case values of 50–60% [15]. Another interesting alternative is the use of carbon/inorganic oxide composites [16]. The carbon phase itself is inactive, but it cooperates with the metal oxides (titania, zirconium or hafnium), so creating a catalyst (80% selectivity) that is highly selective for the aromatization of n-octane into ethylbenzene and o-xylene.

In our laboratory we have been studying the preparation of metal-doped carbon aerogels and their application as catalysts in certain reactions of energy-related or environmental interest for many years [17–21]. However, as far as the author knows, carbon aerogel-based catalysts have never been used as aromatization catalysts. In view of the results previously exposed, it seemed interesting to explore the possibilities of these catalysts in this reaction, because they can be prepared with a large variety of chemical and structural characteristics. As a first step in this new direction, a series of carbon aerogels doped with group-6 metals were prepared using doping or impregnation techniques, and extensively characterized. Their textural and chemical properties were then compared with their catalytic behaviour.

2. Experimental

2.1. Synthesis of the catalysts

Four organic aerogels were synthesized by polymerization of resorcinol and formaldehyde. Resorcinol and formaldehyde (37 wt.%) were mixed in a molar ratio $R/F = 1/2$ with the corresponding amount of metal precursor dissolved in distilled water. Chromium nitrate, ammonium heptamolybdate and ammonium tungstate were used as catalyst precursors. The amount of these compounds added to the solutions was calculated to obtain 1% by weight of the metal in the initial solution. Another aerogel, to be used as a blank, was prepared with the same recipe but without adding any metal salt.

The mixtures were stirred to obtain homogeneous solutions which were cast into glass molds (25 cm length × 0.5 cm internal diameter). After the curing period, the gel rods were cut into 5 mm pellets and supercritically dried with carbon dioxide to form the corresponding aerogels. The aerogels will be referred to as ACr, AMo, AW and A (the blank), respectively, according to the metal that contain. Pyrolisis of the aerogels to obtain the corresponding carbon aerogels was carried out in N_2 flow, 100 $cm^3\,min^{-1}$, by heating up to 500 or 1000 °C with a heating rate of 1.5 $K\,min^{-1}$ and a soaking time of 5 h. The carbon aerogels will be referred to in the text by adding the carbonization temperature to the aerogel name. The exact metal content of the supported catalyst was obtained by burning a fraction of it in a thermobalance at 1123 K under air flow up to constant weight. The metal-doped carbon aerogels were used directly as catalysts, because the precursor salts decompose during the carbonization process. For comparison, a supported catalyst, with a tungsten loading of 5% w/w was prepared by impregnation of the blank sample A1000 with ammonium tungstate, this catalyst will be referred to as A1000-5W and was pretreated 2 h at 500 °C in He or H_2 flow (60 $cm^3\,min^{-1}$) before reaction.

2.2. Procedure of characterization

The textural characteristics of all the samples were obtained by adsorption of N_2 and CO_2 at 77 and 273 K, respectively, and mercury porosimetry up to 4200 $kg\,cm^{-2}$ (Quantachrome Autoscan 60 Pororosimeter). The BET equation was applied to the N_2 adsorption data to obtain the nitrogen surface area, S_{N_2}, and the Dubinin–Radushkevich equation to the CO_2 adsorption data, from which the micropore volume, W_0, and the mean micropore width, L_0, were obtained [22,23]. The following parameters were obtained from mercury porosimetry experiments: pore size distribution, PSD, of pores with a diameter greater than 3.7 nm; pore volume for pores with a diameter of between 3.7 and 50 nm, V_2, referred to as mesopore volume, although in fact the mesopore volume is between 2 and 50 nm [24]; pore volume of pores with a diameter larger than 50 nm, or macropore volume, V_3, and particle density, ρ_p.

The morphology of the sample, the chemical nature and dispersion of the metallic phases were studied by XRD, SEM and TEM. X-ray diffraction experiments, XRD, were carried out with a Phillips PW1710 diffractometer (40 kV and 40 mA) using Cu K_α radiation. SEM experiments were carried out with a ZEISS DSM 950 (30 kV) microscope. TEM was carried out with a Phillips CM-20 electron microscope.

In order to evaluate the surface acidity of the catalyst, the decomposition of isopropanol was studied. Catalytic experiments were carried out in a quartz microreactor at atmospheric pressure with 0.15 g catalyst. The reaction was performed in a He flow saturated with the alcohol at 0 °C. The total flow rate was 60 $cm^3\,min^{-1}$ and the partial pressure of the alcohol 8.44 Torr. Analysis of reaction products was done by online gas chromatography using a Variant gas chromatograph, with a flame ionization detector and a column Carbopack B80/120.

2.3. Catalytic performances in the n-hexane conversion

The aromatization of n-hexane was performed with the same experimental procedure described for isopropanol decomposition. In this case, the reactor was fed with a continuous flow, 60 $cm^3\,min^{-1}$, of a mixture 50%He/50%H_2 bubbled in a hexane saturator cooled to fix the hexane concentration at 2.5% v/v. Products were analyzed by gas chromatography, using a flame ionization detector and a column Chromosorb 102. Conversion was defined on the basis of the n-hexane disappearance and selectivity as the fraction of hexane molecules transformed into each detected product. Prior to any catalytic test, the metal-doped carbon aerogels were heated in a He flow at 200 °C for 2 h to clean their surfaces while the supported A1000-5W catalyst was pretreated as previously commented.

3. Results

3.1. Morphology and textural characteristics

The textural characteristics of the samples are set out in Table 1 and the corresponding pore size distributions (PSD) are shown in Fig. 1. These doped-metal carbon aerogels were mainly macroporous materials, as was the pure carbon aerogel used as a reference material. Mesoporosity was detected only in the case of W-doped catalysts, and is quite insignificant. The macropore volume varied according to the sequence ACr500 < AMo500 < AW500 and decreased with increasing carbonization temperature to obtain AW1000. For the PSD the opposite occurred (Fig. 1). The larger macropores correspond to ACr500 with pores of over 2000 nm in diameter, AMo-500 showed a monomodal PSD centred on pores of

Table 1
Textural characteristics of metal-doped carbon aerogels.

Sample	Metal (%)	ρ_p (g cm^{-3})	S_{N_2} (m^2 g^{-1})	V_3 (cm^3 g^{-1})	V_2	W_0	L_0 (nm)
ACr500	3.6	0.56	397	0.99	0.00	0.17	1.03
AMo500	1.9	0.50	481	1.40	0.00	0.18	1.12
AW500	1.4	0.43	528	1.53	0.05	0.20	1.06
AW1000	2.1	0.54	610	1.32	0.01	0.26	1.06
A1000	–	0.72	470	0.63	0.00	0.27	1.08
A1000-5W (He/500 °C/2 h)	5	0.72	410	0.61	0.00	–	–

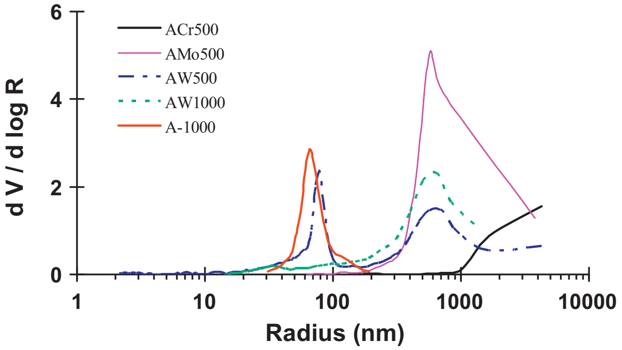

Fig. 1. Pore size distribution (PSD) obtained by mercury porosimetry of metal-doped carbon aerogels.

around 1500 nm in diameter, while AW-500 presented a bimodal PSD with two maxima at around 180 and 1500 nm. The increasing carbonization temperature led to the disappearance of the narrower macropores, while increasing the volume of the larger ones. The blank sample presents a monomodal macroporosity around pores of 130 nm in diameter, and is significantly less porous and therefore denser. The supported A1000-5W catalyst after pretreatment in He flow presents a certain decrease of S_{N_2} regarding the A1000 support, as consequence of the blockage of some porosity by the metal phase deposited, but the macroporosity is not apparently influenced.

The microporosity (W_0), and as a result the surface area values (S_{N_2}), varied in the same order indicated for the macroporosity but were enhanced by the increasing carbonization temperature. The largest micropores (L_0) were detected for the AMo-500 catalyst. The porosity of carbon aerogels was defined by the experimental conditions of four critical steps during the synthesis: (a) gelation (b) drying (c) carbonization and (d) activation. Since the discovery of carbon gels, many papers have analyzed the control of carbon aerogel porosity by adjusting these experimental conditions [21,25–28].

SEM images showing the surface morphology of samples are depicted in Fig. 2a and b, as an example. They are composed of fused microbead particles, and the particle size was strongly influenced by the nature of the metal. The textural properties may be related to the size of the aerogel microparticles. Thus, the smaller microparticles give rise to a pore network containing smaller inter-particle voids which range from macro to mesopores. Results indicate that the morphology and pore texture of the aerogel depended on the nature of the metal salt [17–21]. Intra-particle microporosity is generated during carbonization, thus, W_0 and L_0 increased with carbonization temperature due to the large weight loss during carbonization.

3.2. Chemical nature and dispersion of the metals

The metal nature and dispersion were studied by XRD and TEM. XRD did not show any diffraction peaks for the metal phase. These results are similar to those previously obtained [17] and confirm the good dispersion of the metals. Previous XPS analysis showed a partial reduction of Cr(VI) to Cr (III) and from Mo (VI) to Mo (V), while tungsten remained as W(VI) after carbonization at 500 °C. Fig. 3 shows some examples of the good dispersion obtained in all doped metal catalysts. It is noteworthy that metals are attached to or trapped by the organic gels during gelification and metal particles are formed during the carbonization of the organic aerogels. Thus, there are good contacts or links between both organic and inorganic phases. As can be observed, a high dispersion of metal nanoparticles of different size and morphology is formed on the carbon surface depending of the metal nature and thermal treatment [17,29], indicating that metal-doped catalysts are resistant to sintering given the drastic thermal treatments they have undergone. Nevertheless, the metal particle size observed is large enough to produce XRD diffraction, indicating their amorphous character.

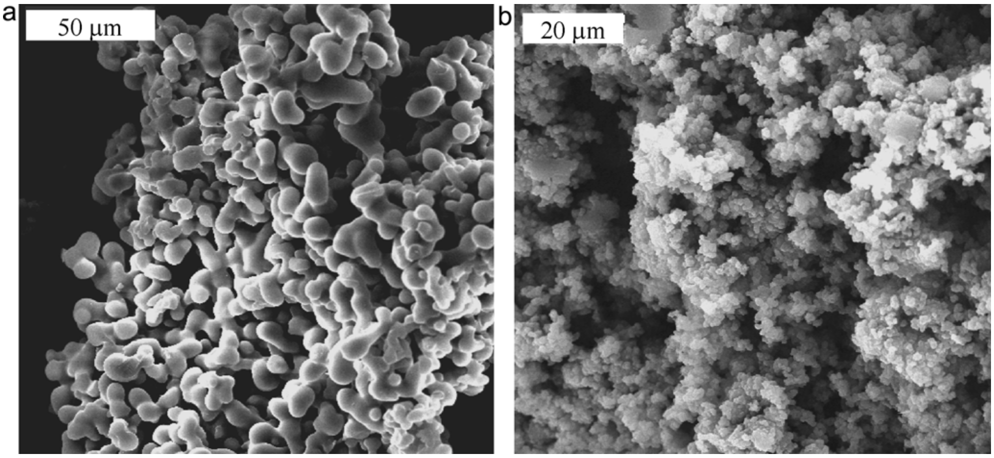

Fig. 2. SEM microphotograph of (a) ACr500 and (b) AW500.

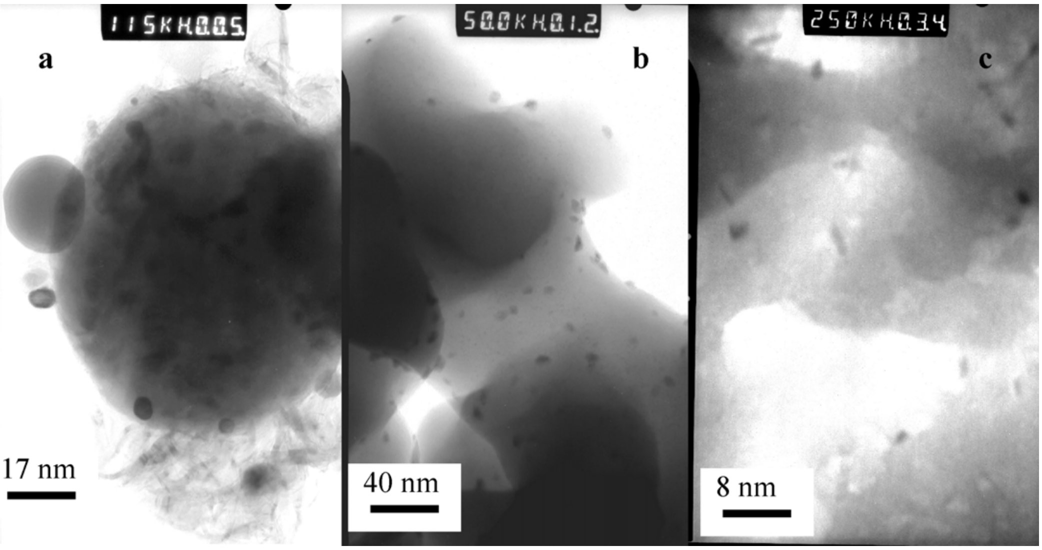

Fig. 3. TEM microphotographs of samples (a) ACr500 (b) AMo500 and (c) AW500.

3.3. *Determination of the acidity of catalysts by isopropanol decomposition*

Metal oxides behave as acid catalysts in the composite, and their performance depends on the nature of the metal oxide and the thermal treatment. Reactions between both metallic and carbon phases are favoured by increasing carbonization temperature (Section 3.2), while the organic carbon phase can be more or less graphitized [17–20,30,31]. On this basis, the acidic characteristics of the samples were studied by isopropanol decomposition as proposed by Ai [32,33] and used previously to characterize carbon aerogels–inorganic oxide composites [17,18,34]. Ai assumed that the dehydration of isopropanol is catalyzed by acid sites, whereas dehydrogenation is catalyzed by both acid and base sites through a concerted mechanism. Thus, the acidity is related to the reaction rate of dehydration to obtain propene, and the basicity to the ratio of the reaction rates for dehydrogenation (to acetone) and dehydration. The results obtained are compiled in Fig. 4. As observed, catalytic isopropanol conversion increased in the order AW500 > AMo500 > >ACr500 and AW500 was strongly more acidic than AMo500 and ACr500, producing a higher propene/acetone ratio (Fig. 4b). When analyze the performance of tungsten-doped carbon aerogels carbonized at 500 and 1000 °C respectively a similar activity was detected for both catalysts. However the product distribution changed significantly and the propene/acetone ratio fell, which is indicative of a lower acidity strength of the acidic sites due to the progressive reduction of the oxide by the carbon matrix with increasing temperature.

3.4. *Aromatization of n-hexane*

The catalytic behaviour of metal-doped carbon aerogels in the n-hexane conversion reaction is summarized in Fig. 5. The pure carbon aerogel used as a reference (A1000) is inactive in n-hexane conversion in the temperature range used. The amounts of the various products expected to be produced by the isomerisation (branched alkanes, methylcyclopentane, and cyclohexane) or intermediate dehydrogenation (olefins) processes are always negligible. Only small quantities of ethylene and butanes (<1%) were sometimes observed, and were evaluated as cracking products. Thus cracking (C_1–C_5) and benzene were the main reaction products. For metal-doped aerogels, the n-hexane conversion increased linearly with temperature but in this sense cracking was progressively favoured versus aromatization, mainly in the case of AW500. All the metal-doped carbon aerogels demonstrated a good stability of the catalytic performance.

As the carbon is inactive, the catalytic performance of the metal-doped carbon aerogels must be related to the properties of the oxide phase. If we compare the results for isopropanol and hexane conversion, we can see that the aromatization ability of the

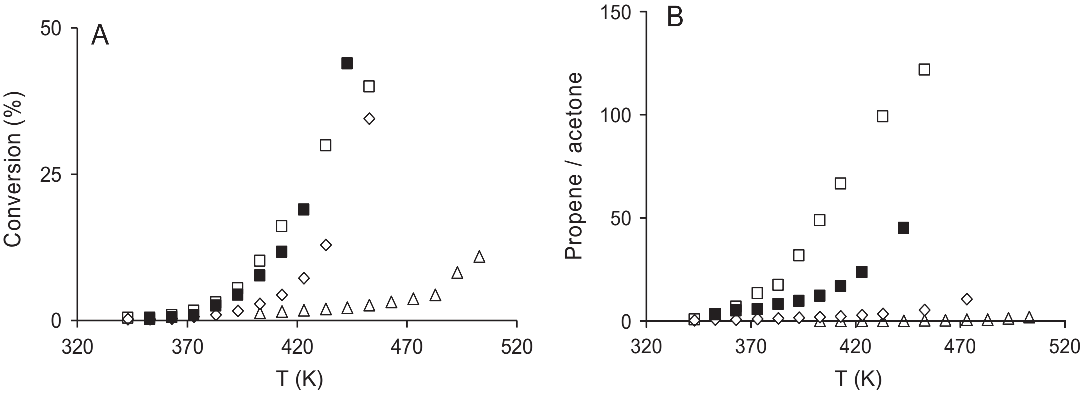

Fig. 4. Variation of (A) isopropanol conversion and (B) propene/acetone ratio against the reaction temperature; △ ACr500, ◇ AMo500, □ AW500 ■ AW1000 (0.15 g of catalyst, flow rate 60 cm^3 min^{-1}, isopropanol partial pressure 8.44 Torr).

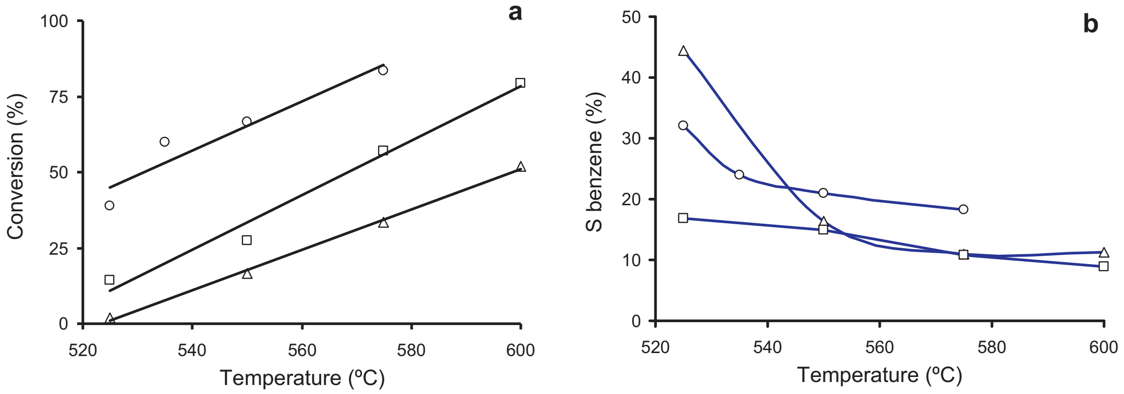

Fig. 5. Catalytic performance of metal-doped carbon aerogels (a) n-hexane conversion (b) selectivity to benzene; □ ACr500 ○ AMo500 △ AW500 (0.15 g of catalyst, 50%He/50%H_2 flow rate 60 cm^3 min^{-1}, 2.5%, v/v hexane).

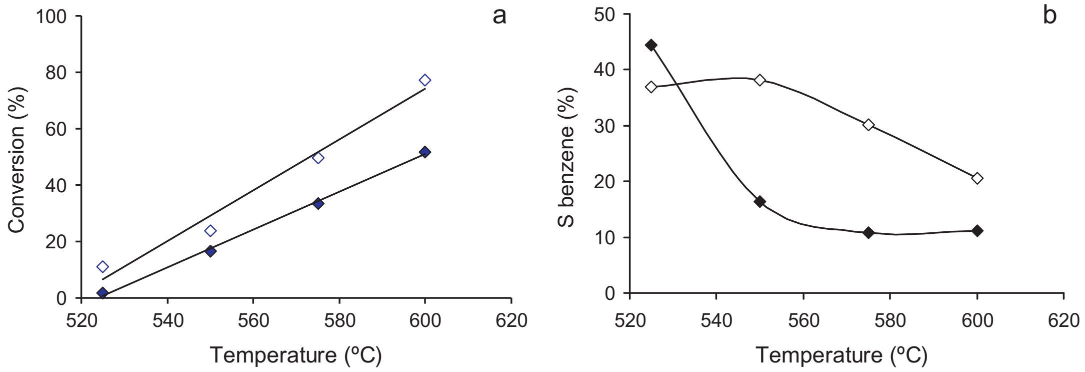

Fig. 6. Influence of the carbonization temperature of tungsten-doped carbon aerogels on their catalytic performance (a) n-hexane conversion (b) selectivity to benzene (♦AW500, ◊AW1000; experimental conditions as in Fig. 5).

catalysts is related at low temperature to their acidic character, varying at 525 °C in the order AW500 > AMo500 > ACr500. However, with increasing temperature, cracking processes are enhanced on acid catalysts in such a manner that AW500 shows from 550 °C an aromatization performance similar to ACr500. AMo500 shows high activity in both processes, indicating a large number of active centres, and these acid centres are weak enough (Fig. 4b) to maintain high aromatization activity. The importance of the strength of the active sites was also pointed out by comparing the catalytic performance of AW500 and AW1000. Thus it can be observed in Fig. 6 that AW1000 is not only more active, but also more selective than AW500 practically over the whole temperature range. Together with the transformations of the metallic phase, the surface area development with increasing carbonization temperature (Table 1) can also favour catalytic activity. Previous authors also indicated that the acidity of supported or bulk oxides catalysts is a possible cause of their aromatization ability [35].

In an attempt to improve the activity and selectivity of tungsten catalysts, a 5%W catalyst (A1000-5W) was prepared by impregnation on the pure carbon aerogel. Two different pre-treatment atmospheres were used (He or H_2) so as to produce a different distribution of active sites. The catalytic results are shown in Fig. 7. Again, the activity observed is similar, but the decline in selectivity is slower when pretreated in H_2 flow. It is also noteworthy that in these experimental conditions aromatization of n-hexane was favoured against cracking over the whole temperature range studied (S Ar > 50%). Fig. 8 shows the catalytic performance of this supported catalyst pretreated in He flow at 525 °C. It is noteworthy

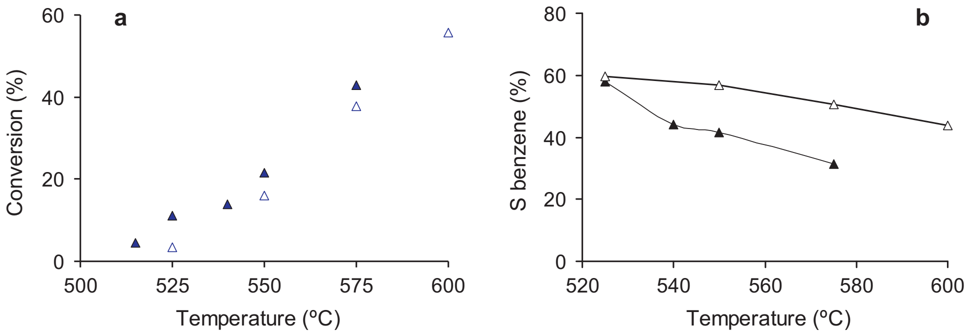

Fig. 7. Influence of the pretreatment atmosphere (△ He/500 °C/2 h, ▲ H_2/500 °C/2 h) on the catalytic performance of A1000-5W catalysts (a) Conversion (b) Selectivity to benzene (experimental conditions as in Fig. 5).

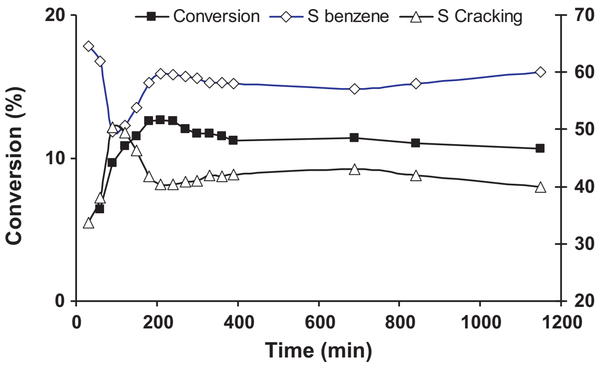

Fig. 8. Stability of the catalytic performance of A1000-5W supported catalyst pretreated in He flow/2 h/500 °C (reaction in continuous flow at 525 °C, 0.15 g of catalyst, 50%He/50%H_2 flow rate 60 cm^3 min^{-1}, 2.5%, v/v hexane).

that the conversion increases at the beginning of the reaction, which suggests certain activation of the surface sites. This is accompanied first by an increase in cracking at the expense of aromatization, however, after that, the opposite was observed, and the stationary state was reached after around 5 h on stream. However, the small changes in the slope of the selectivity curves showing certain oscillations from this point onwards seem to indicate that there is a continuous exchange between aromatization and cracking sites, probably through the deposition/gasification of adsorbed molecules or light coke precursors. The catalyst is stable at 525 °C during at least 20 h on stream with an aromatization selectivity of around 60% at n-hexane conversion values of 12%. This activation effect disappears at high reaction temperatures. In fact, conversion and aromatization decrease slowly at the beginning of the reaction and are quickly stabilized. Similarly, after pretreatment in H_2, aromatization increased at the beginning of the reaction when reaction temperatures were low and slowly decreased at high reaction temperatures. No XRD peaks were detected after pretreatment or even after reaction, suggesting a good dispersion of the active phase and high sintering resistance, but limiting the discussion about the nature of the active sites.

In view of these results the performance of Ni and Co-doped carbon aerogels was also studied. These metal-doped carbon aerogels were selected on the basis of a good dispersion and reducibility of metal nanoparticles, their high porosity and their proven ability (especially of Ni based catalysts) in aromatization processes [36,37]. In this case, both materials have a high mesopore volume and surface area. As occurred previously, both metals are well dispersed inside the carbon matrix and do not present DRX peaks. However, these metals are easily reduced by carbon below 500 °C, according to the Ellhingam diagram, and in fact, both appeared completely reduced after carbonization at 1000 °C [26]. The XRD patterns for the used catalyst present small peaks corresponding to Ni^0, indicating the sintering and reduction of the metallic Ni-particles during reaction and a catalytic system like Pt^0 supported on non-acidic supports was expected. However, the two catalysts only produce the cracking of the n-hexane molecule, with propane as the main reaction product at very low temperature (at around 150 °C) and increasing selectivity to methane with reaction temperature. Only methane is produced from 300 °C onwards in both cases.

4. Discussion

Previous authors proposed that the aromatization of alkanes on metal oxides or metal oxides–carbon composites occurs through a direct 1–6 ring closure reaction of the C_6 chain. The catalysts are considered as monofunctional and it is assumed that there is a stepwise dehydrogenation of the alkane into mono-alkene, diene, triene followed by catalytic or thermal cyclization, the so-called 'triene mechanism' [16]. The bifunctional considerations for the dehydrocyclization of alkanes suggest that aromatic formation develops by cyclization to a five carbon ring followed by ring expansion to a six carbon ring and subsequent dehydrogenation to aromatics. In our case, the fact that there is no isomerisation product under any of the experimental conditions or catalysts tested leads us to the conclusion that the aromatization of hexane in this kind of catalyst takes place according to the triene mechanism.

The gaseous n-hexane should be adsorbed on the catalyst surface, with carbons having bonds with the metallic surface leading to dehydrogenation and weakening the C–C bonds in such a way that rupture occur forming different fragments depending on the adsorption position. In hexane conversion, three different positions C_1–C_2, C_2–C_3 and C_3–C_4 are possible. The C_1–C_5 hydrocarbons can therefore be formed by hydrogenolysis occurring on metallic sites or by bifunctional hydrocracking reactions involving acid and metal sites [38,39]. The coefficient M_f, defined as $M_f = \sum (C_2{-}C_5)/C_1$ provides information about the metal or acidic character of cracking reactions. The M_f values described for acid catalysts are greater than 45, while all of our catalysts present M_f values of less than 5. This also suggests that cracking is produced by hydrogenolysis on metal sites, and that our catalysts behave as monofunctional catalysts.

Although the aromatization selectivity at low reaction temperature may be related to the acidic character of the composite (only the stronger and more active sites are able to perform the reaction), with increasing temperature it is clear that these stronger sites favour cracking at the expense of aromatization. Thus, Mo-500 is the most selective catalyst in the metal-doped series and W1000 is more selective than W500 because of the lower propene/acetone ratio obtained with these catalysts. The formation of metallic species with different oxidation states could enhance the catalytic performance by a synergetic effect. This reduced species can be formed either by increasing carbonization temperature or by using reducing atmospheres for the pretreatment of supported catalysts. However, the reduction of Co or Ni-species until the zero valence leads to very active catalysts. They are active from 120 to 150 °C while the other doped metal aerogels are only active from 500 °C, but only cracking products were obtained. The high hydrogenolysis ability of metals such as Ni or Rh was described by previous authors [37]. Thus, the hydrogenolysis reaction rate in n-heptane conversion using Ni-catalysts was found to be 100 times greater than that obtained using Pt-catalysts. These results were justified in a strong adsorption of the alkane to the Ni-particles by terminal C–C bonds, in such a way that the hydrogenolysis of n-hexane on Ni does not produce $C_1 + C_5$, but the fragment C_5 is so strongly linked to Ni that cleavage continues until n-hexane is converted into six methane molecules [18]. These results clearly indicate that the reduction degree of metal-doped carbon aerogels should be optimized.

Regarding the role of the carbon matrix, it was also suggested [16] that the carbon matrix of the metal–oxide composite enhances the aromatization ability of the corresponding oxide by favouring dehydrogenation, due to the ability of carbon to interact and disperse the hydrogen atoms by spill-over. In spite of the low carbonization temperature used, the nature of the carbon matrix is also strongly influenced by the metal present. Thus, some of them, especially Ni or Cr are highly active inducing the graphitization of the carbon supports [30]. The good contact between both organic and inorganic phases needed to promote the hydrogen spill-over is guaranteed by the synthesis procedure.

As commented in the introduction, we have previously fitted the characteristics of β-zeolite by ionic exchange to optimize its behaviour as Pt-supports [8–11]. The activity of the catalysts decreases with increasing the basicity of the exchanged ion (from Na to Cs) and the selectivity towards aromatic increases in the same sense. At 450 °C the benzene selectivity increased from 10 for Pt supported on Na-exchanged zeolite to 32% for Pt supported on Cs-exchanged zeolite, tending to the 45% reached by PtKL catalysts used as reference [10]. It is noteworthy that in this study, a benzene selectivity of 45% was also reached for tungsten doped carbon aerogel AW500 at 525 °C, increasing this value up to 60% when the catalyst is prepared by impregnation. Similarly, the performance of these metal doped carbon aerogels greatly improves those presented by Trunschke [16]. In this work, authors used composites with around 80% w/w of inorganic phase and obtained an aromatic selectivity of 90% in n-octane conversion regardless of the oxide used, but found that the aromatization centres were largely deactivated. In this work are developed catalysts with good activity and selectivity of around 60%, that was stable for a long time and used catalysts with a metal charge that was always less than 5% w/w. Moreover, it is demonstrated that the catalytic behaviour is intrinsic of each catalyst and that can be fitted by the adequate synthesis and pretreatments. Therefore, the preparation of inorganic–organic composites based on carbon aerogels offers an interesting alternative procedure for developing aromatization catalysts. Many variables such as porosity, the active phase nature and dispersion, loading, interaction between inorganic–organic phases, multiple metal doping, etc. can be explored on the basis of the flexibility of the preparation method.

5. Conclusions

A series of metal-doped carbon aerogels and supported catalysts on carbon aerogels were prepared. The porosity, chemical nature and distribution are greatly influenced by the precursor salt and the thermal treatments. The catalysts are active in n-hexane conversion where only products of cracking and aromatization processes were detected. The catalysts behave as monofunctional catalysts and their activity and selectivity depend on the nature of the active sites. The presence of metal with different oxidation states can improve the catalytic performance through a synergetic effect, because the activation/deactivation process seems to favour alternately either cracking or the aromatization reaction. The carbon matrix largely protects the metal phase from sintering and can facilitate the hydrogen spill-over, in such a way that similar activity was obtained after different treatments. However, the acidic character obviously decreases after additional reducing treatments, typically improving the aromatization ability. Nevertheless, in the case of Ni and Co-doped aerogels, the reduction of metal to the zero valence leads to catalysts that are totally selective to cracking, as a consequence of the strong interaction of n-hexane with the metal particles that avoid the desorption of products until the total cleavage of the n-hexane molecule into six methane molecules is produced. The preparation and optimization of metal-doped carbon aerogels opens a new and interesting route for developing aromatization catalysts.

Acknowledgment

This research is supported by the project CTM2010-18889 of the Spanish MCIN.

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