



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

F.J. Maldonado-Hódar*

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada 18071, Granada, Spain

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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.

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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 Pt/KL 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–ZrO₂ composites. This is favoured by the basicity of the MgO, while on a ZrO₂ rich support isomerization increases at the expense of

* Corresponding author. Tel.: +34 958240444; fax: +34 958248526.

E-mail address: fjaldon@ugr.es

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 Mo⁰. Molybdenum carbide (Mo₂C) 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 \times 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. Pyrolysis of the aerogels to obtain the corresponding carbon aerogels was carried out in N₂ flow, 100 cm³ 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 H₂ flow (60 cm³ min⁻¹) before reaction.

2.2. Procedure of characterization

The textural characteristics of all the samples were obtained by adsorption of N₂ and CO₂ at 77 and 273 K, respectively, and mercury porosimetry up to 4200 kg cm⁻² (Quantachrome Autoscan 60 Porosimeter). The BET equation was applied to the N₂ adsorption data to obtain the nitrogen surface area, S_{N_2} , and the Dubinin–Radushkevich equation to the CO₂ 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 cm³ 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 Carbo-pack 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 cm³ min⁻¹, of a mixture 50%He/50%H₂ 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

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